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Properties of particulate composites: time-temperature effects

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14. ABSTRACT
This project made major contributions to our overarching research goal that the response of low modulus materials to deformations at high strain rates be predicted from experiments per-formed exclusively under low rate loading. In particular, we produced experimental data and modelling frameworks that demonstrate the feasibility of that goal. Further, we designed novel methods for direct measurements of the high rate response, enabling, for the first time, high frequency shear moduli to be measured experimentally. These developments are important for better use of low modulus polymer materials, for example in polymer bonded explosives, pot-ting compounds for protection of electronics in extreme environments, and personal protective equipment. They also have significance for testing of biological materials.

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1 Accomplishments

1.1 Research Objectives

The original project objectives can be summarized as follows:

1) To produce mechanical characterization data for one or more PBS systems, their component polymers, and the polymer-crystal interface, at a range of strain rates and temperatures. Link these using time-temperature superposition.
2) To use these data to design and interpret experiments which can be performed at low rate in microscope and tomography systems but which give understanding of the microscopic behavior at elevated rates, including the formation of damage.
3) Use the Virtual Fields method to allow novel measurements of constitutive response: in particular from experiments in which the strain and/or stress fields are not constant.

These objectives had to be altered because material for the project could not be delivered. We instead moved to investigating model materials consisting of natural rubber filled with spheres, and sugar-filled polyurethane specimens manufactured *in-house*, as well as spending more time on modelling activities. Furthermore, the tomography work was delayed owing to COVID, and we were only able to perform a small number of experiments.

Final accomplishments are listed in the next section.

1.2 Accomplishments during reporting period

This project made major contributions to our overarching research goal that the response of low modulus materials to deformations at high strain rates be predicted from experiments performed exclusively under low rate loading. In particular, we produced experimental data and modelling frameworks that demonstrate the feasibility of that goal. Further, we designed novel methods for direct measurements of the high rate response, enabling, for the first time, high frequency shear moduli to be measured experimentally. These developments are important for better use of low modulus polymer materials, for example in polymer bonded explosives, potting compounds for protection of electronics in extreme environments, and personal protective equipment. They also have significance for testing of biological materials.

Main accomplishments are

1) Demonstration of a model calibration for glassy polymer materials using low temperature data to calibrate the high strain rate response (published).
2) Development of methodologies for interpreting and then predicting the high rate response of low modulus materials (rubbers and filled rubbers).
3) Extensive characterization of elastomeric materials filled with hard particles
    - Glass filled rubbers (papers in preparation)

    - Sugar filled rubbers (paper submitted)

   In addition to the unfilled materials.
4) Constitutive modelling of the above experiments, demonstrating that high strain rate performance can be predicted from low rate response at different temperatures (partly published, papers in preparation).
5) Development of a technique for measuring the high frequency (up to 20 kHz) response of low modulus materials using the Virtual Fields method and high-speed imaging to derive data from strain and acceleration fields in an oscillating specimen. This is known as the high-speed rheometer (published).

The main unmet goal was the in-situ testing to simulate high rate response. This work was delayed because of COVID, during which time we instead performed additional modelling work. We did perform some tomography scans on specimens recovered from various experiments above, and these are being analyzed for inclusion in the paper on glass filled rubbers.

1.3 Dissemination

Papers have been published in leading journals, as listed on the website, with preparation of four more papers in progress. Where relevant, full data sets are available in online repositories. Author Accepted Manuscripts are made freely available on the Oxford University Research Archive following the relevant embargo period for the paper. In addition, two PhD theses have been completed and will be made available on the Oxford University Research Archive. Work has also been presented at leading conferences in the field:

- APS Conference on Shock Compression of Condensed Matter 2018: attended by CR Siviour and A Trivedi.
- Dymat Conference 2018, Archachon, France: CR Siviour and A Trivedi
- Deformation Yield and Fracture of Polymers, Kerkrade, Netherlands, 2018: CR Siviour gave Plenary Lecture *Characterising the response of polymers to high strain rate loading: recent advances and current challenges*
- Society for Experimental Mechanics Annual Conference 2019, Reno, Nevada: Akash Trivedi and Huanming Chen.
- British Society for Strain Measurement 2019: CR Siviour gave Plenary Lecture *Challenges and opportunities in high rate characterisation of soft materials* and A Trivedi won prize for best student paper.
- International Rubber Conference 2019, London UK: CR Sivour, A Trivedi and H Chen.
- Institute of Materials Rubber in Engineering Group 2020, Oxford: UK, A Trivedi
- Society for Experimental Mechanics Annual Conference 2020 (online): Aaron Graham
- Dymat Conference 2021 (online): Akash Trivedi, Aaron Graham.
- IOM^3 Rubber in Engineering Group workshop *Elastomers for High Frequency Applications*, 2021. Invited talk given by Aaron Graham *A novel apparatus and methodology for the high frequency mechanical characterisation of ultra-soft materials.*

2 Impacts

2.1 Development of the principal discipline(s) of the project

Soft polymers, for example rubber, are often used in impact applications. Everyday examples include protective cases for cellphones or other electronic devices. Here, the job of the rubber is to protect the device from damage. In many applications, the properties of the rubber are modified by filling them with particles of a much harder material. These might be used to make the rubber stiffer, or tougher, or to change the electrical or magnetic properties. The ultimate motivation for the research in this project is to improve a class of materials called polymer bonded explosives, or propellants. Here the rubber is filled with particles of an energetic material. The rubber provides strength to the material, allowing it to be cast into different shapes, and makes it safer to handle by preventing the explosive crystals from rubbing against each other.

To use these filled rubbers effectively in impact applications, we need to understand their mechanical response to dynamically applied loads: how stiff and strong are they. These properties can be very different to those seen under static loads. Unfortunately, the dynamic response is difficult to measure, if we take a specimen of rubber and deform it quickly it will wobble, like a jelly. This structural response masks the underlying material behaviour that we need to understand.

In this project, we have made use of two techniques to better understand the dynamic behaviour of filled rubbers. The first is to use the principle of time-temperature superposition. This makes use of the fact that for many polymers, changing the deformation rate has the same effect as changing the temperature. So, we can simulate impact loading by instead performing static tests at reduced temperatures. In previous research, we have demonstrated this technique on unfilled polymer materials, but this is the first comprehensive study of its application to filled and unfilled rubbers. We have shown that it is possible, using relatively simple models, to predict the high rate response based on data obtained statically. These models also include damage formed during the deformation process, which is vital to understanding the lifecycle of the materials.

As part of this activity, we have generated considerable experimental data under both static and dynamic loading, developing further the state of the art in dynamic characterisation. An important development is a technique that combines high frequency oscillation of a specimen with high speed photography. In this way we can measure in real time the structural ‘wobble’ in materials, but then remove the structural effects and instead calculate the underlying material properties. This technique can only be used for small deformations; however, together with the time-temperature superposition work, which we have shown to very large deformations, it provides a comprehensive suite of tools for better understanding, and using, this important class of materials.

2.2 Other disciplines

Many of the challenges faced in characterising rubbers at high strain rates also apply to biomaterials. Time-temperature superposition cannot be used on these materials; however, the high speed rheometer developed here is very well-suited to these measurements, and we are currently demonstrating it on Sylgard and agar (widely used simulants), kidney and brain tissue. This technique has the potential to provide valuable information to support development of personal protective equipment, for example against blast or projectile injury.

2.3 Development of human resources

Three PhD students have been trained as part of this research:

AT – Improved research skills, performed undergraduate teaching and was active in student liaison bodies with the university. AT is now performing post-doctoral research in the same laboratory, supervising a PhD student and also holds a teaching fellowship in the University. His aim is to continue to an academic career. AT is a member of an under-represented group in Engineering (British Asian).

HC – Improved research skills, active in student engineering societies, with which he won prizes in Chinese and UK innovation competitions.

AG – Improved research skills, expected to submit PhD in summer 2022, has also performed undergraduate teaching and been active in student societies, is currently 'Junior Dean', a position mainly concerned with welfare and disciplinary support for undergraduate students living on campus.

2.4 Impact on teaching and educational experiences

The PhD students and I have supported undergraduate students to perform their final year research projects on related topics, including characterization and modelling of elastomers and biopolymers, and design of a low-cost mechanical testing machine. In particular, the latter project was designed in response to the unique requirement to perform an experimental project during the Covid-19 lockdown. With support from AT, the student designed, and built, a system that could be assembled and used at home with only basic tools.

2.5 Impact on on physical, institutional, and information resources that form infrastructure.

We have developed the high speed rheometer described above.

2.6 Impact on society beyond science and technology

Our intention is to obtain further funding to use the techniques developed here to improve understanding of bio-derived and recyclable polymers, to replace, in particular, cross-linked elastomer materials for impact applications. We currently have an EPSRC funded collaboration with the University of Oxford Department of Chemistry, and a Machine Learning research group in Engineering on use of Machine Learning to inform synthesis of these materials.

3 Changes

3.1 Changes in approach

Expected material supply from USAF labs was not realized. Instead we obtained model materials from a research laboratory in the UK (TARRC). This did not significantly change the project objectives.

Because of the COVID lockdown we were not able to perform as much X-ray tomography as originally anticipated, however, we have obtained the data needed to support the development of the methodologies of interest in this project.

3.2 Problems or delays

Covid delays were resolved through a no-cost extension. We also had an earlier no-cost extension to enable recruitment at the start of the project.

3.3 Expenditure Impacts

None

3.4 Significant changes in the use or care of human subjects, vertebrate animals and/or biohazards

None

3.5 Changes to the primary place of performance from that originally proposed

None

4 Technical Updates

Detailed technical reports are available in the theses and papers. Here, a summary is provided with references as appropriate

4.1 Experimental investigations

Comprehensive experimental research was performed to characterise representative filled and unfilled rubber materials. Early in the project, this focused on commercial materials: a neoprene rubber and a carbon black filled polyurethane [1, 2].

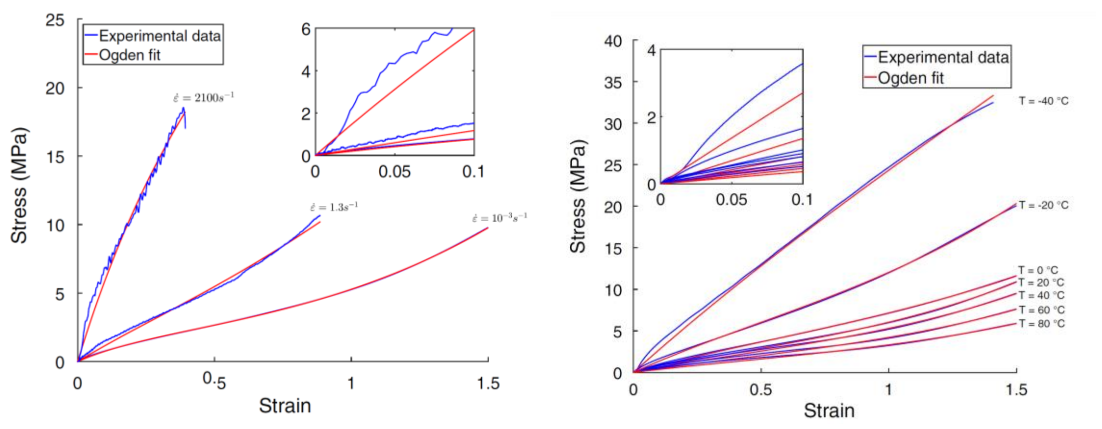

Figure 1. Stress-strain response of neoprene rubber at different strain rates and temperatures [1]

The mechanical responses of the materials were measured at strain rates from 0.001 to c. 5000 s^{-1}, e.g figure 1. The project then proceeded to characterize materials with larger filler sizes (of order 10s to 100s of micrometers), representative of PBXs. We obtained model materials consisting of natural rubber filled with glass beads of nominally 10 and 100 µm. Two loading densities were used, 5% and 50% by volume. Although these are lower than the loading densities found in PBXs and propellants, they were chosen to support model development, and avoid complications of direct particle-particle interactions. These composites, along with the unfilled rubber, were characterized at rates from 0.001 to c. 5000 s^{-1} and quasi-statically down to -80 °C [see chapter 5 in reference 3]; Figure 2 shows the rate dependence.

The second model material was based on a healable polyurethane material supplied by Reading University. This was also characterized on its own [4], and then filled with sugar particles of various sizes. Sugar is commonly used as a mechanical simulant for energetic materials and is available commercially in well-controlled particle sizes. These materials were characterized over a wide range of strain rates, in addition to background thermomechanical characterization, such as differential scanning calorimetry, dynamic mechanical analysis [see chapter 5 in reference 5].

Together, these experiments provide insights into the rate and temperature dependence in these materials, the effects of filler volume fraction on the mechanical response, and the effect of the glass transition in the materials. They also provide information about temperature - rate equivalence in the materials.

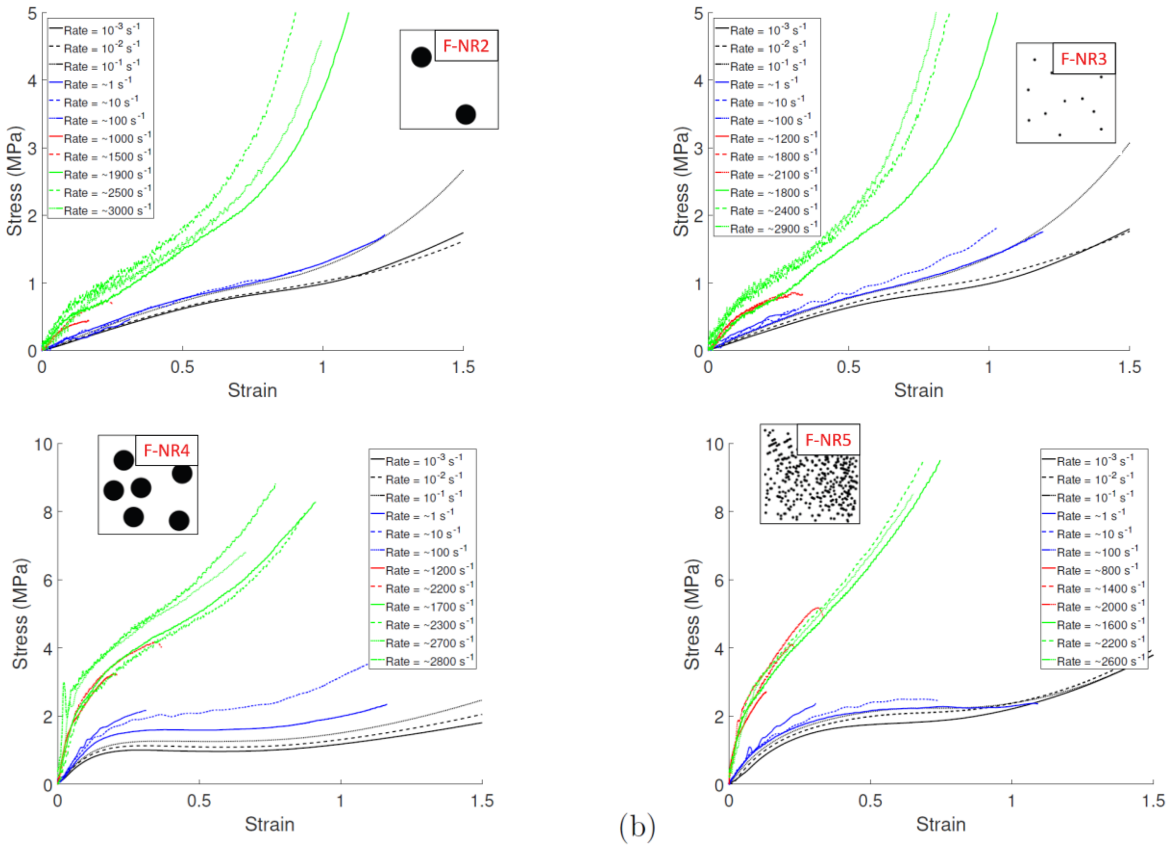

Figure 2. Stress-strain response of glass filled rubbers at different strain rates: F-NR2 100 µm, 5%; F-NR3 10 µm 5%; F-NR4 100 µm 50%; F-NR5 10 µm 50%. [3]

4.2 Modelling efforts

A number of different modelling techniques were explored during the project. The overall strategy was to move from understanding, to describing to predicting polymer response.

Early efforts, making heavy use of time-temperature superposition to understand high rate response, were presented in [1, 6, 7]. Here, the main aim was to explain increases in stiffness / strength observed with increasing strain rate and to justify these using the known temperature and frequency dependence of the modulus. An example, comparing modulus fits to strain rate and temperature is shown in Figure 3.

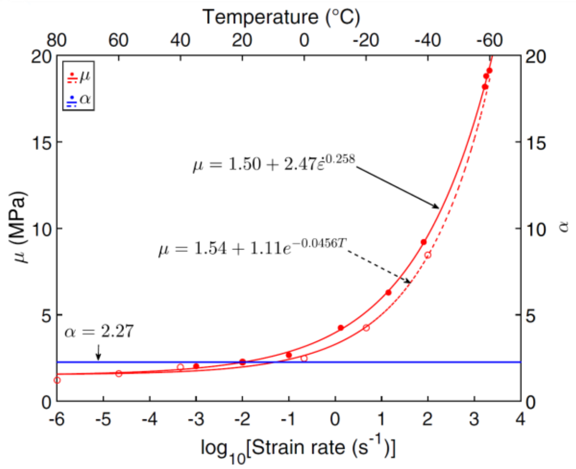

Figure 3. Equivalence of modulus values when fitting models individually to rate and temperature dependent data for neoprene rubber [1]

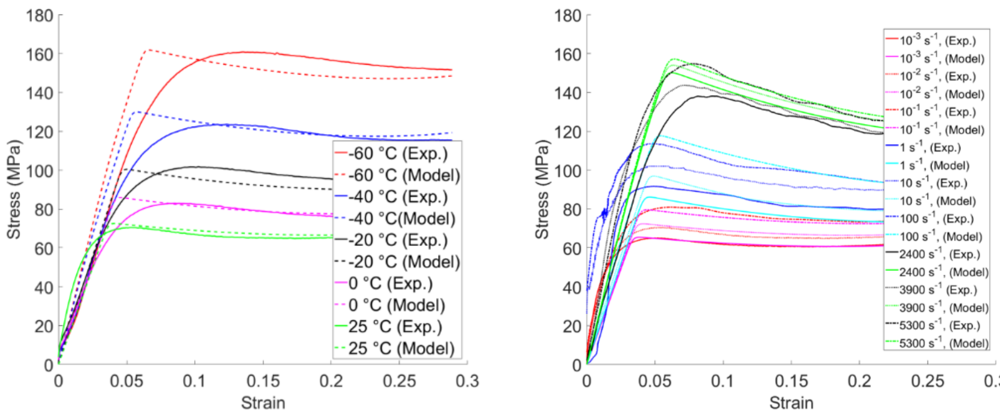

Figure 4. Calibrating (left) and validating (right) a constitutive model for PVC [9].

Further modelling efforts were more predictive. Using data produced in a previous project [8], it was shown that a model can be calibrated at low temperatures and then used to predict the high rate response of poly(vinyl-chloride) [9], figure 4. This work was mainly undertaken because at the time we were unable to obtain the filled rubbers for the current project, however it gave useful insights into the modelling process. Models were then developed for the elastomers, and filled elastomers [2, 3, 4, 5, 10] following a common theme: rheometry and dynamic mechanical analysis were used to provide data on the time and temperature dependence of the complex modulus. This was then combined with an appropriate large strain model, which might contain hyperelasticity, strain softening or damage as appropriate and was calibrated using quasi-static large strain behaviour. Finally, the model developed was used to predict the response at high strain rates. This is demonstrated in Figure 5 for the carbon black filled polyurethane, whilst outputs for the filled supramolecular polyurethane (which used slightly different constitutive and damage models) are shown in Figure 6.

The key contribution of these efforts was to show that high strain rate behaviour of low modulus materials, which is challenging to measure in practice, could be predicted from appropriate models based on the quasi-static response, combined with time and temperature dependent modulus data, all of which can be measured reliably using relatively standard experiments. These techniques are now being used by other projects within my research group to predict high rate elastomer response.

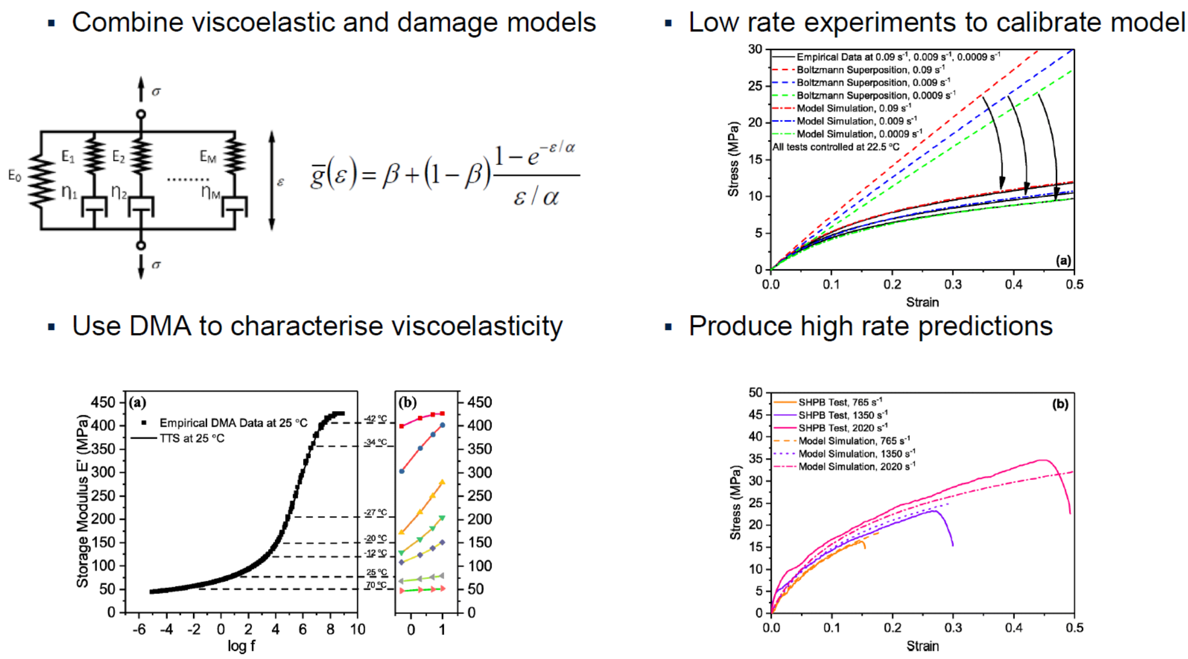

Figure 5. Development and validation of a model for carbon-black filled polyurethane [2].

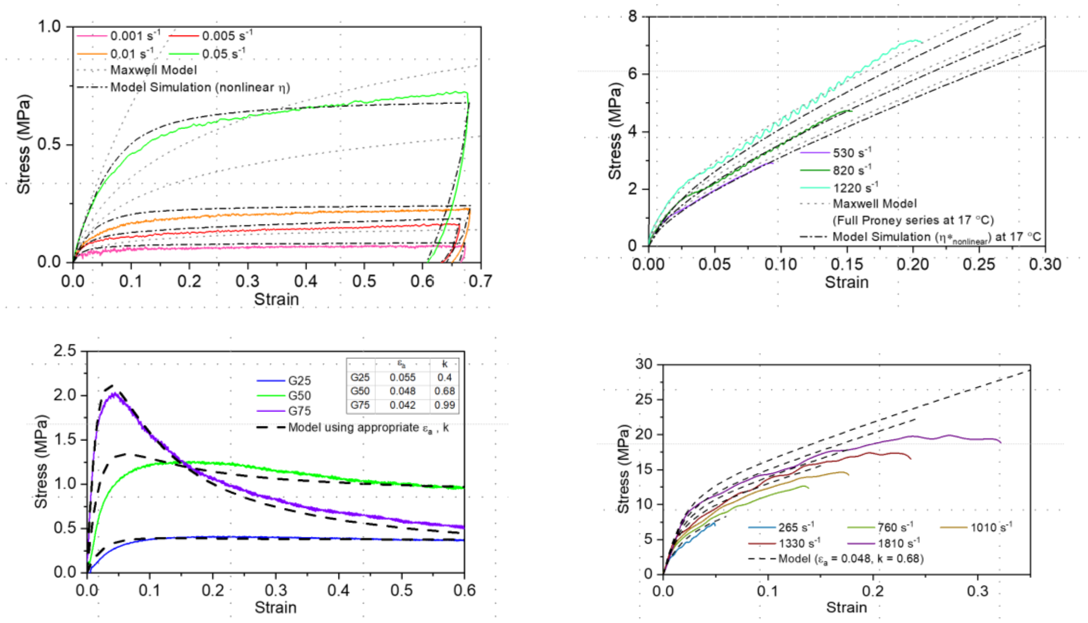

Figure 6. Experimental data and example model outputs: top, unfilled healable polyurethane; bottom, filled healable polyurethane. Graphs on the left are fits to experimental data, whilst graphs on the right are predictions of high rate response [4, 5]

4.3 Technique development

Whilst the use of time-temperature superposition based techniques offers a new method for understanding high rate behaviour of materials, there are some systems in which this cannot work, for example bio-materials or other materials that contain phase changes that do not have time-temperature equivalence. Further, it is still useful to be able to make measurements directly of the high rate, or high frequency response of low modulus materials.

Whilst Hopkinson bar-based techniques can give measurements of the high rate response at large strains, it is well-known that they make unreliable measurements of material modulus. This is a common drawback of compression experiments, but particularly acute at high strain rates because of wave propagation effects. We have, in previous projects, shown that it is possible to make use of travelling waves in low modulus materials as a diagnostic tool for measurements of their dynamic response (e.g. [11]). Here, high speed imaging is combined with a technique called the Virtual Fields Method, which allows the use of displacement and acceleration fields to measure the constitutive behaviour of a material: the acceleration field replaces force measurements in these calculations. This project develops that research further.

To measure the complex modulus of low stiffness elastomers, a torsional pendulum with a variable natural frequency was built. This was excited using piezo-electric shakers and, in turn, used to provide torsional loading of one end of a cylindrical specimen, Figure 7. This sets up a standing wave in the specimen. The amplitude vs displacement profile associated with the standing wave was recorded using high speed imaging, and these full-field data used to extract the mechanical response of the material. A key step in the analysis was to use the knowledge that the specimen was oscillating at discrete frequencies (the desired frequency and some ‘overtones’), the governing equations for the Virtual Fields Method could then be applied in the frequency domain (using a Fourier Transform) which gave very high quality data. The compromise is that by doing this time-dependent information is lost, however if the sample is oscillating at small amplitudes (within the linear viscoelastic regime) at a constant frequency, there is no time-dependence in any case.

The technique has been demonstrated on model silicone elastomers [12, 13], Figure 8, and is currently being applied to a number of other man-made and bio- polymers.

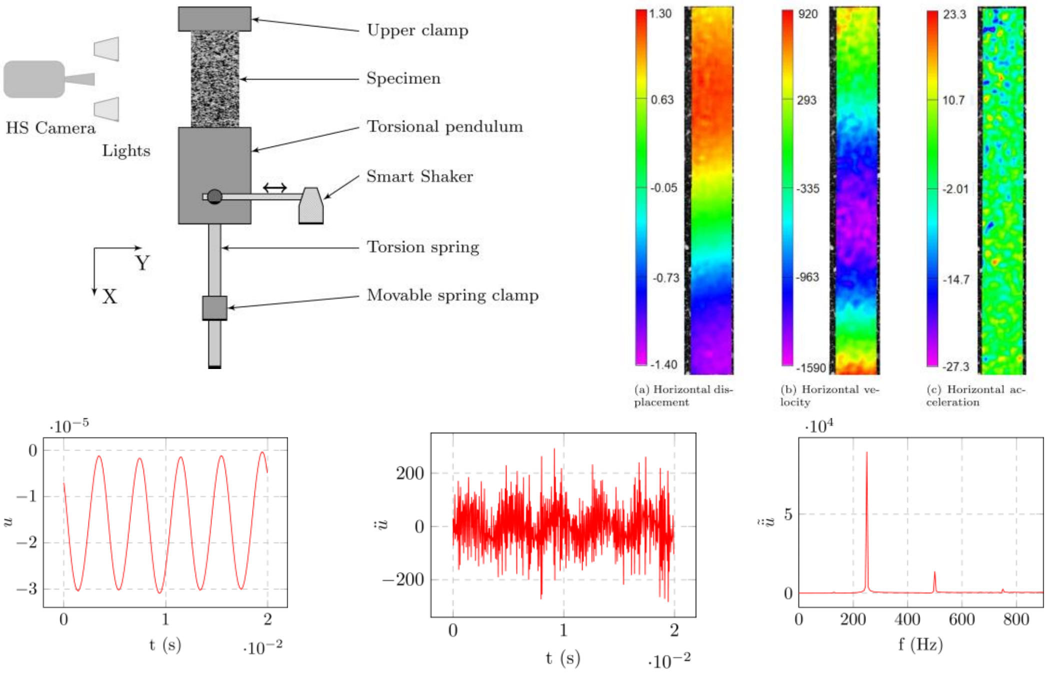

Figure 7. Overview of the new torsion apparatus. Top left, schematic diagram; top right measured displacement fields along the specimen in one of the high speed images; bottom, displacement and acceleration data for a location in the specimen as a function of time [12].

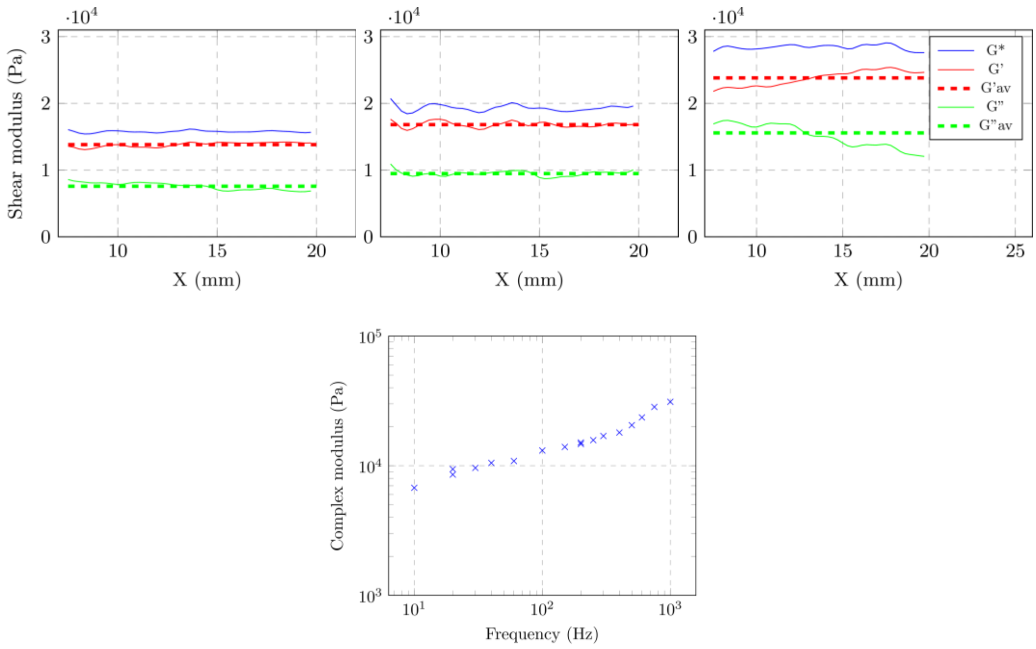

Figure 8. Outputs from the new torsion apparatus. Top, moduli at (left to right) 250, 500 and 750 Hz. Bottom, complex modulus as a function of frequency [13].

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