

# Static Creep and Recovery of Filled Elastomers using Thermomechanometry

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The four-element creep model was used to describe the elastic, viscoelastic and viscous behaviour of silica-filled poly(ethylene-co-methyl acrylate). The analysis model used a stretched exponential function provided the elastic modulus, creep modulus and viscosity, recovery modulus, relaxation time and an asymmetry parameter characteristic of the distribution of relaxation times exhibited by polymers. Molecular characteristics that determined creep and relaxation behaviour were molecular structure, crystallinity and dispersed silica.

## 1. Introduction

Creep is an inherent characteristic of polymers due to their random coil molecular conformation[1]. Creep is defined as a change in strain while a material is under a constant stress. Recovery is the change in strain on removal of the force. Creep-recovery experiments can be performed by static force thermomechanometry (sf-TM).

Creep consists of three components: elastic, viscoelastic and viscous strain. The elastic component is instantaneous reversible deformation and the viscoelastic component is time dependant reversible deformation. The viscous component is time dependent irreversible deformation. During the recovery phase, the elastic component recovers instantaneously, then the viscoelastic component.

Creep-recovery properties of a polymeric material are determined by a group of molecular characteristics such molecular structure[2], crosslinks, dispersed filler[3], free volume, entanglements[4] and crystallinity[5]. Crosslinks inhibit creep and assist recovery by constraining molecular motions giving rise to conformational extension.

Various analysis models[6, 7] have been used to determine many characteristics from creep-recovery data. The most widely used model is the four-element model, or Maxwell-Voigt (MV) model. Another model is the Kohlrausch-Williams-Watts (KWW) model[8]. The MV model is used to describe the elastic, viscoelastic and viscous behaviour of polymers by a combination of three terms with an exponential function as the viscoelastic term at a retardation time (the time for the viscoelastic component to recover to 63.21 %, or  $1-1/e$  of its total deformation). For the KWW model, the relaxation time and the asymmetry parameter are characteristic of the distribution of relaxation times exhibited by polymers.

The KWW equation is a stretched exponential function described by a Weibull distribution function. The asymmetry parameter of the stretched exponential function has been physically interpreted to account for not all molecules being able to start relaxing at the same time. The relaxation time is a measure of mobility of molecules, usually above  $T_g$  (Glass transition temperature). The  $\beta$  shape parameter is a measure of asymmetry related to aforementioned material characteristics governing creep-recovery properties.

## 2. Composite preparation

The selected polymers were: poly(ethylene-co-methyl acrylate) (EMA) 9 %wt methyl acrylate (melting temperature 93 °C, density 0.93 g·cm<sup>-1</sup>) in pellet form supplied by Sigma-Aldrich, and Lotryl 18MA02 poly(ethylene-co-methyl acrylate 19 %wt methyl acrylate (melting temperature 87 °C, density 0.93 g·cm<sup>-1</sup>) in pellet form supplied by Arkema Inc. Silica used was Aerosil® 380 hydrophilic fumed silica (average particle diameter 7 nm, density 2.2 g·cm<sup>-1</sup>) supplied by Degussa.

EMA polymers were dissolved in toluene with heating (at 70 °C) and stirred for 10 min. Silica was added to the dissolved polymer in varying volume fractions (1, 5, 10 and 20 %vol), the composites were then ultrasonified for 6 min at a 20 kHz frequency. The EMA-silica dispersions were then poured into a petri dish and left to dry at room temperature for 48 h. Dried composites were then placed into a vacuum oven to remove any residual solvent. Finally, the composites were pressed into films using a hot press at 100 °C.

Static force-thermomechanometry was performed via a Perkin-Elmer Diamond dynamic mechanical analyser.

### 3. Results and discussion

The EMA composites were cut into specimens with shape dimensions of 0.5 x 10 x 8.5 mm<sup>3</sup>. Data were measured in tensile mode using sf-TM with the instrumental parameters, displayed in Table 1 at constant, ambient temperature and atmosphere:

Table 1 Instrumental parameters employed for mf-TM

Instrumental parameters	Value
Initial force	10 mN
Applied force during creep cycle	5000 mN
Creep time	600 s
Recovery time	Creep time × 4 = 2400 s
Number of creep-recovery cycles	4
Deformation geometry	Tensile mode

The resultant creep-recovery data from sf-TM is shown Figures 1 and 2. The higher filled EMA composites (mainly the 10 %wt SiO<sub>2</sub> and 20 %wt SiO<sub>2</sub> composites) demonstrated an increased resistance to creep, while the lower volume fraction filled composites did not. The higher volume fraction composites demonstrated a shorter viscoelastic phase observed in the curved region. The lower volume fraction composites and pure EMA had viscoelastic regions of their creep phase still increasing at the time of removal of applied force.

The higher volume fraction composites showed an almost instantaneous recovery.. The higher volume fraction composites had flat recovery curves indicating the elastic and viscoelastic components recovered rapidly. Conversely, the lower volume fraction composites and pure EMA demonstrated broader curvature in their recovery phase. This was supported by a lack of flatness (the recovery curves had elongated downward trends) in the recovery until the end of the recovery time.

Comparisons between the EMA 9 % MA and EMA 19 % MA composites reveal that EMA 9 % MA composites indicate the EMA 9 % MA composites are stiffer (due to quicker flattening of curves). The EMA 9 % MA composites are expected to be more crystalline. The seemingly higher strain exhibited by the composites EMA 19 wt% MA 5 %vol SiO<sub>2</sub> may be attributed to the complex interactions between the polyethylene, methylacrylate and silica particles. The silica may be interacting more with the methylacrylate than the methylacrylate is interacting with the polyethylene causing what appear to be outstanding results.

The relaxation models that were applied to creep-recovery data are denoted as follows:

Maxwell Voigt Model (creep phase):

$$\varepsilon = \left( \frac{\sigma}{E_1} \right) + \left( \left( \frac{\sigma}{E_2} \right) \times \left( 1 - e^{-\frac{t}{\left( \frac{\eta_2}{E_2} \right)}} \right) \right) + \left( \frac{\sigma}{\eta_3} \right) \quad \text{Equation 1}$$

Where  $\sigma$  is the applied stress,  $E_1$  is the elastic modulus,  $E_2$  and  $\eta_2$  are the viscoelastic modulus,  $t$  is time and  $\eta_3$  is the viscous modulus. The term  $\eta_2 / E_2$  is equal to  $\tau$ , the retardation time.

Kohlrausch-Williams-Watts Model (recovery phase):

$$\phi(t) = A \times e^{\left[ -\left(\frac{t}{\tau}\right)^\beta \right]}$$

Equation 2

Where  $A$  is a pre-exponential value (initial instantaneous strain on recovery after creep[9]),  $t$  is time,  $\tau$  is the relaxation time and  $\beta$  is the shape fitting parameter.

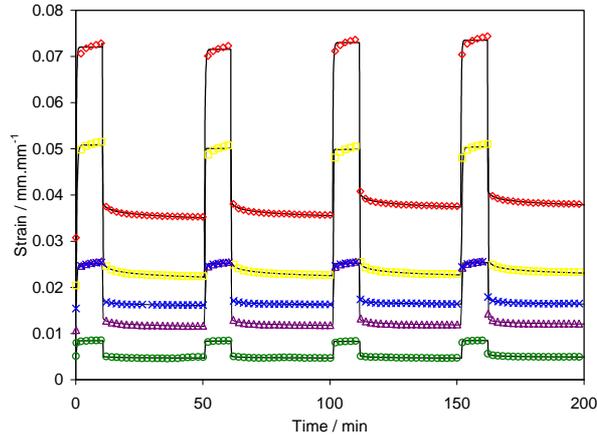


Figure 1 Creep-recovery analysis of EMA 9 wt% MA composites where: EMA 9 wt% MA (-◇-); EMA 9 wt% MA 1 %vol SiO<sub>2</sub> (-□-); EMA 9 wt% MA 5 %vol SiO<sub>2</sub> (-△-);EMA 9 wt% MA 10 %vol SiO<sub>2</sub> (-×-); EMA 9 wt% MA 20 %vol SiO<sub>2</sub> (-○-). Solid lines in creep phase represent MV model fit, while solid lines in recovery phase represent KWW model fit.

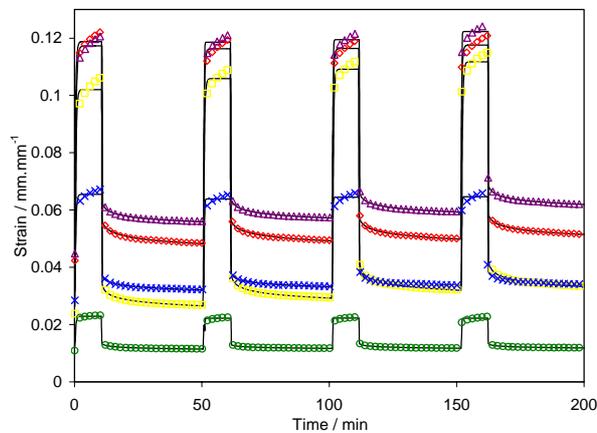


Figure 2 Creep-recovery analysis of EMA 19 wt% MA composites where: EMA 19 wt% MA (-◇-); EMA 19 wt% MA 1 %vol SiO<sub>2</sub> (-□-); EMA 19 wt% MA 5 %vol SiO<sub>2</sub> (-△-);EMA 19 wt% MA 10 %vol SiO<sub>2</sub> (-×-); EMA 19 wt% MA 20 %vol SiO<sub>2</sub> (-○-). Solid lines in creep phase represent MV model fit, whilst solid lines in recovery phase represent KWW model fit)

The resultant variables from applying the MV model to the first cycle of the creep-recovery analysis are seen in Table 2. There was a general increase in the  $E_1$ ,  $E_2$  and  $\eta_2$ , and  $\eta_3$  variables, and a slight decrease in retardation time with increasing silica content indicating a more solid like response. The modulus values obtained for the EMA 9% MA composites were in general higher than their EMA 19% MA composite counterparts, whilst retardation times for the EMA 19% MA composites were slightly higher. With regard to fitting the KWW function, the pre-exponential variable decreased with increasing silica content as did the relaxation time. To account for the slight decrease in  $\tau$ , the  $\beta$  shape parameter changes between each fitted relaxation curve. The  $\beta$  variable can be influenced by various composite properties as mentioned

previously. All of these results are indicators of the composites having restricted flow, hence higher number of crosslinks.

Table 2 Parameters from application of the MV model to creep data in the first cycle of creep-recovery analysis of the EMA 9 % and 19 % MA composites

MA %	SiO <sub>2</sub> %vol	E <sub>1</sub> Pa	E <sub>2</sub> Pa	η <sub>2</sub> Pa·s	η <sub>3</sub> Pa·s	t s
9	0	0.57 × 10 <sup>8</sup>	0.59 × 10 <sup>8</sup>	7.78 × 10 <sup>8</sup>	3.58 × 10 <sup>10</sup>	13
	1	0.59 × 10 <sup>8</sup>	0.73 × 10 <sup>8</sup>	14.55 × 10 <sup>8</sup>	4.42 × 10 <sup>10</sup>	20
	5	1.11 × 10 <sup>8</sup>	1.21 × 10 <sup>8</sup>	24.18 × 10 <sup>8</sup>	7.51 × 10 <sup>10</sup>	20
	10	2.21 × 10 <sup>8</sup>	1.16 × 10 <sup>8</sup>	21.96 × 10 <sup>8</sup>	6.83 × 10 <sup>10</sup>	19
	20	4.49 × 10 <sup>8</sup>	2.80 × 10 <sup>8</sup>	44.80 × 10 <sup>8</sup>	18.17 × 10 <sup>10</sup>	16
19	0	0.47 × 10 <sup>8</sup>	0.28 × 10 <sup>8</sup>	6.13 × 10 <sup>8</sup>	2.60 × 10 <sup>10</sup>	22
	1	0.63 × 10 <sup>8</sup>	0.20 × 10 <sup>8</sup>	4.17 × 10 <sup>8</sup>	3.50 × 10 <sup>10</sup>	21
	5	0.39 × 10 <sup>8</sup>	0.26 × 10 <sup>8</sup>	6.72 × 10 <sup>8</sup>	1.95 × 10 <sup>10</sup>	7
	10	0.45 × 10 <sup>8</sup>	0.38 × 10 <sup>8</sup>	7.59 × 10 <sup>8</sup>	2.25 × 10 <sup>10</sup>	7
	20	1.55 × 10 <sup>8</sup>	1.55 × 10 <sup>8</sup>	29.51 × 10 <sup>8</sup>	9.09 × 10 <sup>10</sup>	5

#### 4. Conclusion

The synthesised composites were analysed via sf-TM employing creep-recovery experiment where elastic, viscoelastic and viscous contributions to the strain were resolved. The creep and recovery data were successfully fitted using a four-element model (Maxwell-Voigt) and an extended model that included a stretched exponential function (Kohlrausch-Williams-Watts Model) to describe the distribution of relaxation times exhibited by polymers. Though the filler reduced creep, the relaxation times for recovery were faster. Increases in all resolved moduli were observed with increasing silica content.

#### 5. References

1. Menard, K.P., *Dynamic Mechanical Analysis - A Practical Introduction*. 1999: CRC Press LLC.
2. Ghannam, M.T., *Creep-recovery experimental investigation of crude oil-polymer emulsions*. Journal of Applied Polymer Science, 2004. **92**(1): p. 226-237.
3. Adalja, S.B. and J.U. Otaigbe, *Creep and recovery behavior of novel organic-inorganic polymer hybrids*. Polymer Composites, 2002. **23**(2): p. 171-181.
4. Bartzczak, Z., *Effect of Chain Entanglements on Plastic Deformation Behavior of Linear Polyethylene*. Macromolecules, 2005. **38**(18): p. 7702-7713.
5. Kolarik, J. and A. Pegoretti, *Non-linear tensile creep of polypropylene: Time-strain superposition and creep prediction*. Polymer, 2006. **47**(1): p. 346-356.
6. Nordin, L.-O. and J. Varna, *Methodology for Parameter Identification in Nonlinear Viscoelastic Material Model*. Mechanics of Time-Dependent Materials, 2006. **9**(4): p. 259-280.
7. Marais, C. and G. Villoutreix, *Analysis and modeling of the creep behavior of the thermostable PMR-15 polyimide*. Journal of Applied Polymer Science, 1998. **69**(10): p. 1983-1991.
8. Mano, J.F. and J.L. Gomez Ribelles, *Mechanical Spectroscopy Studies on a Side-Chain Liquid Crystalline Polysiloxane. Comparison with Dielectric and DSC Data*. Macromolecules, 2003. **36**(8): p. 2816-2824.
9. Fancey, K.S., *A latch-based Weibull model for polymeric creep and recovery*. Journal of Polymer Engineering, 2001. **21**(6): p. 489-509.