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Research Article

Model-Based Study of Creep and Recovery of a Glassy Polymer

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Polyvinyl chloride specimens were subjected to three different constant loads at ambient temperature, and the creep is monitored as a function of time. After a certain time, the load was withdrawn and the strain recovery was followed with time. Although the deformational behavior of such material is conventionally described by the Burger model consisting of elastic, viscoelastic, and viscous components, in the present work, it is shown that the whole creep recovery process is reversible and is described by three viscoelastic components connected in series. Depending on the relative value of the observation and the relaxation times, the viscoelastic components appear pseudo- elastic or viscous. It is found that the model parameters evaluated from the creep data fail to predict the recovery data in both the initial and the end phases, while those from the recovery data can partially reproduce the creep data (satisfactorily in the late phase and with high deviation in the initial phase). The model parameters vary with stress values, but with a good approximation, they could be averaged for a certain stress range to describe creep processes for a specified time period. The proposed model describes creep data better than the Finley and the Weibull models.

1. Introduction

The last century was considered to be the century of polymers, and intensive research had been done on various aspects of the material. The study of deformation behavior of different types of polymers (glassy, rubbery, crystalline, amorphous, and so on) has been done by different methods and techniques, and today, the findings are so established that they are the subject matter of a specialized section called "polymer rheology" in textbooks [1, 2]. Methods for the investigation of the deformation behavior of polymers have been standardized [3, 4]. Among the test methods, studies of tensile behavior at some constant strain rates are the widely applied ones, and the technique that is commercially available for the measurement is the universal testing machine (UTM) or tensile tester. Measuring stress at a constant strain rate, the tensile tester generally generates data for stress development in time, and some very important mechanical parameters of the polymer, such as modulus of elasticity, yield strength, elongation at break, and tensile strength, are reported as an outcome [5]. These parameters, however, are not adequate to characterize the deformational behavior of the polymers, since, with them, it is practically impossible to predict the stress behavior, namely, stress vs. time relation.

Glassy polymers show time-dependent recovery even deformed at stress far below their yield strength and glass transition temperature, and such deformation under long-term constant load is called creep (also known as cold flow) [6]. Recovery of deformation after the load is withdrawn is a prerequisite for dimensional stability of components/parts of a machine/aggregate, especially when they are under stress for a long period. The polymer materials have got versatile applications due to their viscoelastic (time-dependent reversible deformation) properties, but this property does not get adequate attention in the study of deformation by the tensile tester. The stress vs. strain data at some constant strain rate as acquired by a tensile tester might be susceptible to treatment by a mathematical model (corresponding to a mechanical model), but such an approach would face tremendous complication as the deformation behavior is generally described by the combination of several simple models, and for this reason, maybe, the data acquired by tensile tester is used to obtain the parameters like modulus of elasticity, yield strength, elongation at break, and tensile strength, and practically, no effort is made to distinguish the elastic, the viscoelastic, and the viscous components of the deformation of the material.

A model-based study of deformation behavior at constant load, however, is much easier to distinguish among elastic, viscoelastic, and viscous components of a material. This method is also well established and has become part of textbook materials [7–9]. But for the last decades, comparatively less attention has been given to this method, a consequence attributed to the comparatively larger time duration of the experimental work than that in the tensile tester, and "no recognition" of the method as the standard test one. In the meantime, new materials in form of polymer composites have been accumulated which require differentiation of elastic, viscoelastic, and viscous components of materials. These materials are the product of intensive research to improve the mechanical properties of polymer materials and are intended to be used as constructional materials. In those studies, different polymers of mass usages, such as polyethylene [10, 11], polypropylene [12, 13], and poly (vinyl chloride) (PVC) [14], have been extensively used as a matrix material in the preparation of composites. Enormous numbers of papers have been published in scientific journals reporting the improvement in the tensile properties of the polymer by fiber reinforcement [15–19]. Differentiation of viscous and elastic components of these composites would provide valuable information about their dimensional stability and, consequently, their applicability as a constructional material. This is a vast area of study, and a model-dependent deformation study has to be revived. A limited number of research works with the method in modified or unmodified form have already appeared during the last decade [20–23].

Our laboratory has taken the task to study the time-dependent deformation behavior of a polymer. For the study object, a granular PVC material is chosen as available in the local market. This material is imported into the country for use in the manufacture of pipes and some other applications of mass usage. The choice simply grounds the high deformability of the material at room temperature, and that deformation could be recorded with simple distance-measuring devices. A prototype apparatus has been prepared and made functional. The experiment is simple, but the observation is very interesting, which is neither predicted nor disclosed in classical models in the form as they are available in the literature [7–9]. It was interesting to observe that this glassy polymer at ambient temperature under constant load shows a somewhat viscoelastic and viscous component of deformation (typical creep behavior), and no well-defined elastic component (which was so expected from a glassy polymer). As the load is withdrawn, part of the strain is initially recovered but not instantaneously, rather linearly, and the residual strain is gradually recovered at a slow rate (typical viscoelastic behavior), and in the end (days later), no measurable strain remains unrecovered. This is a clear indication of the absence of any viscous deformation during the creep phase. This is a mismatch between the character of deformation in the creep phase (with the "pseudo" viscous component and "no" elastic component) and that in the recovery phase (with undefined initial linear recovery and "no" viscous component). This is a qualitative issue to be analyzed and would be the first task of this work, and to the authors' knowledge, such issue on creep behavior (which is usually described by the Burger model) has not been discussed in literature explicitly. The second task will be to describe the deformation behavior in both the creep and the recovery phases with a mechanical model (and the corresponding mathematical model) and to explore whether a single set of model parameters could describe the deformation in both the phases (creep and recovery) for the model to qualify to be a characteristic for the material itself. For this purpose, the PVC specimens were subjected to three different loads and different creep-recovery times. In this quantitative approach of the model development, it is found that the material continuously attempts to adapt itself under the stress-strain situation, and three successive viscoelastic elements have to be inserted in the mechanical model to describe the deformation behavior. Moreover, it is found that the deformation history is "somewhat deleted from the material memory", and under such conditions, the model parameters describing the deformation progress in the creep phase fail to describe the recovery process. The same failure occurs when attempts are made to reproduce the whole deformation process in the creep phase with the model parameters evaluated for the recovery phase; but interestingly, while the initial and the intermediate portion of the creep is not reproduced well, the late portion of the creep curve is well reproduced by the model parameters from the recovery phase, as if the dynamic behavior developed in the material in the late creep phase is acting in the recovery phase when no external force acts on the material. The model parameters slightly vary with the load as well, but they could be averaged within a tolerable range. The dynamics of model parameter variation along with the progress of strain development have also been studied.

In fact, a number of empirical relations with various mathematical formulations are available in the literature to describe the strain behavior of a polymer material under constant loads [5, 24]. Among them, the Finley model (a power law model) with three adjustable parameters is frequently used as a reference to evaluate other models to describe the creep process. This model constitutes an elastic component and a time-dependent creep component. The creep component does not distinguish between recoverable and irrecoverable strains. Recently, Fancey [23, 25] has proposed a latch-based model to describe creep, recovery, and stress relaxation. It grounds the concept that viscoelastic deformation occurs through incremental jumps and is not a continuous motion, and as such could be described by equations based on the Weibull distribution function. This model has got two independent sets of four adjustable parameters to describe the creep and the recovery of a polymer. This model has appeared to be a powerful tool to describe creep and recovery of polymers and has successfully described the creep process of nylon 6,6/polypropylene and polyether-ether-ketone (PEEK) [25–27]. Ma et al. [28], however, reported that both the creep and recovery data of glued-laminated bamboo fitted well to the Burger model, while the recovery data did not fit well to the Weibull model. Ornaghi et al. [29], on the other hand, successfully applied Fancey's latch model to describe creep, recovery, and stress relaxation of carbon fiber-reinforced polymer (CFRP) composites.

In the quality of an empirical one, the model proposed in this work gives results similar to Finley and Fancey models, but unlike the latter ones, it clearly distinguishes viscoelastic and viscous components of the strain. To the authors' knowledge, in all previous models, the sets of model parameters for the creep and the recovery are independent of each other. In this work, however, it is found that the values of the model parameters assumed in the late phase of the creep process are the same as those in the recovery process. Further intensive study on models describing creep dynamics would exhaustively correlate the parameters in the creep to those in the recovery phase. We admit that the measurement with the present experimental arrangement is not sufficiently precise to make a crucial quantitative estimate of the material property, but still the observation is quite adequate to make a reliable conclusion about the deformation behavior of the polymer material. Data acquired with a more precise arrangement would give more insight into the nature of the material response to the applied external forces, and the researchers will be inspired to develop more reliable instruments capable of studying the deformation behavior of different polymers and polymer composites at short and large strains with varying loads and temperature.

2. Theoretical

2.1. Mechanical Models for Deformation. The deformational behavior of a polymer is represented by mechanical models consisting of different combinations of elastic components (obeying Hooke's law, mimicked by a spring with the modulus of elasticity, E) and viscous components (obeying Newton's viscous law, mimicked by a dashpot with viscosity, η). [30]. The most commonly used mechanical model for studying creep behavior of polymers and their composites is the Burger model or commonly known as the four-element model [31–34]. This model could also be called a three-component deformation model as it comprises elastic ε_e (I), viscoelastic ε_{ve} (II), and viscous ε_v (III) deformation components connected in series (see Figure 1).

This model will not be used to describe the deformation behavior in this work. But each of the three components of the model will give a basic idea and interpretation of the model to be developed.

2.2. Mathematical Modeling of Creep Process. Referring to Figure 1, the material response under the constant stress of σ is represented by the system of Equations (1)–(4).

$$\varepsilon = \varepsilon_e + \varepsilon_{ve} + \varepsilon_v, \tag{1}$$

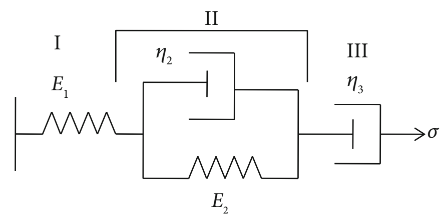


Figure 1: Mechanical model of a material undergoing elastic (I), viscoelastic (II), and viscous (III) deformations.

with

$$\varepsilon_e = \frac{\sigma}{E_1}, \tag{2}$$

$$\varepsilon_{ve} = \frac{\sigma}{E_2}\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \text{ and } \tau = \frac{\eta_2}{E_2}, \tag{3}$$

$$\varepsilon_v = \frac{\sigma}{\eta_3} t, \tag{4}$$

where σ is the stress, ε is the measurable (total) deformation, and t is the time of action of the load. τ has the dimension of time and is called "relaxation time."

It should be noted that a glassy polymer, which is supposed to show only recoverable deformation (elastic and viscoelastic) below glass transitional temperature, shows "somewhat" irreversible deformation (viscous) as well. In fact, experimental observation of all the three components of deformation practically depends on the relative value, t/τ, of the time of observation t and the relaxation time, τ, of the process. For $t/\tau < <1$, the viscoelastic component ε_{ve} will be observed as a viscous one, and for $t/\tau > >1$, the viscoelastic component ε_{ve} will be observed as an elastic one. Thus, the term t/τ determines whether a viscoelastic deformation will be observed as elastic, viscoelastic (in the general case), or viscous type, and observing the nature of the time-dependent creep curve within a given time scale of observation, it is difficult to assess whether a material has undergone truly irreversible deformation or not. For this purpose, the recovery should be followed for a long period.

2.3. Mathematical Model for the Recovery Process. Again, referring to Figure 1, the total strain that has been developed for the creep time t_f is given by the following equations

$$\varepsilon_f = \varepsilon_{e,f} + \varepsilon_{ve,f} + \varepsilon_{v,f}, \tag{5}$$

with

$$\varepsilon_{e,f} = \frac{\sigma}{E_1}, \tag{6}$$

$$\varepsilon_{ve,f} = \frac{\sigma}{E_2}\left[1 - \exp\left(-\frac{t_f}{\tau}\right)\right], \tag{7}$$

$$\varepsilon_{v,f} = \frac{\sigma}{\eta_3} t_f. \tag{8}$$

If the load is suddenly withdrawn after a creep time of t_f, then the elastic component $\varepsilon_{e,f}$ is recovered instantaneously, the viscoelastic component $\varepsilon_{ve,f}$ is recovered in time, but the viscous component being irreversible remains unchanged. Thus, during recovery ($t > t_f$), the remaining strain ε_r at any moment is given by the following equation:

$$\varepsilon_r = \begin{cases} \varepsilon_f, & \text{for } t_r < 0 \text{ with } t_r = t - t_f, \\ \varepsilon_{ve,f} \exp\left(-\dfrac{t_r}{\tau}\right) + \varepsilon_{v,f}, & \text{for } t_r \geq 0. \end{cases} \tag{9}$$

Equations (1) and (9) are mutually supplementary to each other the ideal creep and the ideal recovery equations, respectively. The term t_r/τ determines whether the recovery of viscoelastic deformation will show elastic behavior (instantaneous recovery), or typical exponential curve (in the general case), or an approximated linear relation (linear recovery).

If the deformation mechanism ideally follows that described above, the model parameters determined from the creep phase are expected to be identical with those obtained from the corresponding recovery phase. In other words, the model parameters determined from the creep phase will predict the deformation in the recovery phase and vice versa.

As mentioned in Introduction, besides the Burger model, Finley (Equation (10)) and Weibull (Equation (11)) models are frequently applied to describe creep processes.

$$\varepsilon = \varepsilon_0 + At^n, \tag{10}$$

where ε_0 is the initial instantaneous strain, A and n are the empirical constants, and

$$\varepsilon = \varepsilon_0 + \varepsilon_u \left[1 - \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right)\right], \tag{11}$$

where ε_u is the ultimate time-dependent component of the strain and β is the shape factor.

For $n = 1$, the empirical structure of Equation (10) will be quite identical with that of Maxwell model consisting of the elastic and viscous components (elements I and III in Figure 1) connected in series with $\varepsilon_0 = \varepsilon_e = \sigma/E_1$ (Equation (2)) and $A = \sigma/\eta_3$(Equation (4)). For $n \neq 1$, the creep would seem deviation from Maxwell model, and for $n < 1$, it will give impression of slight trend to leveling off (characteristic of viscoelastic strain). For $\beta = 1$, the empirical structure of Equation (11) will be quite identical with that of the Zener model consisting of the elastic and viscoelastic components (elements I and II in Figure 1) connected in series with $\varepsilon_u = \sigma/E_2$ (Equation (3)).

2.4. Mechanical Model with Time-Dependent Reversible (Viscoelastic) Components in Series. As described in Introduction, the PVC material under investigation did not show well-defined instantaneous deformation, and the recovery was very slow at the end, but the next day, the deformation

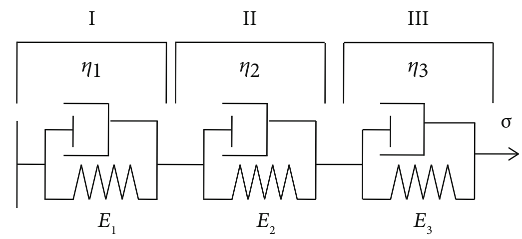


Figure 2: Mechanical model for describing deformation of the material under investigation.

was completely recovered showing no irreversible changes. Leaderman in 1943 also observed the complete reversible behavior in plasticized PVC [35].

For describing the deformation behavior of the present material, a mechanical model consisting of three viscoelastic components in series has been considered (Figure 2).

Referring to the mechanical model in Figure 2, the mathematical model for describing the strain development is as follows:

$$\varepsilon = \frac{\sigma}{E_1}\left[1 - \exp\left(-\frac{t}{\tau_1}\right)\right] + \frac{\sigma}{E_2}\left[1 - \exp\left(-\frac{t}{\tau_2}\right)\right] + \frac{\sigma}{E_3}\left[1 - \exp\left(-\frac{t}{\tau_3}\right)\right], \tag{12}$$

with

$$\tau_1 = \frac{\eta_1}{E_1}, \quad \tau_2 = \frac{\eta_2}{E_2}, \quad \tau_3 = \frac{\eta_3}{E_3}. \tag{13}$$

For a creep period of t_f, the total viscoelastic deformation, ε_f, that has been developed is given by the following equation:

$$\varepsilon_f = \varepsilon_{1,f} + \varepsilon_{2,f} + \varepsilon_{3,f}, \tag{14}$$

with

$$\varepsilon_{1,f} = \frac{\sigma}{E_1}\left[1 - \exp\left(-\frac{t_f}{\tau_1}\right)\right], \tag{15}$$

$$\varepsilon_{2,f} = \frac{\sigma}{E_2}\left[1 - \exp\left(-\frac{t_f}{\tau_2}\right)\right], \tag{16}$$

$$\varepsilon_{3,f} = \frac{\sigma}{E_3}\left[1 - \exp\left(-\frac{t_f}{\tau_3}\right)\right]. \tag{17}$$

The mathematical model describing strain recovery after the withdrawal of the load at the creep time t_f is as follows:

$$\varepsilon_r = \varepsilon_{1,f} \exp\left(-\frac{t_r}{\tau_1}\right) + \varepsilon_{2,f} \exp\left(-\frac{t_r}{\tau_2}\right) + \varepsilon_{3,f} \exp\left(-\frac{t_r}{\tau_3}\right) \text{with } t_r = t - t_f. \tag{18}$$

In this work, the creep data will be fitted to Equation (14) and the recovery data will be fitted to Equation (18), and the model parameters will be evaluated. We shall see later in Results and Discussion that the experimental creep data in a plot with observation time $t > 5$ h will seem to be representable with Equation (1–4) well-differentiating elastic, viscoelastic, and viscous components, rather than the more complicated equations Equations (14–17) consisting of three viscoelastic components with the relaxation times differing one from another in order of magnitude. The recovery curve, in the same way, shows pseudo-unrecoverable deformation. But as the deformation is found recovered the next day, the whole creep and the recovery processes should be represented by the Equations (12) and (18), respectively. The parameters will be determined by the trial-and-error method for the creep and the recovery process separately. As the adjustable parameters (E_i and η_i) are six, it would be difficult to determine them simultaneously by the trial-and-error method. To initiate the method, first of all, the approximate values of the parameters, E_i and η_i, will be determined by the procedure described in Appendix A (Supporting Information (SI) (available here)).

3. Material and Methods

3.1. Materials. The PVC material was collected from a commercial shop in a local market. The polymer might have contained stabilizers, filler, and other additives. This is not much usual for a scientific work to deal with a composition, which is unknown. In this work, however, the primary goal was to gather experience about the efficiency of the existing models to describe the creep and recovery behavior of a polymer material, the required data were meant for bit illustrative purposes, and the exact composition was of secondary importance. To characterize the material under investigation, the melt flow index (MFI) was measured at 180°C and 2.165 kg load by "melt flow index tester-auto cutter" (supplied by International Equipment Company, India) and was found to be 7.2 g/10 min. The thermogravimetric analysis (TGA) done by TGA-50 (a product of Shimadzu) shows that sharp decomposition of the material takes place at the temperature range of 258-348°C leading to a weight loss of 40%, and at around 550°C, the residue is around 20% (Appendix A, Figure S1 (Supporting Information (SI))).

4. Methods

4.1. Preparation of Specimens for Tensile Test. The material was subjected to homogenization (to remove any nonhomogeneity eventually present in the market product) in a double-roller open mixer machine (product of Dongguan Lina Machinery Industrial Ltd.) at 130-150°C for ten minutes. It was then cut into small pieces suitable for loading inside the barrel of an extrusion assembly for specimen preparation.

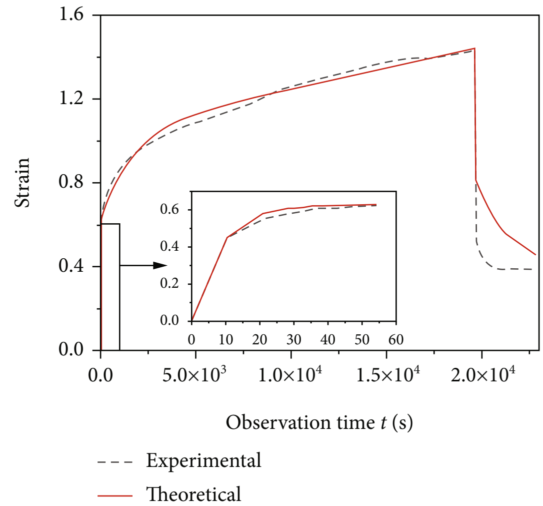


FIGURE 3: Creep model validation (Equation (12)) with load2 for $t_f \approx 317$ min and an overall view of the prediction of subsequent recovery. In inset: expanded view of creep model validation with initial creep data.

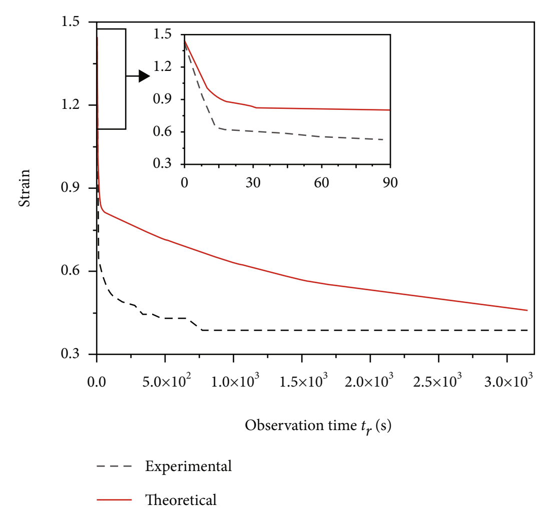


FIGURE 4: Expanded view of the prediction of the whole recovery curve with the parameters evaluated from the creep curve in Figure 3. In inset: expanded view of the prediction of initial recovery data.

The specimens for the test were prepared by a hand-driven compression molding machine extruding at a temperature of 130-140°C. They were dumbbell-shaped with a dimension of $69 \times 8.22 \times 1.16$ mm.

4.2. Creep Tester at Constant Load. The testing instrument for this study is very simple. It consists of a clamp attached to a support. The sample is held still by the clamp, and a load is given at the other end through a light grip equipped with a hook. A flexible meter scale is fixed to the side of the sample, and the elongation was measured initially at an interval of

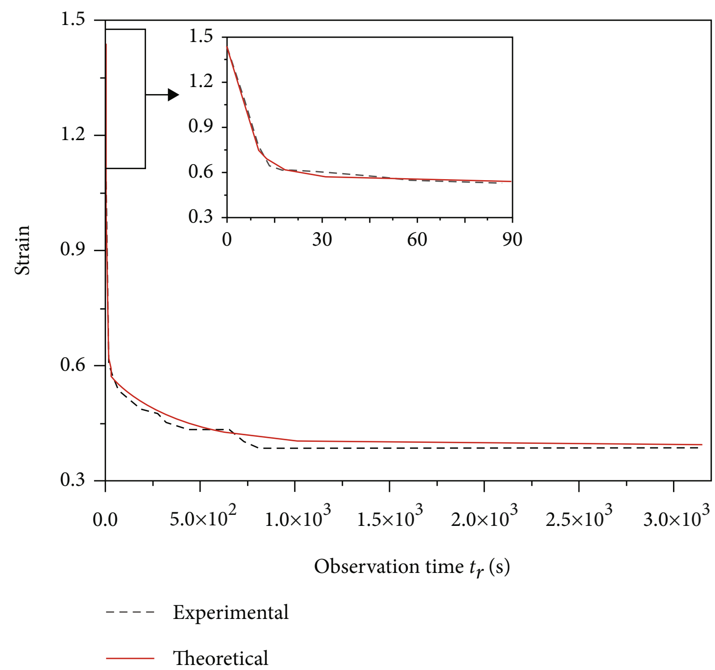


Figure 5: Recovery model validation (Equation (18)) after withdrawal of load2 that has acted on the specimen for $t_f = 317$ min. In inset: expanded view of the recovery model validation with initial recovery data.

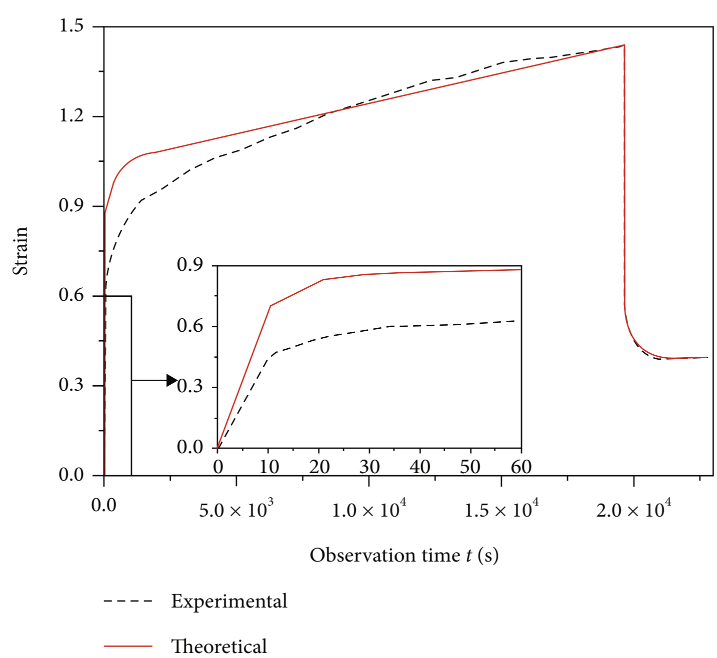


Figure 6: Prediction of the whole creep curve with the parameters evaluated from the recovery curve in Figure 5. In inset: expanded view of the prediction of initial creep data.

seconds, and as the process slows down, the data are collected every 5-10 minutes.

It should be noted here that the few creep testing devices commercially available in the market are automated, but lack the mechanism of instantaneous loading and unloading. In these devices, the load is increased gradually (as a ramp function) until it reaches a certain desired value and then kept constant. In this mechanism, "pure creep" is not observed as the material has already undergone a certain strain before the application of a constant load and that the initial strain is also a function of the load increment rate. A similar picture is observed during the recovery process also. The load is withdrawn gradually, and thus, the material response depends on the load removal rate. Unlike the

Table 1: Fitted model parameters (for the creep and the recovery) of the material for different stresses and creep times.

Fitted parameters	Stress = 0.38 MPa $t_f \approx 333$ min $t_r \approx 50$ min		Stress = 1.51 MPa $t_f \approx 317$ min $t_r \approx 53$ min		Stress = 2.16 MPa $t_f \approx 300$ min $t_r \approx 33$ min	
	Creep	Recovery	Creep	Recovery	Creep	Recovery
$E_1 \times 10^{-6}$ Pa	2.29	2.80	2.44	1.77	2.57	2.16
$\eta_1 \times 10^{-7}$ Pa s	1.73	4.00	1.95	1.07	1.97	2.16
τ_1 s	7.58	14.28	8.00	6.06	7.69	10.00
$E_2 \times 10^{-6}$ Pa	5.97	4.48	3.49	7.81	3.78	5.19
$\eta_2 \times 10^{-9}$ Pa s	5.97	0.14	5.82	2.79	3.98	3.99
$\tau_2 \times 10^{-3}$ s	1.00	0.03	1.67	0.36	1.05	0.77
$E_3 \times 10^{3}$ Pa	5.67	5.67	6.56	6.56	5.55	5.55
$\eta_3 \times 10^{-10}$ Pa s	8.09	8.09	7.54	7.54	6.53	6.53
$\tau_3 \times 10^{-07}$ s	1.43	1.43	1.15	1.15	1.18	1.18

commercial creep testing devices, the instrument used in this study is operated manually, but it gives the opportunity to put the load all of a sudden, and it can be withdrawn instantaneously whenever necessary. Thus, although simple and manual, this device develops pure creep at constant load and shows pure recovery after instantaneous load withdrawal. In Theoretical (Section 2), the mathematical expressions derived for the creep and the recovery analysis are based on the assumptions that the application and the withdrawal of the load are realized instantaneously. Thus, the creep and the recovery study by the present instrument agree with the theoretical formulations described in Section 2.

The stress σ is calculated as follows:

$$\sigma = \frac{W}{A}, \tag{19}$$

where W (N) is the load (that includes the test weight and the weight of the grip and the load cell) and A (m^2) is the cross-sectional area of the specimen.

The strain ε at a given moment t is calculated by the following relation:

$$\varepsilon = \frac{\Delta l}{l_0}, \tag{20}$$

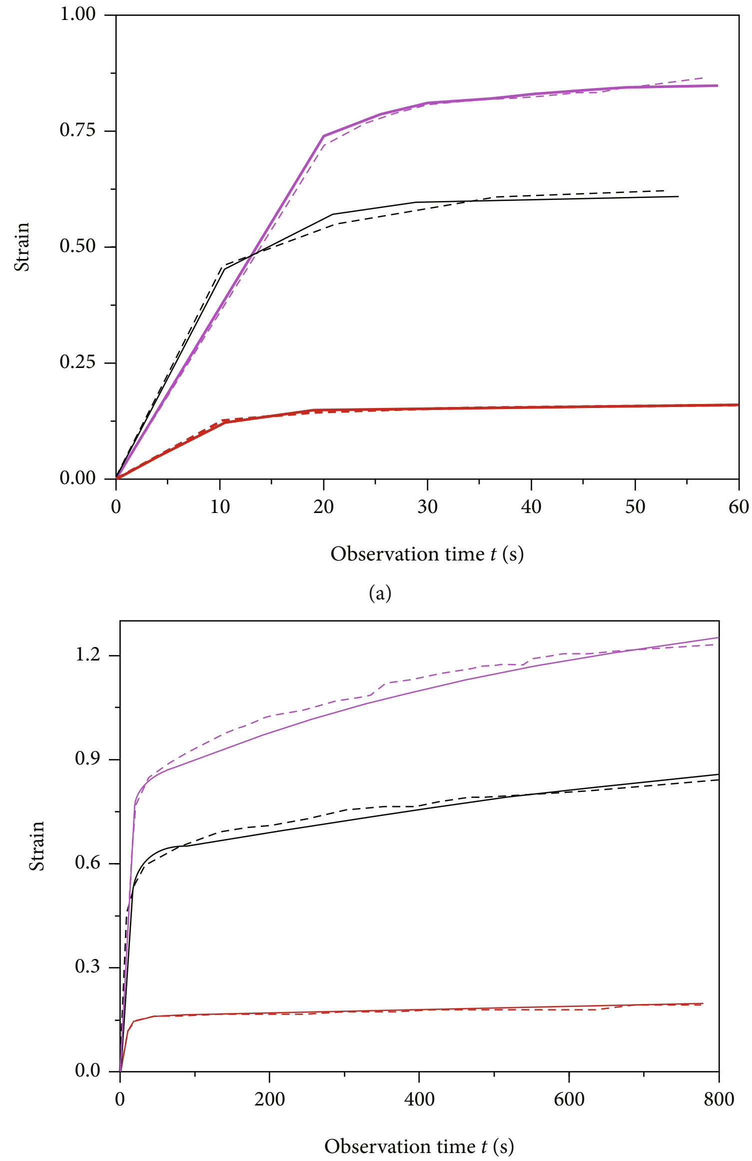
where l_0 (m) is the initial working length of the specimen and Δl (m) is the change in length.

5. Results and Discussion

The specimens were subjected to three different loads (later denoted as load1, load2, and load3, respectively), which were, respectively, equivalent to stresses of 0.38, 1.51, and 2.16 MPa. For all the three loads and time period of action, the total deformations have been recovered practically completely in the next days (left to spontaneous recovery with time) showing that the specimens did not undergo irreversible deformation, but during the regular experimental observation time of creep and recovery, a "pseudo-irreversible" deformation was visible. Thus, to ascertain the ultimate reversibility of the deformation, it was clear from the beginning that the mechanical model would consist of viscoelastic components only, and depending on the relative observation time of the deformation process, some element would appear as "elastic" and some as "viscous" component. Thus, a mechanical model consisting of three viscoelastic components as shown in Figure 2 has been chosen to mimic the deformation behavior, and the corresponding mathematical models for the creep and the recovery are represented by Equations (12) and (18), respectively.

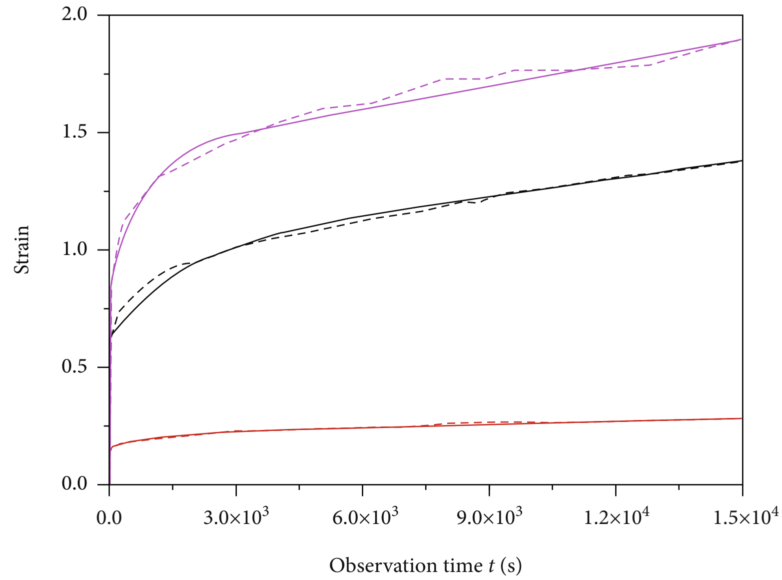
The experimental ε vs. t data for the creep phase have been fitted to Equation (12) and the same for the recovery phase (with the load withdrawn) have been fitted to Equation (18) by a trial-and-error method with formulae written on an Excel Worksheet, and the fitted values of the model parameters have been evaluated for both the phases separately. For the ease of the trial-and-error method, approximate values of E_i and η_i were determined by a method as described in Appendix B (Supporting Information), and with those values, the trial-and-error approach was initiated for determining the parameter values that described the experimental data best.

Figures 3–6 represent validation of the proposed model for the creep phase (Equation (12)) with load2 for the creep duration, t_f of ca. 317 min, and for the recovery process (Equation (18)) for ca. 53 min. Treatments of the creep and the recovery data have also been done with load1 (for the creep duration of ca. 333 min and recovery time of ca. 50 min) and with load3 (for creep duration of ca. 300 min and recovery time of ca. 33 min), and the observations were found similar as those for load2 (shown in Appendix B of the Supporting Information). The fitted values of the parameters (E_1, η_1, E_2, η_2, E_3, and η_3) for both the creep and the recovery phases for the three loads have been evaluated separately (Table 1), and attempts have been made to predict the recovery curve with the parameters evaluated from the creep curve and vice versa.



(b)

Figure 7: Continued.



(c)

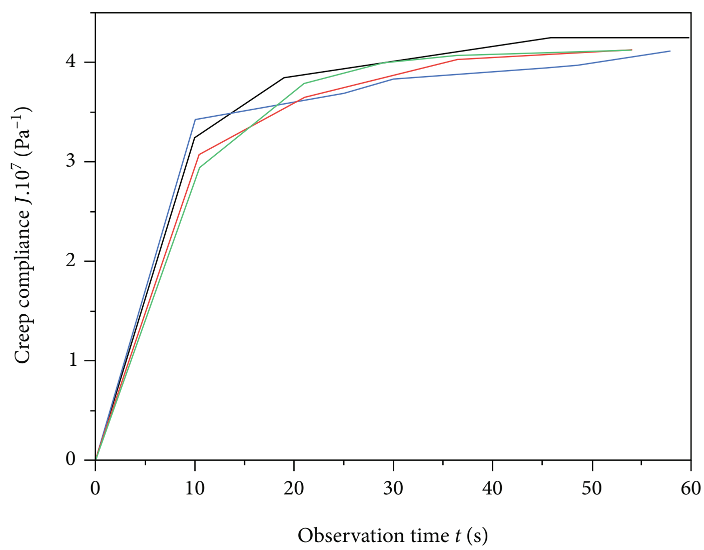
Figure 7: Creep data fitted to Equation (12) with loads1-3 for specified creep time: (a) $t_f = 1$ min, (b) $t_f = 13$ min, and (c) $t_f = 250$ min. The dotted line and solid line represent the experimental and the model-fitted data, respectively. The red, black, and purple lines represent load1, load2, and load3, respectively.

Table 2: Fitted values of the model parameters with different stresses for creep durations 1 min, 13 min, and 250 min.

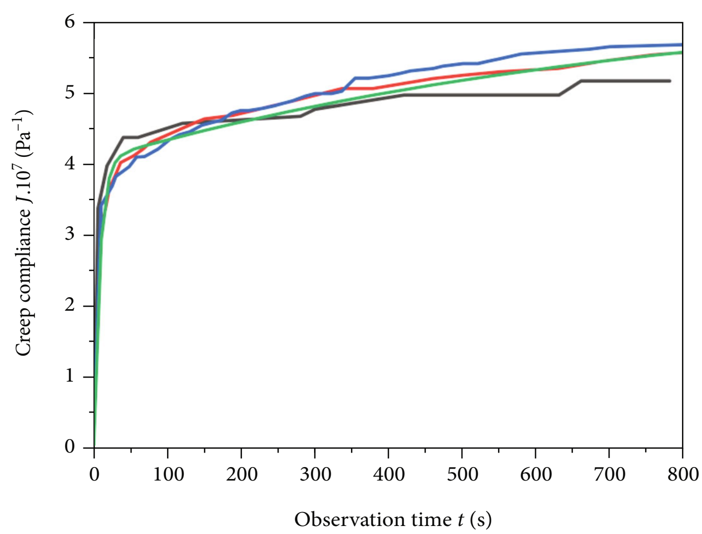
Load	Creep time t (min)	$E_1 \times 10^{-6}$ Pa	$\eta_1 \times 10^{-7}$ Pa s	$E_2 \times 10^{-6}$ Pa	$\eta_2 \times 10^{-9}$ Pa s	$E_3 \times 10^{-3}$ Pa	$\eta_3 \times 10^{-10}$ Pa s
	1	2.27	1.67	—	—	—	—
Load1	13	2.29	1.73	5.96	3.73	—	—
	250	2.32	1.76	6.28	7.84	6.70	8.88
	1	2.47	1.90	—	—	—	—
Load2	13	2.44	2.30	3.26	3.83	—	—
	250	2.43	1.74	3.97	6.61	6.56	6.03
	1	2.54	2.49	—	—	—	—
Load3	13	2.66	2.05	3.53	2.21	—	—
	250	2.57	1.97	3.78	3.98	5.55	6.53

As seen in Figure 3, the model consisting of three viscoelastic components describes the whole creep process in the short-term (expanded view, in the inset of Figure 3) as well as in the long-term aspects quite satisfactorily. But the parameters determined from the creep phase do not predict the recovery data satisfactorily (seen well in Figure 3) neither in the long-term nor in the short-term aspect (shown in expanded view in Figure 4). It is presumed that as the creep process proceeds, the state of the supramolecular structure constituting the material body continuously changes, and for a long-term creep process, these structures have undergone substantial changes and the recovery process could not be described by the same model parameters. As seen in Table 1, the creep and the recovery are presented by different sets of model parameters. Two different sets of model parameters for the creep and the recovery have been reported also by Fancey [25]. In this study, however, the task was to explore whether a single set of model parameters could describe both processes. As this is not achieved, it is assumed that as the load is withdrawn, the material property would correspond to the state at which the test specimen has reached at the creep time, t_f.

Figure 5 validates the recovery model for load2. As seen in figure (with an expanded view of initial recovery in inset), the same mechanical model (Figure 2) describes the whole recovery process quite satisfactorily, but with parameter-values different from those in the creep process (Table 1). Unlike the parameter values determined from the creep data, those determined from the recovery data describe the creep process at the later phase ($t > 83$ min) of development quite satisfactorily (Figure 6), but fail to describe the initial and the intermediate creep development process within a tolerable range of deviation. A similar picture has been observed for the creep and the recovery processes with load1 and load3 (Appendix C (Supporting Information)). It is presumed that the model parameters that correspond to the mechanical

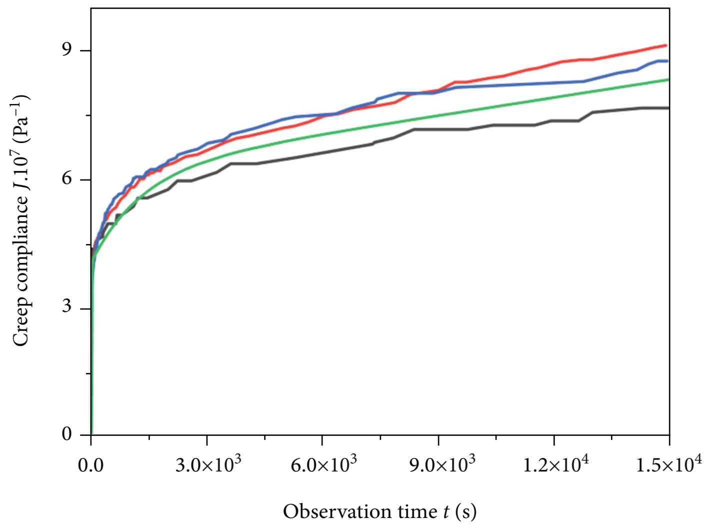


(a)



(b)

FIGURE 8: Continued.



(c)

Figure 8: Compliance J vs. creep time t curves with loads1-3 for creep time: (a) $t = 1$ min, (b) $t = 13$ min, and (c) $t = 250$ min. The green line represents the predicted compliance value with the model parameters averaged for the three loads. The black, red, and blue lines represent data for load1, load2, and load3, respectively.

state of the test specimen at the end of the creep process are almost the same as those valid for the recovery phase. Successful description of the creep process near the end, but failure to do so at the initial and the intermediate phase (Figure 6), indicates that as the creep process develops, the model parameters undergo changes in conformity with the changes undergone in the supramolecular structure of the test specimens, and the previous state is deleted from the material memory. Thus, the model parameters for the recovery process will depend on how long the creep process has continued. In that case, creep data acquired for a specified creep duration might be more convenient to analyze for stress effect on model parameters.

As seen in Table 1, the model parameters vary with the stresses, which have been reported by previous authors [25, 32] too. But if the model parameters are not stress-independent nor correlated in a defined manner with the stress, the model will have only qualitative significance with parameter-values different for different specimens and that will mean that the model will not be a predictive one at all and that would be an unfortunate end.

As discussed above, the model parameters change with the advancement of the creep process, and for this reason, the parameter values determined from the creep phase do not describe the recovery process. Then, it will be interesting to get some idea about the dynamics of variation of the model parameters with the advancement of the creep process. This analysis has been done for three specified creep durations, namely, 1 min, 13 min, and 250 min. For all the three stresses, the model parameters have been evaluated with the creep data acquired in the mentioned periods. The creep duration-dependent model validations have been presented in Figure 7, and the corresponding fitted values of the parameters for the three different loads have been presented in Table 2.

As seen in Table 2, the creep data for the creep duration of 1 min is described by a single viscoelastic component. For the creep duration of 13 min, however, two viscoelastic components connected in series describe the creep data, and finally, to describe the creep behavior for 250 min, three viscoelastic components connected in series are required. The number of model components increases with the advancement of the creep processes. Definitely, in some portion of the creep curve, the consecutive viscoelastic components could overlap, but in the present study, due to the large difference in the relaxation time of the three components (of the order 3-4), the appearance of the successive viscoelastic components is well differentiated. Thus, in efforts to describe the creep behavior with a single set of model parameters, while the stress dependence of the parameters appears to be a stumbling block, the creep duration dependence of the number of model components is a total barrier.

For a model to characterize a polymer material, it is desired that the model parameters would predict the creep behavior adequately within a tolerable range of deviation. But as seen earlier in this section, the creep duration affects the model components and the parameter-values, both. Thus, the model has to be defined for specified creep duration and also for a given stress. This will be then a very restricted characterization of the material. An attempt could be made to define some stress-independent averaged model parameters to predict the creep process within a range of stress and for specified creep duration. The question is how much deviation in the prediction of the deformational behavior has to be put up with if the model is represented by stress-independent averaged parameters? It should be admitted that the reproducibility of data for the polymer specimens (which have undergone specific preparation steps) will vary within a certain range. Therefore, it is curious to check to what extent the averaged values of the model

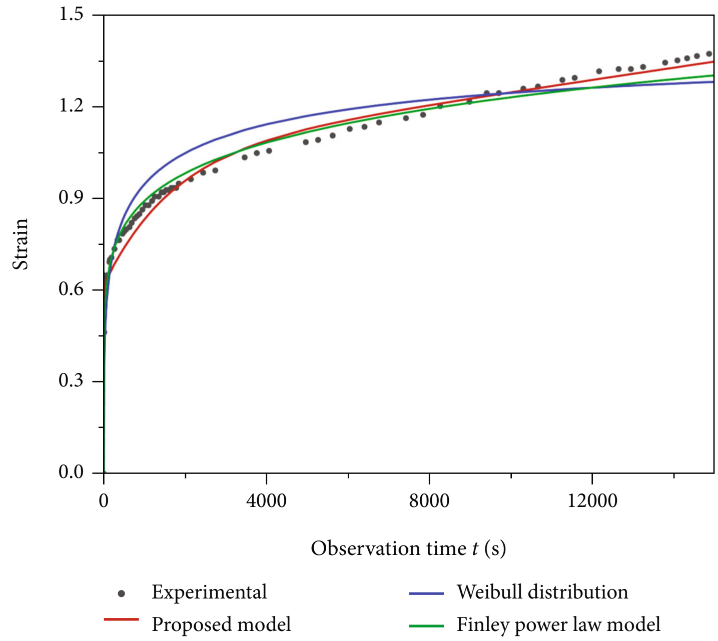


Figure 9: Model validation for creep time 250 min: Finley and Weibull models vs. the proposed model for load2.

parameters obtained from creep data for different stresses, but for a specified creep duration would describe the creep process adequately. This analysis is described below, and for that end, for each creep duration $t_f = 1$ min, 13 min, and 250 min, the parameters have been averaged to predict the creep behavior.

To eliminate the stress effect, the data are presented in terms of compliance J (defined as $J = \varepsilon/\sigma$) vs. time t in Figure 8 for $t_f = 1$ min, 13 min, and 250 min, respectively. As seen in Figure 8, the averaged values of the parameters for the specified creep time predict the creep compliance for the three loads within a tolerable deviation range of 10%. Thus, it may be concluded that within a tolerance limit of 10% deviation, the creep process could be described by a single set of averaged model parameters for a certain stress range. This result is optimistic and gives an opportunity to propose some stress-independent model parameters within specified stress ranges.

It is curious to verify whether the proposed model misses some information that would be accessible through the Finley and the Weibull models. Figure 9 presents a comparison of strain predictions by the proposed model and the Finley and the Weibull models for load2 for creep time 250 min. As seen in the figure, prediction by the Finley model is competitive with the proposed one. The deviation of the prediction by the Weibull model is higher than the Finley and the proposed ones, and this is expected, as, for high creep time; the curve will approach a limiting value for the Weibull model (Equation (12)). Similar is the case with creep data for load1 and load3 (Figures S11 and S12 in Appendix D (Supporting Information)). The values of the adjustable parameters of the Finley and Weibull models are given in Table S1 (Appendix D (Supporting Information)).

6. Conclusion

From the experimental observation of the creep and the subsequent recovery process of a glassy polymer material, it may be concluded the following:

(i) The creep process could be described only by viscoelastic components connected in series, and the number of these components depends on the extent of strain that has been developed. With the appearance of a new component, the parameter-values of the previous components undergo slight changes. Three viscoelastic components appear adequate to describe a long-term creep process. Depending on the relative value of the observation and the relaxation times, the viscoelastic components may seem to be elastic or viscous

(ii) The recovery process is also described by the same three-component viscoelastic model as that for the creep process, but the parameter-values are different for the creep and the recovery processes

(iii) The model parameters evaluated from the creep data predict the recovery process neither in the short-term nor in the long-term aspect, but those estimated from the recovery data reproduce well the late phase of the creep process but fail to do so for the initial phase

(iv) The number of viscoelastic components of a model depends on the creep duration, and that is a barrier to the development of a single model for characterizing the deformation behavior of a polymer material

(v) The model parameters for the creep process depend on the stress value too. But the averaged parameter values could reproduce the creep data within a tolerable range of 10% for a certain stress range with specified creep duration

(vi) The proposed and the Finley models describe the creep data better than the Weibull model. The proposed one is competitive with the Finley model in describing the creep data empirically, but the first distinguishes irrecoverable strain from recoverable one, while the latter fails

Data Availability

Authors can make the data available on request.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Materials

Supporting Information is available. Appendix A shows the thermogravimetric analysis of PVC material. Appendix B includes the method for determining the approximate value of model parameters. Appendix C includes the creep and recovery model validation and the prediction of the one with the parameters obtained from the other for load1 and load3. Appendix D shows the comparison of the proposed model with the Finley and the Weibull models. *(Supplementary Materials)*

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