Relaxation Models Applied to Modulated Force Thermomechanometry of a Silica Filled Flexible Polymer

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Relaxation of silica-poly(ethylene-co-methyl acrylate) composites was measured using modulated force thermomechanometry. Isothermal frequency dependant storage and loss modulus data were described using Debye, Cole-Cole, Cole-Davidson, and Havriliak-Negami models. Terminal and plateau responses were predicted by the Havriliak-Negami model. Superposition of frequency-modulus data at a series of temperatures was performed using the Williams-Landel-Ferry principle to provide data extending into the terminal and plateau frequency regions.

1. Introduction

The relaxation time of a polymer composition is the time-dependent molecular response of that system to an external stimulus. Relaxation times depend upon the morphological scale and measurement technique. Relaxation times derived from mechanical analysis are often obtained by application of a static force. Under static deformation, an empirical measure of a relaxation time is the time for the strain to recover to 0.3679 ($=1/e$) of the maximum strain[1]. Alternative measures of relaxation time are obtained by fitting data to various relaxation models. Relaxation times for static force data are available from the Kohlrausch-Williams-Watts[2] and Maxwell, Voigt models[3]. Relaxation times for modulated force data are available from the Debye[4], Cole-Cole[5], Cole-Davidson[6], and Havriliak-Negami[7] models. The aim of this research was to describe the dynamic relaxation of polymer-silica nanocomposites using various models. Objectives were to construct Time–Temperature–Superposition[8] (TTS) mastercurves, fit the mastercurve data to Debye, Cole-Cole, Cole-Davidson and Havriliak-Negami equations and to interpret the results in terms of macromolecular motions and polymer-filler interactions (there may be filler-filler interactions, but these forces may not be applicable within the linear viscoelastic region). The measurements used an applied force with sinusoidal modulation, with frequency and temperatures as complementary variables.

2. Sample preparation

The two selected EMA polymers were: poly(ethylene-co-methyl acrylate) 9 %wt methyl acrylate (hardness 35-40 Shore D, melting temperature 93 °C, density 0.93 g·cm^{-1}) in pellet form supplied by Sigma-Aldrich, and Lotryl 18MA02 poly(ethylene-co-methyl acrylate) 19 %wt methyl acrylate (hardness 83 Shore A, metling temperature 87 °C, density 0.93 g·cm^{-1}) in pellet form supplied by Arkema Inc. Silica used were Aerosil® 380 hydrophilic fumed silica (average particle diameter 7 nm, density 2.2 g·cm^{-1}) supplied by Degussa.

EMA polymers were dissolved in toluene with heating (at 70 °C) and stirred with a magnetic stirrer for 10 min. Silica was added to the dissolved polymer in varying volume fraction (1, 5, 10 and 20 %vol)which then ultrasonfication for 6 min at a 20 kHz frequency. The ultrasonicated, dissolved EMA-silica mixtures 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 via hot press at 100 °C.

Measurements were performed using modulated force thermomechanometry (mf-TM) alternatively called dynamic mechanical analysis (DMA) or dynamic mechanical spectroscopy (DMS). Measurements were performed in tensile mode using rectangular polymer specimens, 0.5 x 10 x 15 mm^3, under dry nitrogen purge, at the frequencies and temperatures shown in Table 1. Storage modulus (E′, in-phase), loss modulus (E″, out-of-phase) and the ratio E″/E′ = tan(δ) were the frequency–temperature dependant variables.

Table 1 Instrumental parameters employed for mf-TM

Instrumental parameters	Value
Strain amplitude value	20 m
Minimum tension force	0.01 mN
Tension force gain	1.5
Force amplitude default value	100 mN
Atmosphere	Dry nitrogen purge
Deformation geometry	Tensile mode
Analysed frequencies	0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 100 Hz
Heating program	Isothermal-step mode
Temperature range	-80 – 60 °C with 10 °C increments

3. Results

It was found that with increasing silica content, the storage and loss moduli increased. Isothermal frequency sweeps where converted into mastercurves via the time-temperature superposition principle. This is the principle whereby high temperature analysis is equated to low frequency and low temperature analysis is equated to high frequency analysis. Mastercurves were created by shifting isothermal frequency curves along a horizontal, log(frequency) axis in relation to a reference temperature (for this research, the reference temperature was 20 °C). Once all isothermal frequency data has been shifted by a shift factor, a_T, only a single mastercurve remains. The Williams Landel Ferry (WLF) model was used to relate shift factors to temperature for each composite. The resultant mastercurves predict the material response to frequencies extended beyond its normal frequency analysis range.

Dynamic relaxation models were applied to these mastercurves to determine the infinite and zero modulus (E_∞ and E_0 respectively) and the relaxation time. The models applied were:
Debye (D) Model

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty} = \frac{1}{1+i\omega\tau}$$ **Equation 1**

Cole-Cole (CC) Model

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty} = \frac{1}{1+(i\omega\tau)^\alpha}$$ **Equation 2**

Cole-Davidson (CD) Model

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty} = \frac{1}{(1+(i\omega\tau))^\beta}$$ **Equation 3**

Havriliak-Negami (HN) Model

$$\frac{\varepsilon^*(\omega)-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty} + \frac{1}{(1+(i\omega\tau)^\alpha)^\beta}$$ **Equation 4**

It was found that the HN model fitted the mastercurve data most accurately, followed by the CC, CD and finally D models. The accuracy of the HN model can be attributed to it having two shape parameters effecting both the symmetry and skewness of the fitting curve. The accuracy of the fitting curves was determined by the Wicket error function, which is

$$f = \frac{\sum_{E'} \left| \log\left(\tan(\delta)_{exp}\right) - \log\left(\tan(\delta)_{calc}\right) \right|^2}{\sum_{E'} \left| \log\left(\tan(\delta)_{exp}\right) \right|^2}$$

Equation 5

Where $\tan(\delta)_{exp}$ is the experimentally determined loss factor and $\tan(\delta)_{calc}$ is the calculated loss factor derived from the fitted relaxation models. For this function, the closer the error value to zero, the more accurate is the fitting. From the Wicket error figures displayed in Table 2, it can be seen generally the HN model is by far the best fitting model, with the CC model next, then the CD model and finally the D model.

Table 2 Wicket errors for relaxation models fitted to experimental data

MA %	SiO$_2$ %vol	D model	CC model	CD model	HN model
9	0	6.42	0.49	0.56	0.32
	1	3.07	0.65	0.77	0.038
	5	2.30	1.09	0.77	0.089
	10	3.06	0.34	0.55	0.066
	20	8.70	0.48	1.11	0.35
19	0	11.65	4.24	9.96	0.21
	1	10.08	4.06	6.41	0.26
	5	15.53	2.84	8.88	0.35
	10	14.80	1.12	3.563	0.18
	20	8.18	0.58	1.31	0.18

Figure 1 is a typical representation of fitting the relaxation models to mastercurve data, in this case the data are fitted by the Cole-Cole plot of EMA 9 % MA mastercurve data.
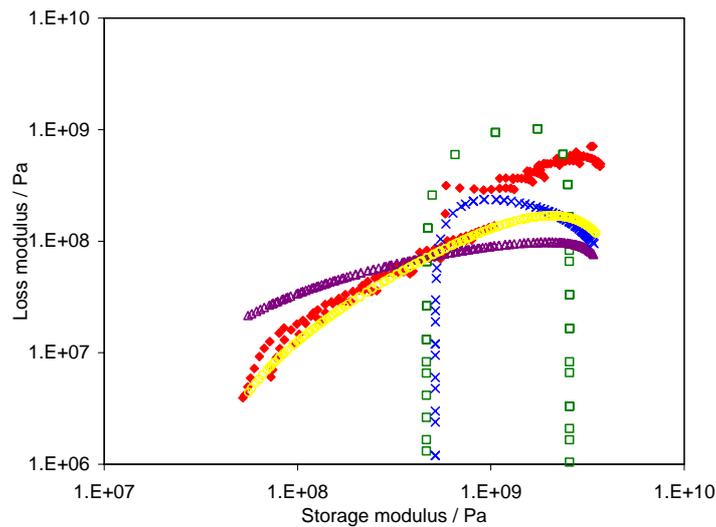

Figure 1 Relaxation models fitted to Cole-Cole plot of mastercurve data for EMA 9 % MA (-◆-) with: Debye model (-□-); Cole-Cole model (-△-); Cole-Davidson model (-×-); Havriliak-Negami model (-○-).

Patterns were observed in the fitting curves. In each model, the relaxation time increased with increasing silica content. This is attributed to the increasing stiffness of the

filled EMA. The infinite and zero moduli increased with increasing silica content. However the increase in infinite modulus between the 10 %vol SiO_2 and 20 %vol SiO_2 composites was small as the composites were approaching their terminal E_0 value. As the mastercurve approaches higher frequencies, the filler effect on the EMA is less noticeable. This is seen in the relaxation model fits where the infinite modulus values change little at higher volume fractions of SiO_2 (i.e. they plateau). These high frequencies equate to low temperatures where little molecular and segmental rotation could occur in the EMA regardless of filler content. The zero modulus is a better measure of the filler effect on the EMA since it is at low frequencies which are equivalent to high temperatures. At higher temperatures, molecular and segmental rotation can occur, therefore the effect of the physical crosslinks created by the SiO_2 can be better observed in the zero modulus. This accounts for the larger increase in zero modulus with subsequent additions of SiO_2 compared with the infinite modulus.

4.   Conclusion

Superposition of frequency and temperature based on the Williams-Landel-Ferry (WLF) principle provided data extending into the terminal and plateau regions. Modulus data were fitted to the frequency dependent models mentioned above. The Havriliak-Negami model provided the best fit of the data. Molecular relaxation times were obtained and the equations allowed the data to be extrapolated to low (terminal region) and high (plateau region) frequencies The relaxation time was found to shorten with increasing filler content while the zero and infinite moduli were found to increase. There was a larger increase in the zero modulus due to it being at lower frequencies equating to higher temperatures where molecular and segmental rotation can occur.

5.   References

1.   Menard, K.P., *Dynamic Mechanical Analysis - A Practical Introduction*. 1999: CRC Press LLC.
2.   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.
3.   Genovese, A. and R.A. Shanks, *Time-temperature creep behaviour of poly(propylene) and polar ethylene copolymer blends.* Macromolecular Materials and Engineering, 2007. **292**(2): p. 184-196.
4.   Debye, P., *Polar Molecules*. 1929: The Chemical Catalog Company, Inc.
5.   Cole, K.S. and R.H. Cole, *Dispersion and absorption in dielectrics. I. Alternating-current characteristics.* Journal of Chemical Physics, 1941. **9**: p. 341-51.
6.   Davidson, D.W. and R.H. Cole, *Dielectric relaxation in glycerol.* Journal of Chemical Physics, 1950. **18**: p. 1417.
7.   Havriliak, S. and S. Negami, *A complex plane analysis of a-dispersions in some polymer systems.* Polymer Preprints (American Chemical Society, Division of Polymer Chemistry), 1965. **6**(2): p. 818-22.
8.   Williams, M.L. and J.D. Ferry, *Dynamic mechanical properties of polyvinyl acetate.* Journal of Colloid Science, 1954. **9**: p. 479-92.