Predicting the high strain rate behaviour of particulate composites using time-temperature superposition based modelling

Akash R Trivedi[*] and *Clive* R Siviour

Department of Engineering Science, University of Oxford, Parks Road, Oxford, OX1 3PJ, UK

Abstract. Polymeric particulate composites are widely used in engineering systems where they are subjected to impact loading – at a variety of temperatures – leading to high strain rate deformation. These materials are highly rate and temperature dependent, and this dependence must be well understood for effective design. It is not uncommon for many of these materials to display mechanical responses that range from glassy and brittle to rubbery and hyperelastic [1-3], due to their polymeric constituents. This makes accurate measurements and modelling not only necessary, but challenging. This is made more difficult by experimental artefacts present when traditional tools such as the split Hopkinson pressure (SHPB) or Kolsky bar are used to interrogate the high rate response of low-impedance materials. The transition from isothermal to adiabatic conditions as the rate of deformation increases also has an effect on the mechanical response, which cannot be neglected if the high rate behaviour is to be accurately predicted. In this paper, time-temperature superposition based frameworks that have enabled the high rate behaviour of neoprene rubber [4] and (plasticised) poly(vinyl chloride) [5] to be captured, will be extended to explore the high strain rate behaviour of unfilled natural rubber and several grades of glass microsphere filled natural rubber particulate composites.

1 Introduction

Particulate composites are commonplace in Engineering applications, ranging from concrete used in construction through to polymer bonded explosives (PBX) used in advanced weapons systems [6,7]. As in these examples, the filler may enhance the mechanical properties of the material, or the overall material may be designed to transport the filler itself. These composites are often used in systems where they can be subjected to impact loading, leading to high rate deformation, at a variety of temperatures. When the matrix constituent in these composites is a polymer, the overall behaviour is likely to be highly temperature and rate dependent. This makes characterisation and modelling challenging, but also necessary.

One of the standard tools to measure the high rate response of materials is the split-Hopkinson pressure bar (SHPB, also known as the Kolsky bar [8]). However, at high strain rates (> c.10 s^{-1}), characterising the behaviour of low-impedance materials becomes

---

[*] Corresponding author: akash.trivedi@eng.ox.ac.uk

increasingly difficult. The main challenges are low wave-speeds leading to a time to static stress equilibrium on the order of the experimental duration [9], and experimental signals from which force is calculated are too small to measure accurately [10]. In the past, these challenges have been overcome with modifications including pulse-shaping to change the incident stress wave, reduced cross-section bars [10], piezoelectric pressure transducers [11], or through the use of full-field, time-resolved displacement measurements [12].

In this paper, we present our novel methodology in which the behaviour at high rates will be explored using modelling frameworks calibrated with data obtained from simple, low rate experiments. An advantage of focusing on lower strain rate experiments to understand the high rate behaviour (either through experimental simulations [13,14] or calibrated models [4,5]) is that a wider range of diagnostic tools may be used to interrogate the mechanical response (e.g. Scanning Electron Microscope, X-ray tomography, etc.)

2 Material

In previous studies [1,14], temperature and rate dependence has been explored through the use of model materials. In this paper, unfilled and glass microsphere filled natural rubbers are used to investigate these dependences in low-impedance particulate composites. Despite being model materials for this project, filled and unfilled natural rubber (F/U-NR) are used extensively in industrial applications such as energy absorbers, vibration dampers and seals. Here, they also experience high rate deformation at a variety of temperatures.

Natural rubber forms the basis of the EDS 19 grade used in this study. Plates measuring $230 \times 230 \times 5$ mm were manufactured at the Tun Abdul Razak Research Centre in Hertfordshire, UK. The full formulation can be found in [15]. To make the F-NR composites, glass microspheres (from Blagden Specialty Chemicals) were mixed homogenously into the EDS 19 gum prior to curing. Two grades of spheres were used with an order of magnitude difference in the mean particle size. Basic properties of these constituent materials can be found in Table 1. With each grade of spheres, two sets of composites were produced, with a 5% and 50% volume filler fraction. These F-NRs are depicted diagrammatically in Figure 1.

Table 1. Material properties for the composite constituents.

Material	Density (kg m^{-3})	Elastic Modulus (MPa)	Mean particle size (µm)	Particle range (µm)
EDS 19 (U-NR)	966	0.52 (23 °C, 2% strain, 0.1 Hz)	N/A	N/A
Spheriglass 2429	1570	69,000	70-100	53-106
Spheriglass 5000	1620	69,000	7-10	7-10
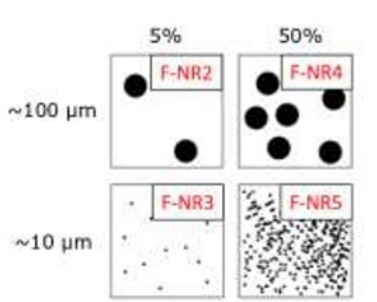
Figure 1. Schematic diagram of the different grades of F-NR composites.

3 Experiments

The modelling framework is calibrated with data from simple thermomechanical characterisation experiments and low rate compression data. High rate compression data are then used to validate the model's predictive capability. Dynamic Mechanical Analysis (DMA) experiments form the basis of the time-temperature superposition method, allowing the modulus at an ambient reference temperature to be obtained for a wide range of frequencies. The Cox-Merz rule [16] can then be used to infer the rate dependence of the modulus. Modulated Differential Scanning Calorimetry (MDSC) experiments allow the temperature dependent heat capacity to be obtained, and subsequently used in the estimation of the expected temperature rise due to adiabatic self-heating. This is observed at high strain rates as the heat generated from plastic work cannot diffuse out of the specimen on the duration of the experiment. This phenomenon needs to be integrated into the modelling framework as it can lead to the thermal softening of the mechanical response.

3.1 Dynamic Mechanical Analysis (DMA)

For each material, isothermal frequency sweeps were performed on a TA Instruments Q800 in single cantilever configuration with specimens measuring $5 \times 2 \times 40$ mm. At each temperature step, seven frequencies were tested, comprising three values per decade of frequency. The duration of these experiments is considerable, and because of technical limitations preventing the DMA cooling apparatus being used continuously for more than 5 days, two sets of DMA experiments were performed for each material: from -80 to -40 °C and from -50 °C to +40 °C. The results were subsequently stitched together.

Using the frequency dependent (storage) modulus data for each isotherm, a suitable time-temperature superposition (TTS) algorithm can be employed to construct a master curve showing the modulus dependence for a given reference temperature over a wide range of frequencies. In this study, the algorithm presented in [5] is used. Figure 2a shows the master curve for each grade of rubber at a reference temperature of 25 °C.

3.2 Uniaxial compression

Uniaxial compression experiments were performed at varying strain rates and varying temperatures on right circular cylinders of 5 mm diameter and length. This dimension was chosen to reduce the inertial stress contributions at high rates [17]. Varying rate experiments at 25 °C (Figure 2b) were conducted on the Instron 5980 universal testing machine ($10^{-3} - 10^{-1}$ s^{-1}), hydraulic press ($1 - 100$ s^{-1}) and the SHPB (c.10^{3} s^{-1}), which was also used in a Direct Impact Hopkinson pressure bar (DIHPB) configuration to facilitate larger strains. Varying temperature experiments at 10^{-2} s^{-1} (Figure 2c) were conducted using a 3119-600 Series environmental chamber. Each sample was held at temperature for 30 minutes to ensure thermal stability.

(a)
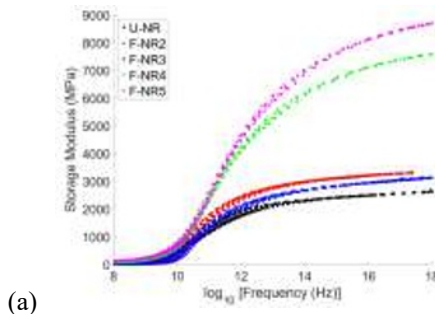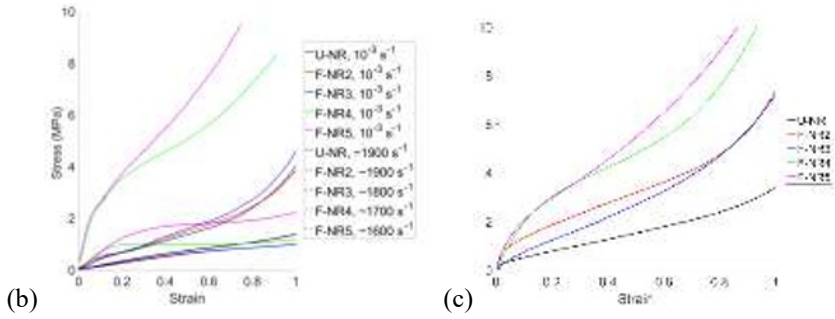
Figure 2. (a) Master curve for each material generated at a reference temperature of 25 °C. (b) Highlighting selected varying strain rate experiments at 25 °C and (c) low temperature experiments at -40 °C and 10^{-2} s^{-1}.

4 Modelling Framework

In our previous research, time-temperature superposition based frameworks have been applied to capture the high rate behaviour of neoprene rubber [4] and predict the high rate behaviour of (plasticised) poly(vinyl chloride) [5]. In this paper, by observing the rate-temperature equivalence in experimental stress-strain results, it is shown that the ambient, high rate response of both U-NR and F-NR particulate composites can be predicted, with model parameters solely calibrated with simple experiments at low rates.

The varying rate data in Figure 2b represent hyper-viscoelastic behaviour: low-strain viscoelasticity, followed by large-strain hardening. For this reason, a constitutive model was used where the overall stress is the sum of the viscoelastic and the hyperelastic components: $\sigma = \sigma_v + \sigma_h$. The viscoelastic stress was obtained by fitting Prony series models to the master curves shown in Figure 2a and subsequently using the Boltzmann superposition principle:

$$\sigma_v(t) = \int_{-\infty}^{t} E(t - \zeta)\, \dot{\varepsilon}(\zeta) d\zeta \qquad (1)$$

where $E(t)$ is the modulus as obtained from the Prony series and $\dot{\varepsilon}(\zeta)$ is constant. The hyperelastic stress was captured with a one-term Ogden model:

$$\sigma_h(t) = \frac{2\mu}{\alpha}\left(e^{\alpha \dot{\varepsilon} t} - e^{-\frac{1}{2}\alpha \dot{\varepsilon} t}\right) \qquad (2)$$

where the strain rate is constant and the value of μ in this research was fixed using the simple relation $\mu = E_\infty / 3$ (E_∞ is the long-term rubbery modulus, obtained also from the results of the DMA experiment). A strain activated damage model [1,18] was incorporated to this basic framework to allow the behaviour of the composites to be predicted. The damage is expressed as is a function of the input mechanical energy, w, and its effect on the mechanical response is modelled is using the following expression:

$$E_d = (E_c - E_r)\left[1 - \exp\left(-\frac{w_0}{w}\right)\right] + E_r \qquad (3)$$

where E_d is the damaged modulus, E_c is the relaxation modulus of the composite, E_r is the residual modulus of the damaged material, and w_0 is the activation energy for damage. Where the U-NR stress response is simply the sum of the expressions in Equations 1 and 2, the F-NR

behaviour is captured by applying this continuum damage model across both viscoelastic and hyperelastic stress branches.

In this model, there are four parameters that need to be calibrated: the hyperelastic convexity, α; the composite modulus, E_c; the residual modulus, E_r; and the damage activation energy, w_0. To make the model predictive with respect to the high rate behaviour, the four parameters were calibrated with the results of ambient and low-temperature compression experiments. To optimise the quasi-static calibration of parameters, α and E_r were calibrated with low temperature experiments whereas E_c and w_0 were calibrated under ambient conditions. In future iterations, E_c will be taken directly from the DMA results. Predictions of the high rate behaviour are compared to the experimental data are in Figure 3. For the U-NR, there is a slight under-prediction of the stress, however the general trend is well captured. The stress response for the 5% F-NR composites are excellently predicted, but the larger strain response for the 50% F-NRs is lower than expected. These are promising results, but there is room for improvement.
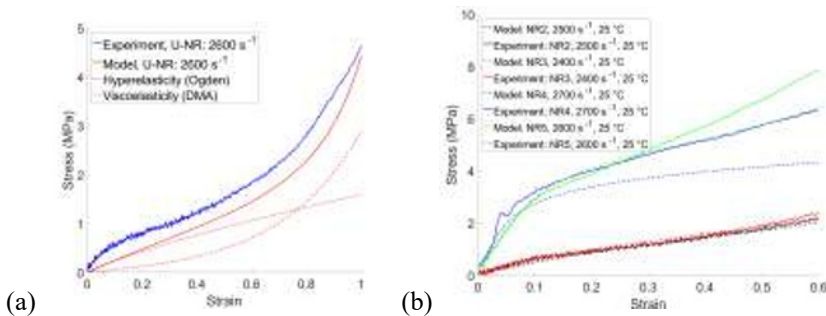
Figure 3. Comparing model predictions with experimental data for (a) unfilled natural rubber (U-NR) and (b) the four grades of filled particulate composites (F-NR).

5 Conclusions

This paper has shown that a damage augmented hyper-viscoelastic model can be calibrated using simple, low-rate data and subsequently used to predict the high-rate response of both unfilled and filled natural rubber particulate composites. Improvements to the modelling approach can be made by using the results of DMA experiments to obtain the composite modulus directly, examining samples *post-mortem* to improve damage definitions, and allowing the predictive capability to extend to simulations below the glass transition of the rubber. In future, the development of modelling strategies presented here will form a good foundation for further investigations of filled and unfilled polymers.

6 Acknowledgements

References

1. C. Siviour, P. Laity, W. Proud, J. Field, D. Porter, P. Church, P. Gould, and W. Huntingdon-Thresher, *High Strain Rate Properties of a Polymer-Bonded Sugar: Their Dependence on Applied and Internal Constraints*, Proc. R. Soc. A Math. Phys. Eng. Sci. **464**, 1229 (2008).

2. P. J. Rae and D. M. Dattelbaum, *The Properties of Poly(Tetrafluoroethylene) (PTFE) in Compression*, Polymer. **45**, 7615 (2004).

3. E. N. Brown, P. J. Rae, and E. B. Orler, *The Influence of Temperature and Strain Rate on the Constitutive and Damage Responses of Polychlorotrifluoroethylene (PCTFE, Kel-F 81)*, Polymer. **47**, 7506 (2006).

4. A. R. Trivedi and C. R. Siviour, *A Simple Rate–Temperature Dependent Hyperelastic Model Applied to Neoprene Rubber*, J. Dyn. Behav. Mater. **6**, 336 (2020).

5. A. R. Trivedi and C. R. Siviour, *A Novel Methodology for Predicting the High Rate Mechanical Response of Polymers from Low Rate Data: Application to (Plasticised) Poly(Vinyl Chloride)*, Mech. Time-Dependent Mater. **1** (2020).

6. D. M. Williamson, C. R. Siviour, W. G. Proud, S. J. P. Palmer, R. Govier, K. Ellis, P. Blackwell, and C. Leppard, *Temperature–Time Response of a Polymer Bonded Explosive in Compression (EDC37)*, J. Phys. D. Appl. Phys. **41**, 085404 (2008).

7. D. R. Drodge, D. M. Williamson, S. J. P. Palmer, W. G. Proud, and R. K. Govier, *The Mechanical Response of a PBX and Binder: Combining Results across the Strain-Rate and Frequency Domains*, J. Phys. D. Appl. Phys. **43**, (2010).

8. H. Kolsky, *An Investigation of the Mechanical Properties of Materials at Very High Rates of Loading*, Proc. Phys. Soc. Sect. B **62**, 676 (1949).

9. G. T. (Rusty) Gray III and W. R. Blumenthal, *Split-Hopkinson Pressure Bar Testing of Soft Materials*, ASM Handbook Volume 8, Mechanical Testing and Evaluation (ASM International) (2000).

10. W. Chen, B. Zhang, and M. J. Forrestal, *A Split Hopkinson Bar Technique for Low Impedance Materials*, Exp. Mech. **39**, 81 (1999).

11. M. J. Kendall, D. R. Drodge, R. F. Froud, and C. R. Siviour, *Stress Gage System for Measuring Very Soft Materials under High Rates of Deformation*, Meas. Sci. Technol. **25**, 075603 (2014).

12. F. Pierron and M. Grédiac, *Towards Material Testing 2.0. A Review of Test Design for Identification of Constitutive Parameters from Full-Field Measurements*, Strain **57**, 12370 (2020).

13. M. J. Kendall and C. R. Siviour, *Experimentally Simulating Adiabatic Conditions: Approximating High Rate Polymer Behavior Using Low Rate Experiments with Temperature Profiles*, Polym. (United Kingdom) **54**, 5058 (2013).

14. M. J. Kendall and C. R. Siviour, *Experimentally Simulating High Rate Composite Deformation in Tension and Compression: Polymer Bonded Explosive Simulant*, J. Dyn. Behav. Mater. **1**, 114 (2015).

15. MRPRA, Natural Rubber Engineering Data Sheet - EDS 19, 1980.

16. W. P. Cox and E. H. Merz, *Correlation of Dynamic and Steady Flow Viscosities*, J. Polym. Sci. **28**, 619 (1958).

17. D. A. Gorham, *The Effect of Specimen Dimensions on High Strain Rate Compression Measurements of Copper*, J. Phys. D. Appl. Phys. **24**, 1489 (1991).

18. R. Cornish, D. Porter, P. Church, P. Gould, T. Andrews, B. Proud, D. Drodge, and C. Siviour, *Comparison of Porter-Gould Constitutive Model with Compression Test Data for HTPB/SUGAR*, in *AIP Conference Proceedings*, Vol. 955 (2007), pp. 777–780.