Supporting Information

Model-based study of creep and recovery of a glassy polymer

*Myisha Ahmed Chowdhury, Md. Mohibul Alam, Md. Mostafizur Rahman, Md. Akhtarul Islam**

Center for Environmental Process Engineering, Department of Chemical Engineering and Polymer Science, Shahjalal University of Science and Technology (SUST), Sylhet-3114, Bangladesh.

*E-mail: mislam@sust.edu

Appendix A Thermogravimetric analysis of PVC composition

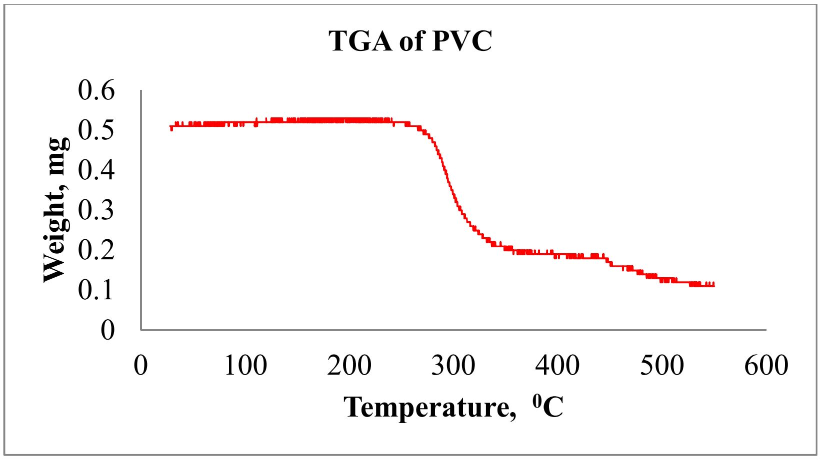


Figure S1: Thermogram of the PVC composition under investigation

Annexure B: Determination of the approximate value of model parameters

Model parameters from creep data

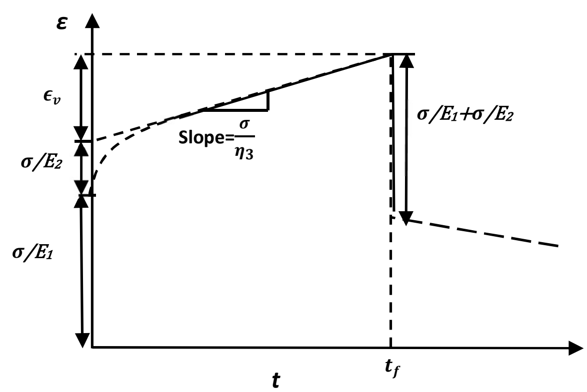


Figure S2: Determination of the model parameters for creep and recovery

The creep curve is idealized in Figure S2 for $t< t_f$. It is assumed that the viscoelastic deformation of the components I & II in Figure 2 is fully developed for the creep time $t=t_f$, but that of the third component is still at the beginning of development. This is equivalent to assume that $t_f/\tau_1\rightarrow\infty$, $t_f/\tau_2\rightarrow\infty$ and $t_f/\tau_3<<1$.

Under these conditions, the deformation components in the creep process (see Equations (12, 13)) are as follows:

$$\varepsilon_{1,f} \approx \varepsilon_{1,\infty} \approx \frac{\sigma}{E_1}, \qquad \varepsilon_{2,f} \approx \varepsilon_{2,\infty} \approx \frac{\sigma}{E_2}, \qquad \text{and } \varepsilon_{3,f} \approx \frac{\sigma}{\eta_3} t \qquad \text{(S1-S3)}$$

The creep curve is extrapolated to the ordinate axis ($t\rightarrow0$) at point C, and an asymptotic is drawn on the creep curve, which intersects the ordinate axis at point B. Referring to Figure S2, the approximate value of E_1 and E_2 are estimated from the Eqs (S1) & (S2) respectively. The value of η_3 is determined from the slope of the asymptote (Eq. (S3)).

The value of E_3 or τ_3 has not been determined from the creep curve. Its approximate value could be determined from recovery data.

Rewriting the Eq. (12) with approximation in Eqs. (S1-S3) and then linearizing one obtains:

$$Y \approx \frac{t}{\tau_2} \quad with\, Y = -ln\left(1 - \frac{\varepsilon - \frac{\sigma}{E_1} - \frac{\sigma}{\eta_3} t}{\frac{\sigma}{E_2}}\right) \qquad \text{(S4)}$$

The Y vs. t plot gives τ_2 (and subsequently η_2).

In expanded view (in the inset of Figure 3), we see that near $t \to 0^+$, there is no instantaneous strain, rather a gradual increase in strain is quite evident (compare the compressed and the expanded view of the initial recovery in Figure 3 in the main text). The value of τ_1 is determined from this section of the curve as follows:

$$\varepsilon_1 = \frac{\sigma}{E_1}\left[1 - \exp\left(-\frac{t}{\tau_1}\right)\right] \tag{S5}$$

Where ε_1 is the strain developed in the first component of the model in Figure 2. The exponential part of Eq. (S5) is expanded in series, and neglecting the second and the higher-order terms, the Eq. (S5) is reduced to

$$\varepsilon_1 \approx \frac{\sigma}{E_1 \tau_1} t = \frac{\sigma}{\eta_1} t \tag{S6}$$

This is equivalent to assume that t and τ_1 are in the same order of magnitude.

The creep data near $t \to 0$ fitted to Eq.(S6) will give η_1. Thus, the approximate values of E_1, η_1, E_2, η_2, and η_3 are determined, but E_3 is not determined yet.

Model parameters from recovery data

The recovery curve is idealized in Figure S2 for $t > t_f$, and it is assumed that the parameter values in the recovery process are the same as those in the creep process. A new strain-axis is drawn at $t = t_f$. Then $(\varepsilon_{1,f} + \varepsilon_{2,f})$ is intercepted from ε_f from the top dropping to the point D, as shown in Figure S2. Now the slope of the line joining the point D and the endpoint of the recovery curve will give the approximate value of τ_3 (see the 3rd component of Eq. (18) and its development below).

$$\varepsilon_{r,3} = \varepsilon_{3,f} \exp\left(-\frac{t_r}{\tau_3}\right) \text{ with } t_r = t - t_f \tag{S7}$$

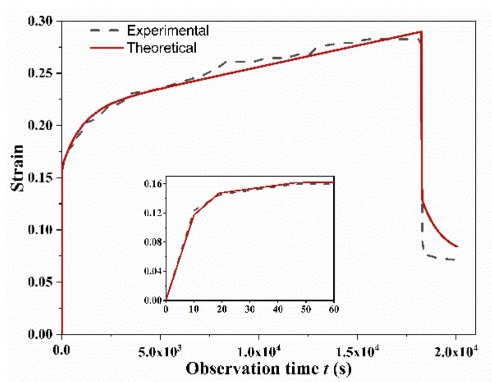
Expanding the exponential term of the Eq. (S7), and neglecting higher-order terms, one obtains

$$\varepsilon_{r,3} = \varepsilon_{3,f}\left(1 - \frac{t_r}{\tau_3}\right) \tag{S8}$$

Thus, a combined (creep and recovery) data treatment approach will give a complete set of parameter-values (E_i, η_i, and/or E_i, τ_i). We shall see in the main text that if the recovery process is monitored at $t = t_f^+$ in expanded view, similar to creep curve at $t = 0^+$, there is no instantaneous recovery, and the recovery of the 1st and the 2nd components of the model (Figure 2 in the main text) proceeds simultaneously, and it is difficult to distinguish them.

One must keep in mind that the values determined by the described method based on idealized curves are highly approximated, but they are a good basis for initiating trial and error method for the determination of the model parameters that would satisfactorily describe both the creep and the recovery data.

Annexure C: Creep and recovery model validation, and the prediction of the one with the parameters obtained from the other



Figures S3: Creep model validation (Eq. (12)) with load1 for $t_f = 333$ min, and an overall view of the prediction of subsequent recovery. In inset: expanded view of creep model validation with initial creep data

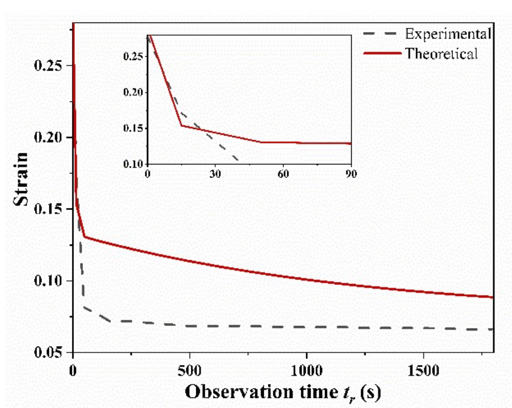


Figure S4: Expanded view of the prediction of the whole recovery curve with the parameters evaluated from the creep curve in Figure S3. In inset: expanded view of the prediction of initial recovery data

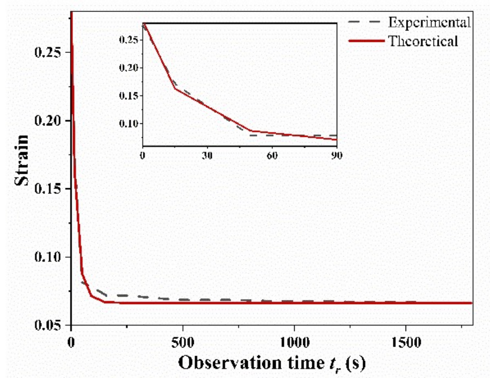


Figure S5: Recovery model validation (Eq. (18)) after withdrawal of the load1 that has acted on the specimen for $t_f \approx$ 333 min. In inset: expanded view of the recovery model validation with initial recovery data

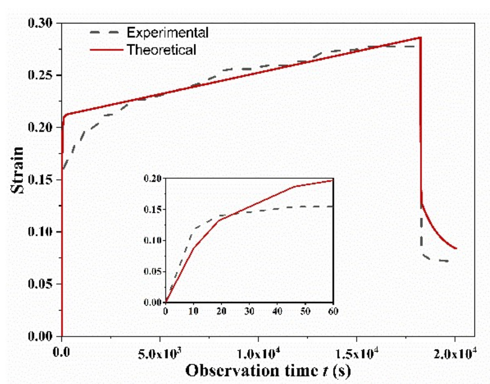
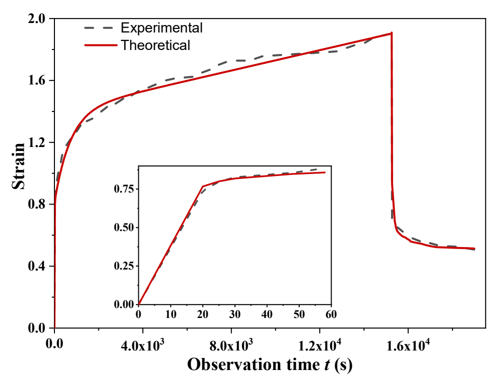


Figure S6: Prediction of the whole creep curve with the parameters evaluated from the recovery curve in Figure S5. In inset: expanded view of the prediction of initial creep data



Figures S7: Creep model validation (Eq. (12)) with load3 for t_f = 300 min, and an overall view of the prediction of subsequent recovery. In inset: expanded view of creep model validation with initial creep data

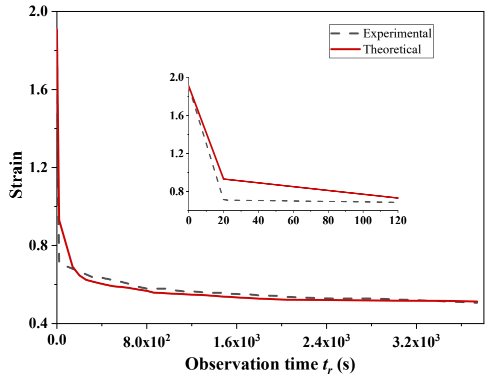


Figure S8: Expanded view of the prediction of the whole recovery curve with the parameters evaluated from the creep curve in Figure S7. In inset: expanded view of the prediction of initial recovery data

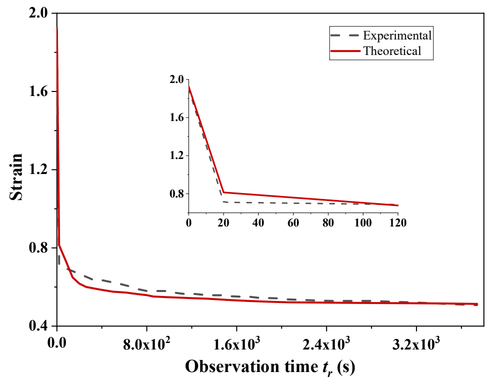


Figure S9: Recovery model validation (Eq. (18)) after withdrawal of the load3 that has acted on the specimen for t_f= 300 min. In inset: expanded view of the recovery model validation with initial recovery data

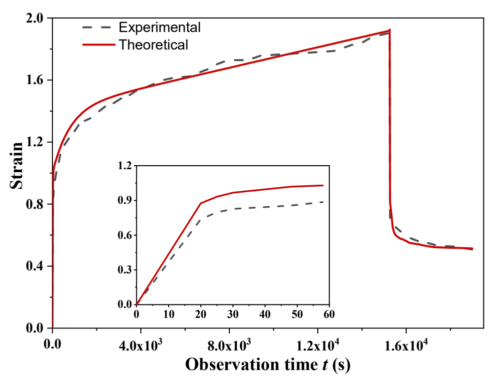


Figure S10: Prediction of the whole creep curve with the parameters evaluated from the recovery curve in Figure S9. In inset: expanded view of the prediction of initial creep data

Annexure D: Prediction of creep process: Proposed model vs. the Finley and the Weibull models

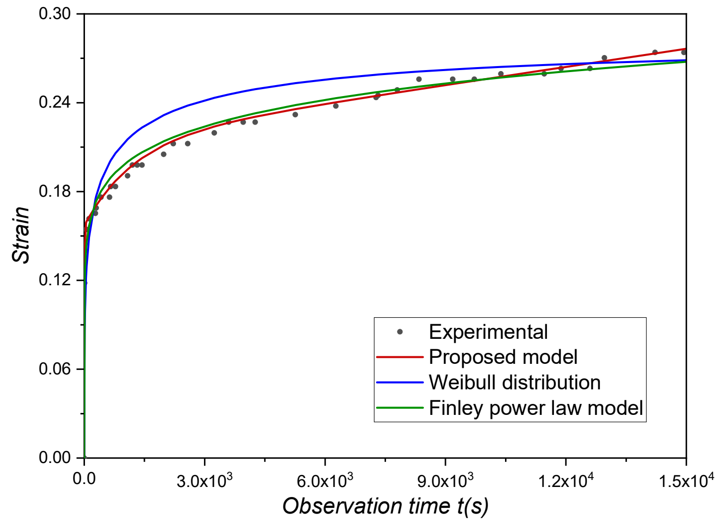


Figure S11 Model validation for creep time 250 min: the Finley and the Weibull models vs. the proposed one for load1

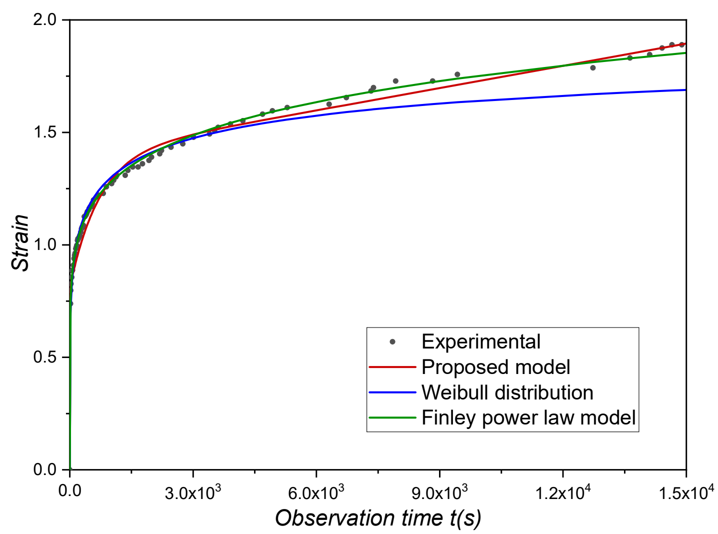


Figure S12 Model validation for creep time 250 min: the Finley and the Weibull models vs. the proposed one for load3

Table S1: Fitted values of the parameters of the Finley and the Weibull models for creep time 250 min

Load designation	Finley model parameters			Weibull model parameters			
	ε_0	A	n	ε_0	ε_u	τ	β
Load1	0	0.09	0.11	0	0.28	299.87	0.30
Load2	0	0.34	0.14	0	1.39	632.80	0.30
Load3	0	0.50	0.14	0	1.91	563.03	0.24