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**A Method for Predicting the
Perceived Hardness of Soft-
Touch Elastomeric Coatings
and Over-Mouldings**

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ABSTRACT

The perceived and physical hardness of surfaces play a key role in our assessment of product quality and performance expectation. Thin rubbery overmouldings are now commonly used to impart a soft 'feel' to consumer goods such as golf clubs and screwdriver handles to influence prospective purchasers.

In a recent study we demonstrated a very strong correlation between the perceived hardness of materials and that measured by an indentation method following the Shore A scale. The ASTM standard that describes the Shore hardness method emphasizes the need to make measurements in relatively thick samples, well away from edges to avoid any potential edge effects. Such 'edge effects' are usually unavoidable in over-moulded coatings. In this study we report an approach to predicting the Shore hardness of a limited range of carbon-filled thermoplastic elastomers for a number of different geometries that include such edge effects. This enables prediction of the effective 'softness' of products. Results were validated against Shore Hardness measurements.

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1 INTRODUCTION

Our perception of a material or object is based on a range of inputs including touch. The ‘feel factor’ plays an important role in the customers perception of quality i.e. it feels ‘soft’, ‘warm’, ‘luxurious’. During the past decade the concept of soft-touch feel has been applied to plastic mouldings. Many soft-touch plastics are thermoplastic elastomers, TPE’s, which have a rubbery feel and are simpler to process and recycle than materials such as PVC films. Examples of use include golf club and screwdriver handles. A previous report (Tomlins et al, 2005 [1]) describes methods that can be used to measure a number of key physical attributes of soft-touch materials including surface texture, surface friction, thermal diffusivity and mechanical ‘compressibility’.

Soft-touch materials are typically assessed by compression during prodding, stroking or gripping. This approach is similar to measuring the indentation of a probe that is commonly used to determine the ‘hardness’ of ‘soft’ materials according to the Shore A scale. Indeed we have recently demonstrated a very strong correlation between measurements of Shore hardness and the perceived hardness of this class of materials, see Figure 1 (Petrie et al, 2004 [2]). This finding can be potentially exploited to improve the efficiency of product design. Products that have a soft-touch finish are typically developed using prototypes which enables different material types, colours, and textures to be explored. However, by utilising the link between perceived and physical hardness it should be possible to assess the feel of a product in a virtual environment. This goal can be achieved by using a force-feedback joystick of the type employed in keyhole medicine assuming that the physical hardness of the over-moulding can be modelled- the topic of this report.

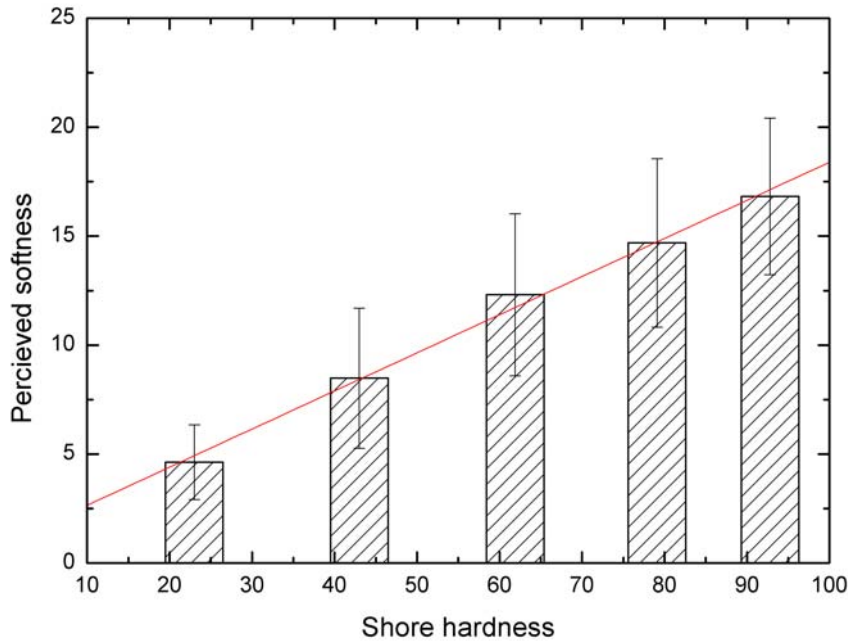
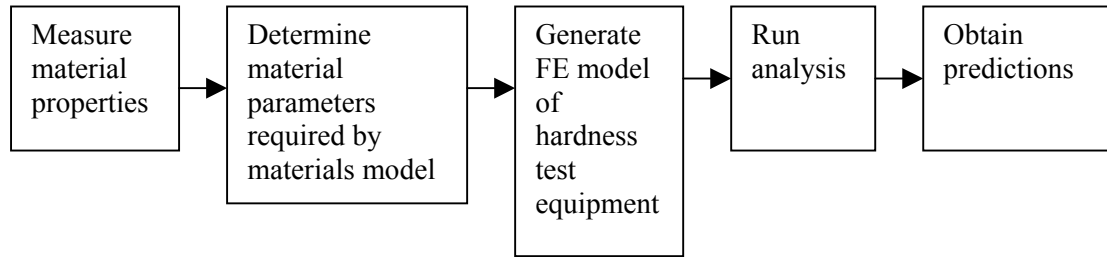


Figure 1: Relationship between physical hardness (Shore A hardness) and perceived softness for Multiflex carbon-filled TPE's [2]

There are five key stages in the prediction of Shore hardness, which is calculated using the finite element (FE) method. These are shown below:



Hardness predictions are based on a mathematical model of the Shore A hardness test equipment. This equipment measures the penetration of a probe into the test material after a given time for a given load. The calculations that predict the hardness of the material therefore require a knowledge of how the material deforms in response to a given loading. These materials models are complicated for soft, rubbery viscoelastic materials. As a consequence materials data needs to be obtained from a range of techniques including stress relaxation and dynamic mechanical tests, details of which are presented in Appendix 1. Methods for modelling viscoelastic behaviour are provided in Appendix 2 and details of the FE modelling are given in Appendix 3.

2 MATERIALS

The styrene-ethylene-butlyene-styrene, (SEBS) thermoplastic elastomer copolymers (TPEs) (Multiflex, Pan Polymers) can be modified to produce a range of soft-touch compounds that span the Shore hardness scale by adding additives such as carbon black. Medium and high carbon content materials were chosen, Table 1, as these are more of a challenge to model than materials with lower filler content.

Specimens 150 mm x 150 mm were injection moulded according to the conditions listed in Table 2, either nominally 2.6 mm or 3.9 mm thick, using a purpose built edge-gated mould design that has been described in detail elsewhere (Rides et al, 1996 [3]). Briefly the mould cavity was developed to provide a uniform flow field for molten material as it fills the mould. This is achieved by creating a domed structure between the sprue and weir-edge gate.

Table 1: Specimen details

Trade Name	Sample Code	Nominal Carbon Content
Multiflex G90A 520 N0200 12615 Black	AAAT F001	High
Multiflex G60A 21 BT Z3519 N0104 Black	AAAT F004	Medium

Table 2: The injection moulding conditions for the specimens

Material	Melt Temp. (°C)	Mould Temp. (°C)	Cycle Time (s)	Injection Time (s)	Hold Pressure (bar)	Hold Time (s)	Cooling Time (s)
AAAT F001	180	50	77	0.80	20	20	50
AAAT F004	180	30	95	0.72	30	20	60

Care was taken to keep the materials clean during both the moulding process and cooling after ejection from the mould. Moulded specimens were individually placed on paper on a wooden table and allowed to cool naturally at room temperature. Immediately after ejection from the mould tool, the sprue was removed. The specimens were packaged in packs of five, each specimen being separated by a sheet of paper and stored in re-sealable plastic bags.

3 MEASUREMENT OF SHORE HARDNESS

The deformation produced by applying a known force to an indenter for a specific time is commonly used to measure the physical hardness of polymers, expressed using the Shore (or Durometer) scale [4].

Figure 2 shows a schematic representation of a typical Shore A indenter, which terminates in a truncated cone. During the test, the indenter is pushed into the material under a controlled load for a specified time period. The time delay is to allow for the strain relaxation behaviour of the elastomer. At the end of the time period, the remaining depth of the indenter is measured and a value from 0 (full protrusion) to 100 (no protrusion) is quoted. The standard test, ASTM D 2240-04 [4], recommends a minimum thickness for the material and areas where measurements should not be made. This requirement is designed to eliminate any undesirable contributions to the measurement from the underlying substrate or from edge effects.

Hardness data are used for qualitative purposes only since there is no simple relationship between these measurements and any fundamental material properties due to the complex stress state that arises during indentation.

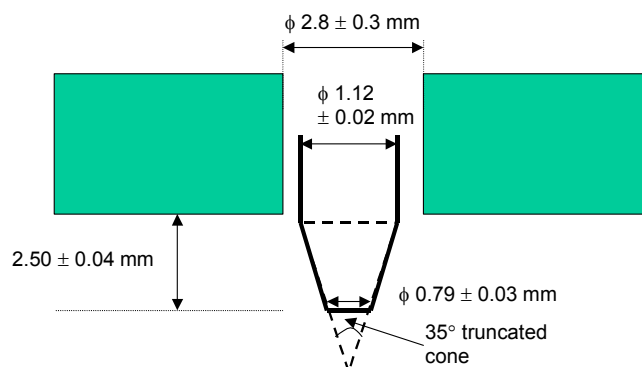


Figure 2: A schematic representation of the indenter used to measure hardness on the Shore A scale (Redrawn from ASTM D 2240-04)

Measurements of Shore hardness using the A scale were made using a Ray-Ran digital durometer (model WS777) following the procedures described in ASTM D 2240-04 [4]. A type A indenter was used and the indentation load was controlled at 1 kg. Each test was carried out at least 12 mm from any edge and the dwell time was set to 15 seconds.

The results of the Shore hardness (A scale) measurements of the two carbon-filled rubbers are shown in Table 3. Two of the samples of each material tested were stacked to ensure a minimum thickness of 6 mm according to the recommendations of ASTM D 2240-04 [4]. At least ten measurements were made per sample.

Table 3: The mean and standard deviations of Shore A hardness data for samples of different thickness.

Sample	Sheet thickness (mm)	Shore A hardness
AAAT F001	2.6	92.7 (0.1)
	3.9	93.0 (0.2)
	6.5	92.8 (0.2)
	7.8	92.8 (0.6)
AAAT F004	2.6	65.4 (1.4)
	3.9	62.7 (0.8)
	6.5	62.9 (1.2)
	7.8	61.9 (0.4)

4 PREDICTIONS OF SHORE HARDNESS

Finite element analysis has been used to model the Shore A hardness test. This section of the report is concerned only with the FE predictions of Shore hardness values. Information of measuring the material properties and parameters are given in Appendix 2. Details of the finite element model are provided in Appendix 3.

A series of FE analyses were undertaken to investigate the effect of geometry, i.e. specimen thickness and diameter (specimens were cylindrical due to use of axisymmetric elements). Analyses were run for each material with a diameter of 50 mm and thickness' of 7.8, 6.5, 3.9 and 2.6 mm, matching those available for experimental validation. Specimen thickness' of 6, 3 and 1 mm were also analysed and, to investigate edge effects, diameters of 25 and 12.5 mm were used. Figure 3 shows examples of the predicted indentation deformation for the two materials studied. A higher degree of indentation is observed with the medium-filled material.

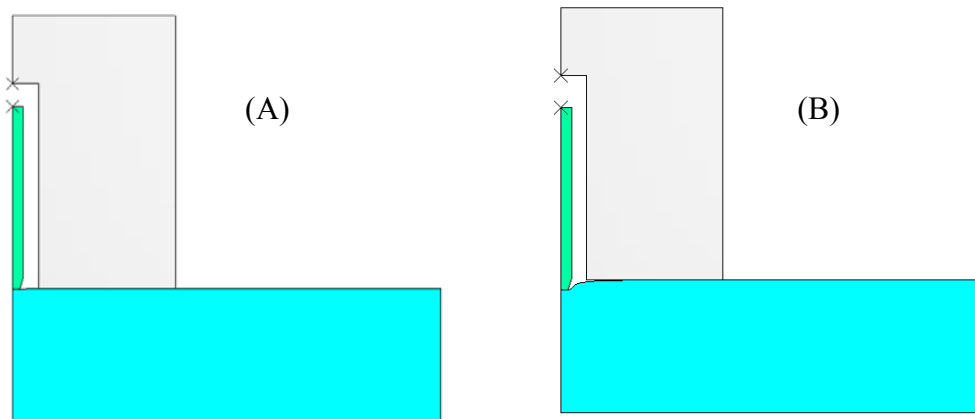


Figure 3: Deformed plots obtained from Shore A hardness predictions of materials AAAT F001 (plot A) and AAAT F004 (plot B).

The predicted hardness values are presented in Table 4. It can be seen that in the softer material the hardness values are higher at smaller specimen thickness, while specimen thickness makes very little difference in the harder material. This corresponds to the trends seen experimentally. The radius of the specimen makes no significant difference in either material, so it would seem that, at these dimensions, edge effects are not affecting results. Edge effects may become more substantial if testing is carried out any closer to the edge.

Table 4: Predicted Shore A hardness values for a range of specimen dimensions for both AAAT F004 and AAAT F001 materials

Specimen Dimensions, Height x Diameter (mm)	Predicted Shore hardness (A scale)	
	Medium Filled (AAAT F004)	High Filled (AAAT F001)
7.8 x 50	75.9	97.6
6.5 x 50	76.3	97.6
6 x 50	76.5	97.6
6 x 25	76.4	97.6
6 x 12.5	76.1	97.5
3.9 x 50	78.0	97.7
3 x 50	79.4	97.8
3 x 25	79.4	97.8
3 x 12.5	79.1	97.7
2.6 x 50	80.5	97.9
1 x 50	88.1	98.5
1 x 25	88.0	98.5
1 x 12.5	87.9	98.4

5 COMPARISON OF EXPERIMENTAL DATA AND PREDICTED VALUES

The experimentally measured hardness values are shown together with the predicted values in Table 5, for both materials. It can be seen that the predicted values are higher than the experimentally measured values. This difference is greatest for the softer material (AAAT F004).

Table 5: The measured and predicted Shore A hardness data for samples of different thickness

Sample	Sheet Thickness (mm)	Measured Shore A Hardness	Predicted Shore A Hardness
AAAT F001	2.6	92.7 (0.1)	97.9
	3.9	93.0 (0.2)	97.7
	6.5	92.8 (0.2)	97.6
	7.8	92.8 (0.6)	97.6
AAAT F004	2.6	65.4 (1.4)	80.5
	3.9	62.7 (0.8)	78.0
	6.5	62.9 (1.2)	76.3
	7.8	61.9 (0.4)	75.9

A few checks were made to investigate these differences. An FE analysis was run with the specimen modelled as an elastic steel. When a Shore A hardness reading is taken on a very hard specimen, the indenter displacement should be 2.5 mm giving a hardness value of 100. The FE analysis predicted a value of 99.98. Experimentally, the same check was carried out, using a steel block. The measured value was 97.5. This indicates that there is a degree of error or uncertainty in the experimental values obtained. Because the test is based on the response of a linear spring, this should be a linear error, and therefore the experimental results can be corrected for this by multiplying the values by a factor of 100/97.5. The corrected values are presented in Table 6.

Table 6: The corrected measured and predicted Shore A hardness data for different thickness samples

Sample	Sheet Thickness (mm)	Corrected Measured Shore A Hardness	Predicted Shore A hardness
AAAT F001	2.5	95.1	97.9
	4	95.4	97.7
	6.5	95.2	97.6
	7.8	95.2	97.6
AAAT F004	2.5	67.1	80.5
	4	64.3	78.0
	6.5	64.5	76.3
	7.8	63.5	75.9

The measured and predicted values for the hard material (AAAT F001) are now much closer. There is still a sizeable difference in the values for the softer material (AAAT F004). The predicted and measured hardness values were plotted against thickness, see Figure 4.

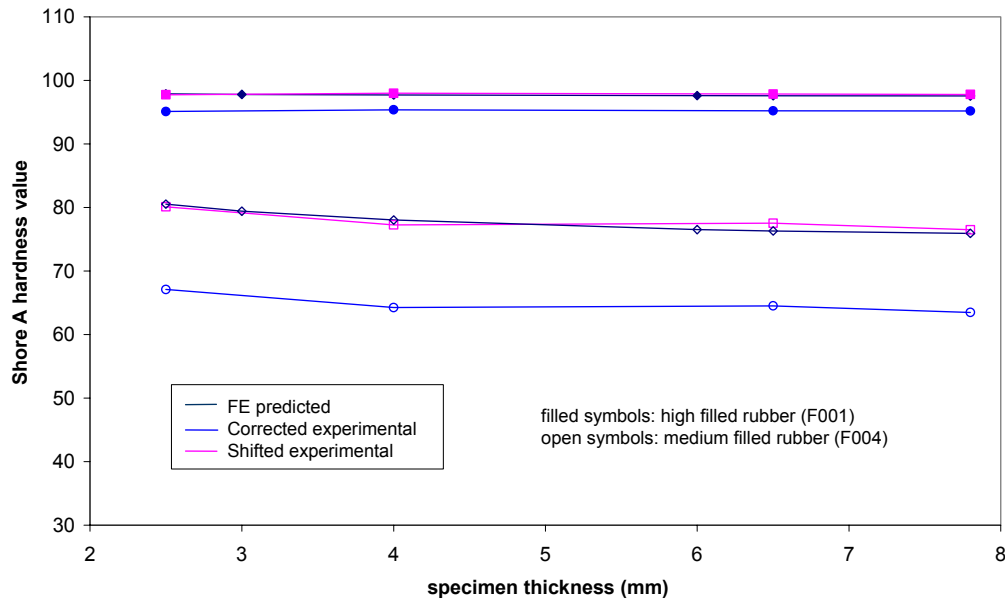


Figure 4: Shore A hardness value plotted against specimen thickness for both materials.

The corrected experimental data are shown in Figure 4. These data have also been shifted, placing the curves onto the predicted values. The curves demonstrate that the same trend in thickness is observed in both the experimental and predicted cases.

There are a few possible sources of error, one of which may be the test apparatus. There is the known error in the hardness measurement of steel, and the results have been corrected to take this into account. In the FE analyses we have assumed a spring stiffness for the indenter (see Appendix 3 for details), but this may be different to that for the actual spring.

The FE predicted values depend largely on accurate representation of the rubber material. The FE model itself has been verified by the prediction of a hardness of nominally 100 for an elastic steel specimen. In the analyses of the carbon-filled rubbers a hypoelastic material model was chosen. This best represents the material behaviour as it allows for non-linearity at low strains, a phenomenon observed in these materials. It is possible that the data used for the hypoelastic materials model could be inaccurate. The parameters have been obtained from tensile mechanical tests, while indentation is a compressive loading mode. No analyses have been carried out to assess the sensitivity of the hypoelastic model to the parameters used.

Friction has not been included in the above analysis, but the presence of friction between the specimen and indenter and the specimen and casing may influence the indentation and hence the hardness. The friction coefficient for this system is not known, so FE analyses of the 6.5mm x 50mm medium-filled specimen have been undertaken with friction coefficients of 0.1 and 0.3. It was found there was no difference in the predictions of Shore A hardness. Studying the displaced FE plots

during the analysis showed no movement of the mesh underneath the tip of the indenter, which confirms that including friction would have little effect.

The deformed plots presented in Figure 3 show that in the softer material the deformation area around the indenter is quite large. It is not possible to observe the deformation around the indenter experimentally, but it may be that the FE analysis is not modelling the indentation of the relatively sharp indenter accurately. Figure 5 shows the maximum principal strain predictions for both materials. The contour plots show a high strain gradient along the surface elements of the rubber, ranging from 0 – 0.048 for the high-filled rubber. In the medium-filled rubber the values range from 0 – 0.15, which are outside the strain range modelled in the hypoelastic model (up to 0.05). These factors could explain why better correlation is obtained for the harder material where less indentation is occurring, and the strain range is lower.

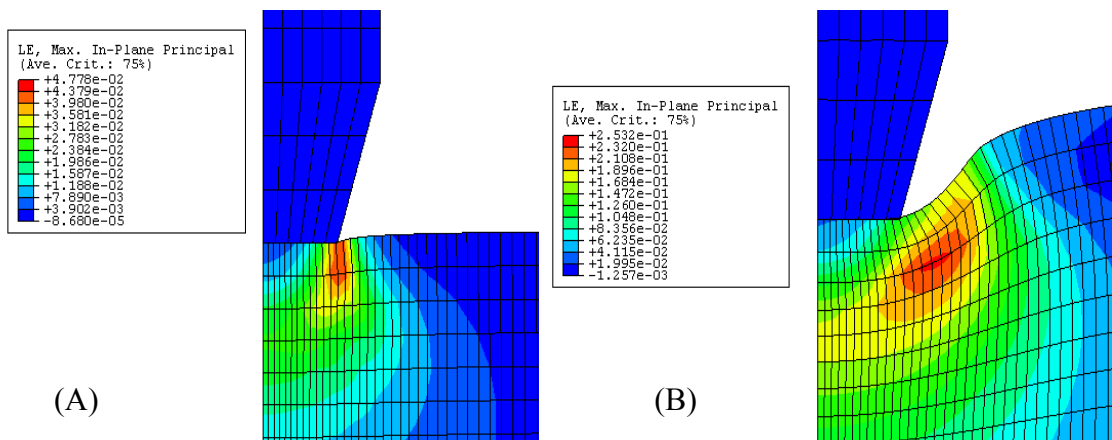


Figure 5: Maximum principal strain contour plots for (A) AAFF F001 and (B) AAFF F004.

To investigate this a Shore O indenter was used instead of the Shore A indenter. The Shore O indenter is a 3/32" spherical indenter (see Figure 6), which is normally used for softer materials with a Shore A hardness below 20. An FE model was also generated for the Shore O indenter, and analyses were run for both materials.

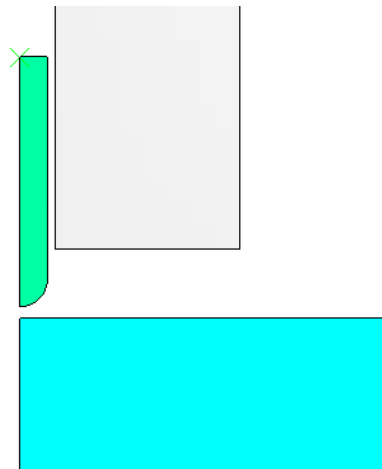


Figure 6: Diagram of spherical Shore O indenter.

The deformed plot obtained from using the Shore O indenter and the softer material (AAAT F004) is shown in Figure 7. In this analysis, the specimen deformation is following the shape of the indenter much more closely.

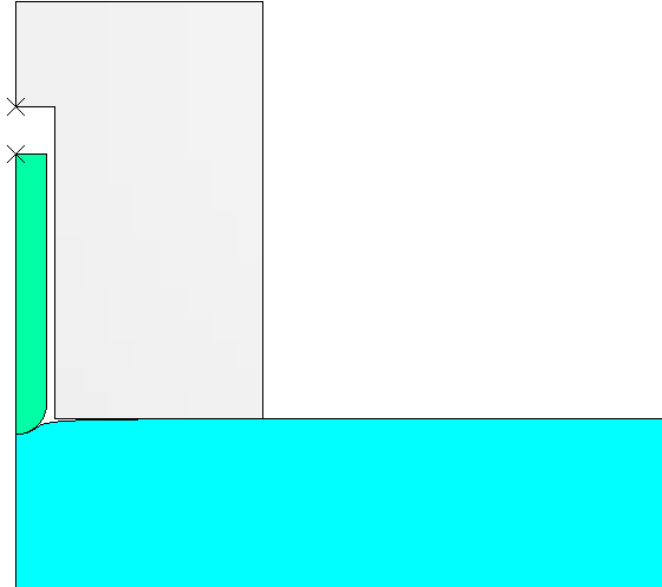


Figure 7: The deformed plot obtained from an analysis using the Shore O indenter and the medium filled rubber (AAAT F004).

Figure 8 shows the maximum principal strain contour plots obtained for both materials in the Shore O hardness analyses. With the Shore O indenter the strains in the surface elements are uniform and much lower than observed with the Shore A indenter. The strains predicted are within the bounds of those modelled with the hypoelastic model in the harder material, and only go slightly outside the bounds for the softer material.

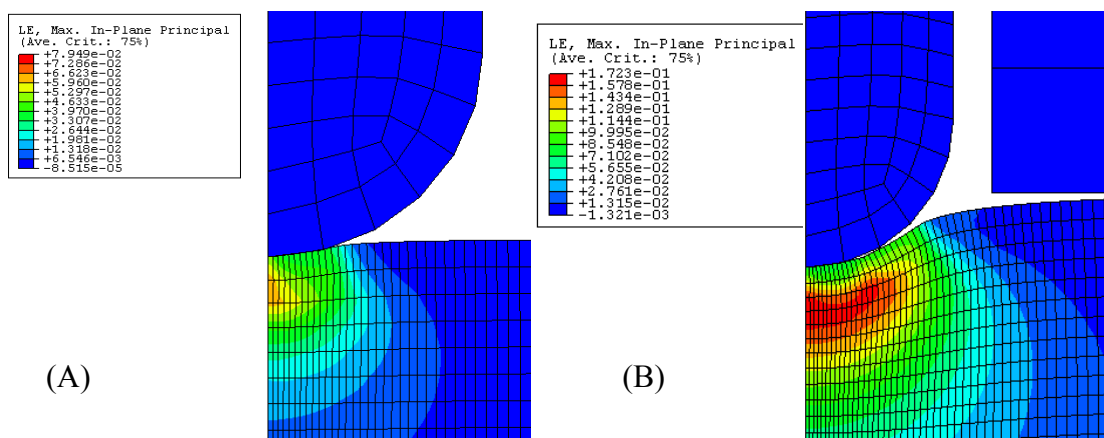


Figure 8: Maximum principal strain contour plots for (A) AAAT F001 and (B) AAAT F004.

The predicted values for the Shore O hardness test, given in Table 7, are much closer to the experimental values. This implies that the material parameters for the hypoelastic material model are reasonable, as good correlation is obtained for the spherical indenter, but that the analysis is sensitive to both indenter shape and the resulting deformation for softer materials.

Table 7: The corrected measured and predicted Shore A hardness data for different hardness samples

Sample	Sheet Thickness (mm)	Measured Shore hardness (O scale)	Predicted Shore O hardness
AAAT F001	6.5	96.4 (0.1)	95.7
AAAT F004	6.5	78.8 (0.4)	78.8

6 DISCUSSION

PREDICTING THE FEEL OF RUBBERS

There is a linear relationship between the perception of the hardness of the TPE's, Figure 1, that have been modelled in this investigation. The link between perception and a physical measurement is excellent and provides a basis for assessing the 'feel' of overmoulded materials based on their predicted hardness. The results presented in this report show that it is possible to predict the hardness of thin soft-touch materials using finite element analysis. This method could be used to predict the thickness required to give a specific hardness (for example, one perceived as feeling 'luxurious') on a rigid surface.

Shore A hardness measurements were carried out on the two carbon-filled rubbers studied. Finite element analyses of the Shore A hardness test using a hypoelastic material model were able to qualitatively predict the thickness effects observed in the two materials, although the actual values predicted were slightly high for the hard rubber and significantly higher for the softer material. A slight error was found in the experimental values and this was corrected for.

Inspection of the deformed finite element plots revealed a larger area of deformation around the Shore A indenter for the softer rubber, with minimal deformation in the hard rubber. Investigation of the strains along the top surface of the specimens showed a high strain gradient with high peak strains. Use of the spherical Shore O hardness indenter provided much better correlation between experimental and predicted hardness values.

The parameters in the hypoelastic model were derived from experimental data up to a maximum strain of 0.05. In the Shore A test, strain levels predicted by the FE analysis approach 0.2. The use of the model with the parameters derived here to predict behaviour at these high strain levels may introduce errors that explain the differences

between measured and calculated hardness values obtained from this test. The Shore O test, having a more blunt indenter, produces lower, more uniform strains in the rubber. This may well account for the better agreement between experiments and predictions for this test.

KEY POINTS

- The Shore hardness values of the Carbon-filled rubbers studied appear insensitive to specimen thickness.
- The Shore O hardness of thin soft-touch materials can be predicted using finite element analysis.
- This method could be used as a design tool to predict the thickness required to give a specific hardness on a rigid surface, allowing manufacturers to design for perceived ‘softness’ properties.

7 ACKNOWLEDGEMENTS

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8 REFERENCES

1. Tomlins, P., Rides, M., Dawson, A., Gee M., Dean G., Hobbs, G., Allen, C., Gnaniah, S., Calver, A. and Darling, R., Physical Characterisation of Soft-Touch Materials, NPL Report, DEPC MPR 024, July 2005.
2. Petrie, H., King, N. and Tomlins, P.E., Investigations into sensation of softness and perception of the tactile properties of ‘soft touch’ thermoplastic elastomers, NPL report, DEPC MPR 017, December 2004.
3. Rides, M and Dean G.D. Evaluation of mould designs for preparing standard plate specimens of plastics by injection moulding, NPL Report CMMT(A)30, May 1996.
4. ASTM D 2240-04 Standard Test Method for Rubber Property—Durometer Hardness.
5. “ABAQUS/CAE User’s Manual”, Version 6.4, ABAQUS Inc., USA, 2003.

APPENDIX 1: Viscoelastic Material Behaviour

A1.1 Overview

A1.1.1 Linear Viscoelastic Behaviour

Rubbers are viscoelastic materials i.e. their mechanical properties depend on the measurement timescale. This time-dependence increases as the measurement temperature approaches the glass-to-rubber transition temperature. The mechanical properties of viscoelastic materials are commonly determined using stress relaxation or creep experiments. In a stress relaxation test, a constant strain, ϵ_s , is applied and the time varying stress, $\sigma(t)$, is measured. If a uniaxial tensile strain is applied, then a tensile stress relaxation function can be determined using the equation:

$$E(t) = \sigma(t)/\epsilon_s \quad (A1.1)$$

The quantity $E(t)$ can then be considered as a time-dependent Young's modulus. If $E(t)$ is independent of the magnitude of ϵ_s , then behaviour is linear viscoelastic.

Mechanical properties can also be conveniently determined using dynamic mechanical tests in which a sinusoidal, time-varying strain is applied and the time-varying stress is measured. For a viscoelastic material, the stress and strain waveforms are out of phase. If the stress and strain waveforms are tensile and have amplitudes σ_0 and ϵ_0 respectively, and the phase difference is δ , then a dynamic tensile modulus E' can be determined using the equation:

$$E' = \frac{\sigma_0 \cos \delta}{\epsilon_0} \quad (A1.2)$$

This dynamic modulus (also referred to as storage modulus) depends on the measurement frequency and can be correlated with the stress relaxation modulus in Equation (A1.1) through expressions that relate the frequency to an effective time in a stress relaxation test.

A test under a constant deformation rate is commonly used to determine the mechanical properties of elastic materials. A plot of stress against strain is a straight line at small strains where the behaviour is linear. With viscoelastic materials, the stress/strain plot is a curve, even when behaviour is linear viscoelastic. The shape of the curve varies with strain rate. The gradient of a stress/strain curve therefore depends both upon strain and strain rate. These phenomena are a direct consequence of the variation of deformation behaviour with time under load, and consequently, this method has limited value for determining properties such as modulus.

A1.1.2 Non-Linear Behaviour

Rubbers are often loaded with carbon black to improve their mechanical properties or to reduce material costs. The presence of carbon particles increases properties such as $E(t)$ and E' in Equations (A1.1) and (A1.2) and makes them strain dependent and time dependent. Doubling the strain in a measurement of this type of material does not lead to a doubling of stress, and the deformation behaviour is therefore referred to as non-linear. In the case of carbon particle reinforcement, the non-linear behaviour is

significant at small strains (in the region of 1% and less) and is attributed to a breakdown of the particle structure with increasing strain level. The breakdown is recoverable, but the recovery is not immediate and can take hours depending on the type of carbon black and the maximum strain sustained in a test.

A1.2 Experimental Methods

A1.2.1 Stress Relaxation Tests

Stress relaxation measurements were made in tension using a Dynamic Mechanical Analyser (TA2980). The specimen length between clamps was about 15 mm for each specimen tested. Cross-section dimensions were typically 5 mm by 4 mm. The applied strain, held constant in these tests, was determined as the ratio of the clamp displacement to the original clamp separation. The value for the strain determined this way is susceptible to a small error arising from the compliance of the apparatus and movement of the specimen within the clamps. Although the magnitude of these errors has not been evaluated, they are expected to be small because of the low stiffness of the specimens. Measurements of stress $\sigma(t)$ with time under strain were made at selected strains ϵ_s starting at the lowest strain and then moving progressively to higher values. A time interval between tests of at least the duration of the previous test was imposed to allow the specimen to recover from the applied strain before the next measurement began. Values for stress relaxation modulus have been derived using Equation (A1.1) and are plotted against time under the applied strain.

Figures A1 and A2 show stress relaxation results for the two rubber materials studied in this project. For each material, the stress relaxation modulus is seen to decrease with increasing time and applied strain. The dependence of modulus on strain is greatest for the material where the reinforcing effect of the carbon is highest (AAAT F001). This data will be analysed further in Appendix 2.

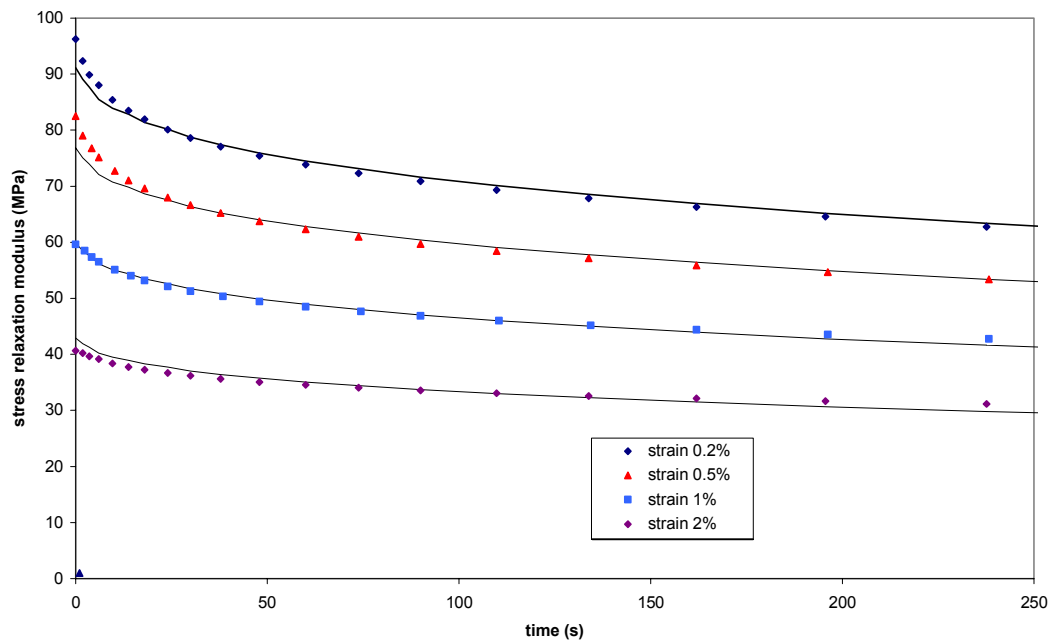


Figure A1.1: Stress relaxation results for the material AAAT F001 at different strain levels. The continuous curves are obtained using Equation (A2.1) with parameter values given in Table A2.1.

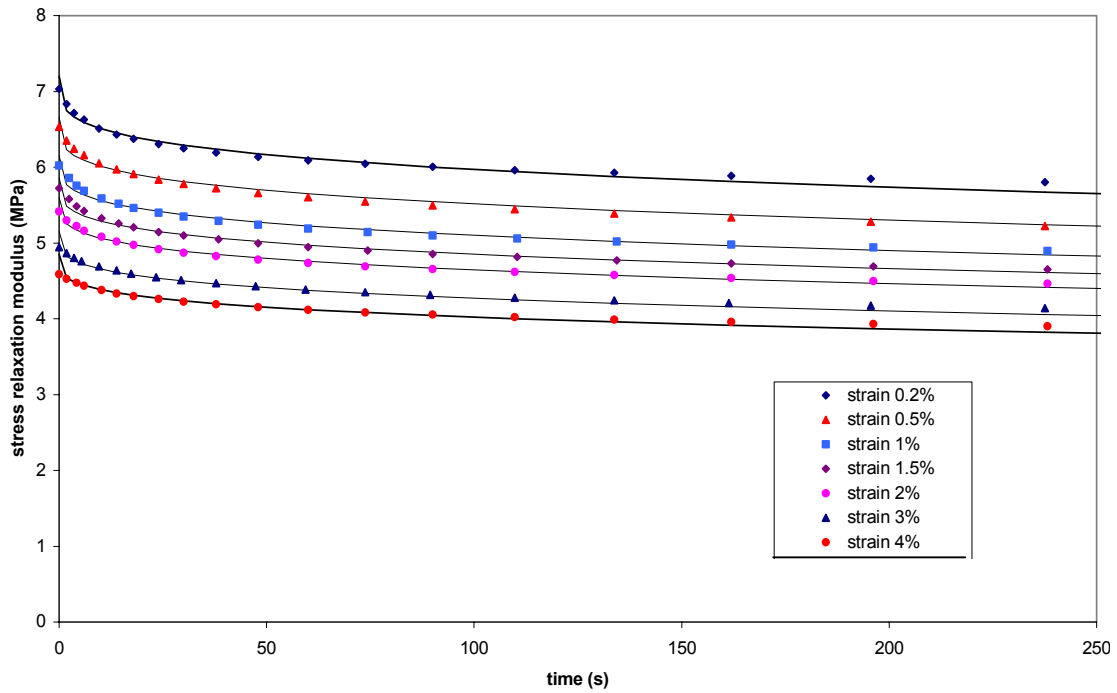


Figure A1.2: Stress relaxation results for material AAAT F004 at different strain levels. The continuous curves are obtained using Equation (A2.1) with parameter values given in Table A2.1.

A1.2.2 Dynamic Mechanical Tests

Measurements of dynamic mechanical properties were made on the same TA Instruments machine used for the stress relaxation tests. The same specimen and inter-clamp length were also used in both tests to facilitate correlations of results from the two test methods. Dynamic mechanical tests are commonly used to determine the variation of the dynamic modulus with temperature. The method can also be readily used to explore the dependence of modulus on the dynamic strain amplitude (see Appendix 2).

APPENDIX 2: Modelling Viscoelastic Behaviour of Thermoplastic Elastomers

The time and strain dependent behaviour of the two rubber materials introduced in Appendix 1 is illustrated in this appendix using results from stress relaxation tests and dynamic mechanical tests. Results are modelled using simple equations. In Section A2.3, the use of these equations is explored for predicting behaviour under a constant applied strain rate.

A2.1 Modelling the Strain Dependence of the Effective Stress Relaxation Modulus

The stiffness behaviour of the carbon-filled rubbers studied here can be characterised using stress relaxation tests to determine a stress relaxation modulus which is a function of time and the strain level. This behaviour can be modelled using separable functions of strain and time. The analysis of stress relaxation results is illustrated using the data from material AAAT F004 in Figure A1.1 (medium carbon content). A function commonly used to analyse stress relaxation results is:

$$E(t) = E_R (1 - kt^n) \quad (\text{A2.1})$$

E_R is the effective stress relaxation modulus at zero time, k is a parameter related to the inverse of a mean stress relaxation time and n is a parameter used to introduce a distribution of relaxation times into the relaxation process.

Values for the E_R , k and n giving best fits to the results in Figure A1 were obtained by first estimating the magnitude of E_R that gives a linear plot of $\log \left(1 - \frac{E(t)}{E_R} \right)$ against $\log t$. The associated parameters k and n were then obtained from the gradient and intercept of the linear plot. It was found that each of the curves in Figure A1.1 could be accurately described with the same values for $k = 0.054$ and $n = 0.25$. The curves obtained using these parameters are compared with experimental data in Figure A1.1. The dependence of modulus on the level of strain is therefore defined by the parameter E_R . This observation implies that the influences of strain and time on stress relaxation modulus are separable. Thus the dependence on time is not influenced by the level of strain and vice versa. Values for the parameter E_R giving the fits to data in Figure A1.1 at each strain are listed in Table A2.1.

Table A2.1: Variation of the parameter E_R in Equation (A2.1) with strain

Strain ϵ_s %	E_R (MPa)	
	F001 ($n = 0.25$, $k = 0.092$)	F004 ($n = 0.25$, $k = 0.054$)
0.2	102	7.2
0.5	86	6.7
1	67	6.2
1.5		5.9
2	48	5.6
3		5.2
4		4.9

A similar procedure was used to obtain a best fit using Equation (A2.1) to the stress relaxation results shown in Figure A1.2 for the higher carbon content material studied (AAAT F001). The best-fit curve is shown with the data in Figure A1.2, and the parameter values associated with the curve are recorded in Table A2.1. Only four values are shown for the high carbon content material as data were only obtained at four strain levels.

It can be seen that the value for n does not seem to change with the amount of carbon. The greatest changes with filler content are in the parameter E_R , which shows more dependence on the applied strain, ϵ_s .

The dependence of the values of E_R in Table A2.1 with strain ϵ_s is plotted for each rubber material in Figures A2.1 and A2.2. The variation with strain has been described using the function:

$$E_R = E_o (1 - a \epsilon_s^m) \quad (\text{A2.2})$$

where E_o , a and m are material parameters based on a best fit of Equation (A2.2) to data in Table A2.1. Values for these parameters giving best fits to the data were obtained by estimating a value for E_o and plotting $\log(1 - E_R/E_o)$ against $\log \epsilon_s$. The value for E_o was systematically changed to give the closest representation of data to a straight line from which values for m and a were obtained from the gradient and intercept. Values for the parameters E_o , a and m are listed in Table A2.2.

Table A2.2: Values for the stress relaxation parameters in Equation (A2.2) for each material

Material	E_o (MPa)	a	m
AAAT F001 (High filled)	121.1	2.5	0.33
AAAT F004 (Medium filled)	8.0	1.2	0.30

The dependence of stress relaxation modulus on strain and time can be accurately modelled by combining Equations (A2.1) and (A2.2):

$$E(t) = E_o (1 - a \epsilon_s^m) (1 - k t^n) \quad (\text{A2.3})$$

The parameters E_o , a , m , k and n are constant for a particular rubber.

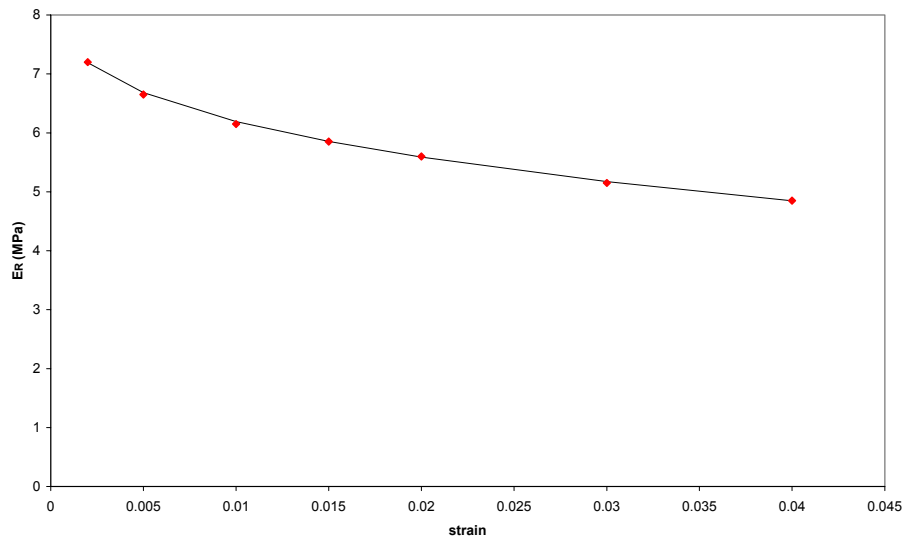


Figure A2.1: Plot of the parameter E_R in Equation (A2.1) against strain obtained from the analysis of the stress relaxation results in Figure A2.1 for the medium filled rubber (AAAT F004). The continuous line is derived using Equation (A2.2) with parameter values in Table A2.2.

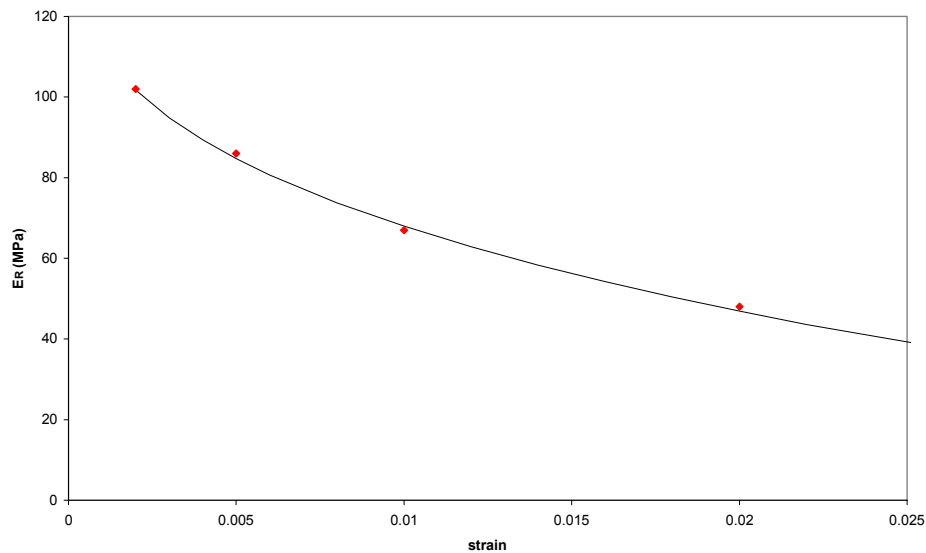


Figure A2.2: Plot of the parameter E_R in Equation (A2.1) against strain obtained from the analysis of the stress relaxation results in Figure A2.2 for the high filled rubber (AAAT F001). The continuous line is derived using Equation (A2.2) with parameter values in Table A2.2.

A2.2 Modelling the Strain Dependence of the Dynamic Modulus

The dependence of modulus on strain can be more conveniently demonstrated using dynamic mechanical tests.

Figure A2.3 shows the dependence of modulus on dynamic strain amplitude for the material AAAT F004 at three frequencies of 0.01, 0.1 and 1 Hz. At the end of each test, specimens were maintained for a period of 1 hour before the start of the next test to allow the carbon structure to recover prior to testing again at the lower strains. No attempt has been made, however, to monitor recovery to establish whether this time

period is sufficient. These results have been analysed to explore whether the dependence of E' on dynamic strain amplitude ϵ_0 and frequency is separable, as observed for stress relaxation in Equation (A2.3) and, if so, whether the strain dependence is identical to that found for stress relaxation results in Equation (A2.2). If this were found to be the case, then the time and strain dependent properties could be characterised with a single stress relaxation test and a single dynamic mechanical test.

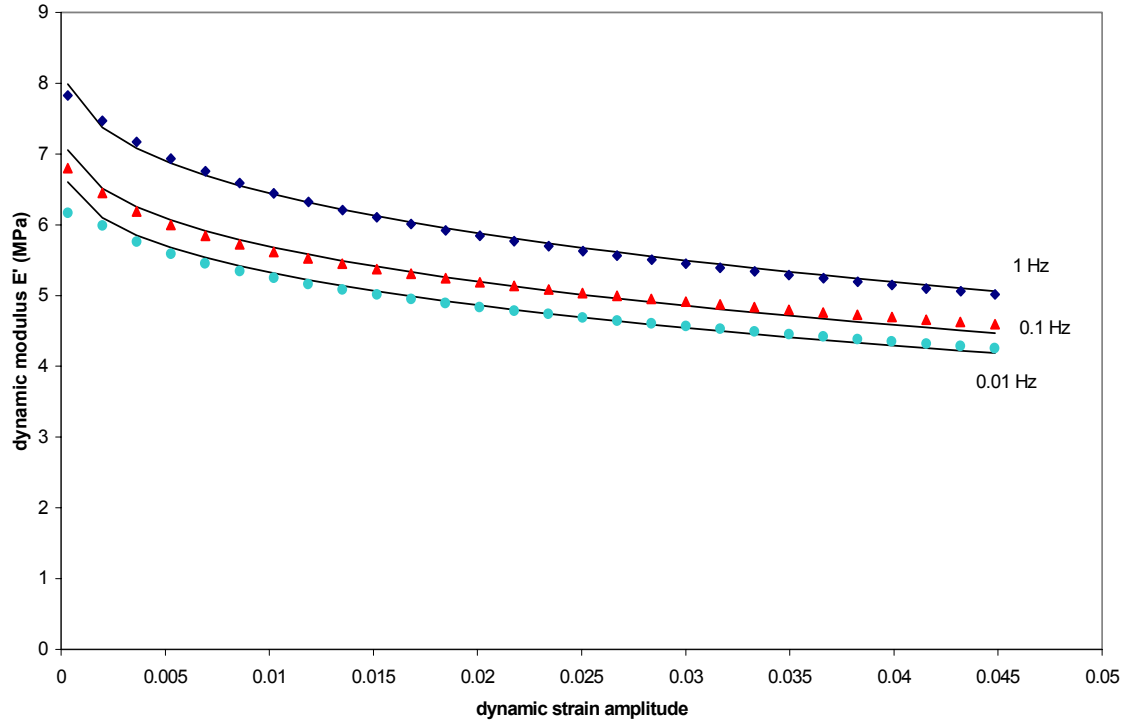


Figure A2.3: Variation of the dynamic modulus of the medium filled rubber with dynamic strain amplitude at different frequencies. The continuous curves are obtained using Equation (A2.4).

The data in Figure A2.3 at each frequency have been analysed using the equation:

$$E' = E'_0 (1 - b \epsilon_0^q) \quad (\text{A2.4})$$

where E'_0 , b and q are parameters that may depend on frequency. Values for these parameters giving the best fit to data were obtained by estimating a value for E'_0 and plotting $\log\left(1 - \frac{E'}{E'_0}\right)$ against $\log \epsilon_0$. The value for E'_0 was then systematically varied to give the best linear representation from which values for q and b were deduced.

The fits to experimental data shown in Figure A2.3 were obtained using values for $b = 1.05$ and $q = 0.3$ that are independent of frequency. The frequency dependence of E' is contained within the parameter E'_0 , which has the values shown in Table A2.3 at the test frequencies in Figure A2.3. The experimental E'_0 shown in Table A2.3 is determined by fitting Equation (A2.4) to the experimental data shown in Figure A2.3.

Table A2.3: Variation of the dynamic parameter E'_0 in Equation (A2.4) with frequency for material AAAT F004

Frequency (Hz)	E'_0 (MPa) (experimental)	E'_0 (MPa) calculated using Eqns (7) and (8)
1	8.8	8.4
0.1	7.8	7.9
0.01	7.3	7.3

The dependence of E' on dynamic strain, given by Equation (A2.4), can be compared with the dependence of $E(t)$ on static strain, given by Equation (A2.3). The powers to which the strain is raised, q and m , in these equations are the same magnitude. It is not clear, however, whether a dynamic strain ϵ_0 and a static strain ϵ_s of the same magnitude have the same effect on non-linear behaviour, although the coefficients of strain, a and b (see Sections A2.1 and A2.2, respectively), are of similar magnitude.

The time and frequency dependent terms, $E_0(1 - kt^n)$ and E'_0 , respectively, can be compared to explore whether the dynamic modulus E'_0 at any frequency f can be correlated with a stress relaxation modulus at some effective time t_e related to f . Thus:

$$E'_0(f) = E_0(1 - kt_e^n) \quad (\text{A2.5})$$

The results for the medium filled rubber in Figures A1.2 and A3.3 are not sufficiently accurate to enable a clear correlation between f and t_e to be determined. However, the approximate relationship:

$$t_e = 1/f \quad (\text{A2.6})$$

gives calculated values for $E'_0(f)$ using Equation (A2.5) that are comparable with experimental values as shown in Table A2.3.

It is not clear, from the results reported here, whether a sinusoidal strain of amplitude ϵ_0 has the same non-linear response as a static (stress relaxation) strain ϵ_s of the same magnitude. A correlation of the strain-dependent behaviours from dynamic and stress relaxation tests is further complicated by the uncertainty in the effective time of a cyclic strain. Exploration of methods for correlating strain-dependent behaviour from these tests is a subject for further study. This may lead to a procedure for characterising strain and time-dependent behaviour using a single dynamic test at an appropriate frequency and a single stress relaxation test at an appropriate strain.

A2.3 Constant Strain Rate Tests

The model for stress relaxation behaviour can be used to predict the stress response to more complex strain histories. This is illustrated here by predictions of stress/strain curves resulting from constant strain rate tests at a variety of strain rates.

As explained in Section A1.1.1, the stress/strain response of a viscoelastic material is a curve whose gradient decreases with increasing strain when tested under a constant applied strain rate. The gradient at any strain increases with increasing strain rate. The curve for any particular strain rate can be predicted, as shown below, from knowledge of the stress relaxation function. This is straightforward for a material showing linear viscoelastic behaviour, but the validity of the procedure is uncertain for non-linear behaviour such as that exhibited by the carbon-filled rubbers. The procedure for calculating stress/strain curves from stress relaxation data is now illustrated with reference to results for the medium filled rubber.

A tensile test at constant strain rate can be considered as a series of step increases in strain with strain increment $\Delta\epsilon$ for periods Δt . For strain levels where behaviour is linear, the stress response to the step loading can be derived by superposition of tensile stress relaxation curves:

$$\sigma(t) = E(t) \Delta\epsilon + E(t - \Delta t) \Delta\epsilon + E(t - 2\Delta t) \Delta\epsilon + \dots \quad (\text{A2.7})$$

The superposition is strictly valid only for linear behaviour where the response to any increase in strain, $\Delta\epsilon$ is independent of the strain level at which the increase is applied. For carbon-filled rubbers, the stress relaxation function $E(t)$ depends on strain as shown by Equation (A2.3). Within this equation the strain- and time-dependencies are separable which suggests that the dependence on time is *independent* of the level of strain. The significance of this with regard to the validity of superposing stress relaxation behaviour given by substituting Equation (A2.3) into Equation (A2.7) is not clear, but we will proceed on the assumption that any associated errors are acceptable.

The situation where the strain is applied smoothly at constant velocity can be realised by letting $\Delta\epsilon \rightarrow 0$ in which case Equation (A2.7) reduces to the integral equation:

$$\sigma(t) = \int_0^t E(t-s) \frac{d\epsilon}{ds} ds \quad (\text{A2.8})$$

where s is a dummy time variable.

By defining a new time variable $u = (t - s)$ and noting that $d\epsilon/ds = \dot{\epsilon}$, Equation (A2.8) becomes:

$$\sigma(t) = \dot{\epsilon} \int_0^t E(u) du \quad (\text{A2.9})$$

Taking the stress relaxation function for carbon-filled rubbers as Equation (A2.3), $E(u)$ is given by:

$$E(u) = E_0 (1 - a \epsilon^m)(1 - k u^n) \quad (\text{A2.10})$$

Substituting Equation (A2.10) into Equation (A2.9) and noting that $\dot{\epsilon} = \epsilon/t$, we obtain the equation of a stress/strain curve under constant strain rate as:

$$\sigma(\epsilon) = E_0 \epsilon (1 - a \epsilon^m) \left(1 - \frac{k \epsilon^n \dot{\epsilon}^{-n}}{(n+1)} \right) \quad (\text{A2.11})$$

Equation (A2.11) demonstrates the non-linear variation of stress with strain and a dependence on strain rate. For a material with $a = 0$, there is no contribution from the carbon to non-linear behaviour. Also it can be seen that when k is very small, the dependence on strain rate is also small, which is consistent with the associated reduction of the viscoelastic (time-dependent) response in E given by Equation (A2.1).

Taking values for the parameters E_0 , a and m in Table A2.2 and for k and n in Table A2.1, Equation (A2.11) has been used to calculate stress/strain curves for the medium filled rubber (AAAT F004), and these are shown at different strain rates in Figure A2.4. The separation of each curve with strain rate is a consequence of time-dependent behaviour whilst the curvature arises from both non-linear as well as time-dependent behaviour.

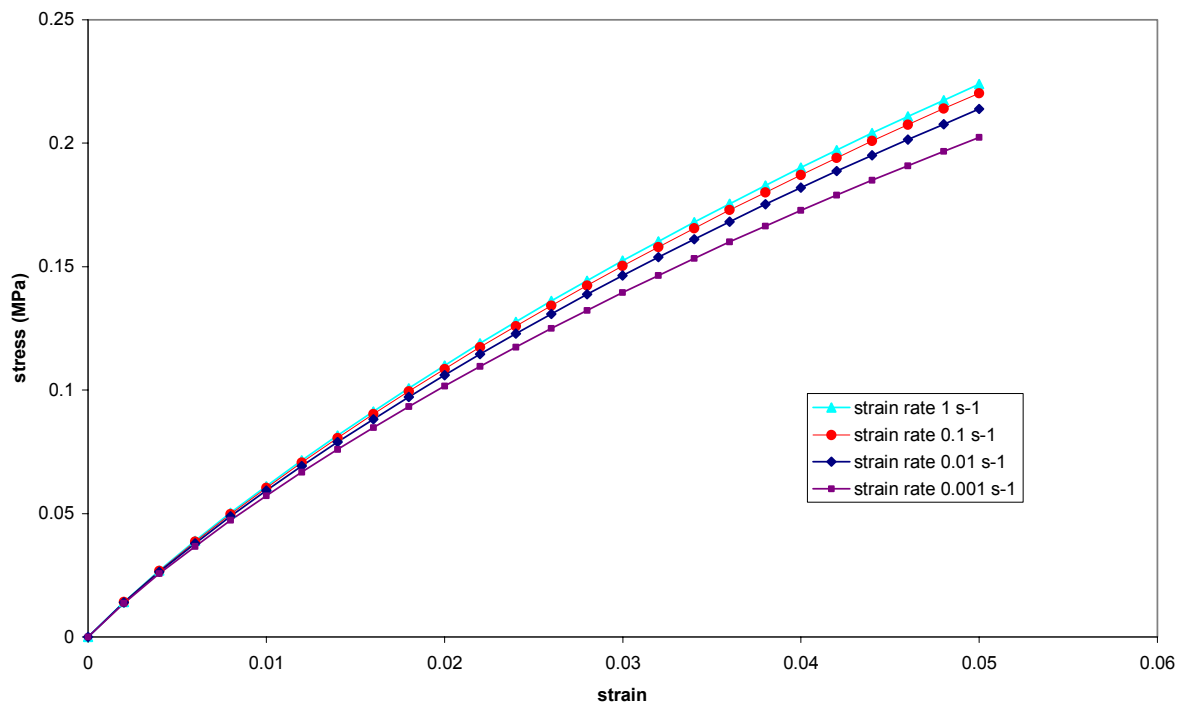


Figure A2.4: Stress/strain curves under constant strain rate predicted for the medium filled rubber at different strain rates using Equation (A2.11).

There is an assumption with this procedure that stresses can be calculated by superposition of the stress responses from every strain change. This is strictly only valid for materials whose stiffness behaviour is linear. The magnitude of any errors for the materials studied here should be investigated through comparisons of predictions of results for constant strain rate tests with experimental measurements. These studies would allow the suitability of the functions introduced here to describe strain and time-dependent behaviour to be explored for a wider variety of rubber materials and over wider ranges of strain and time. The sensitivity of predictions to the accuracy in the determination of model parameters could also be explored.

APPENDIX 3: Finite Element Modelling

A3.1 Finite Element Mesh Generation

A finite element analysis (FEA) has been used to model the Shore A hardness test. ABAQUS/CAE [5] was used as a preprocessor, to create the geometry, mesh and constraints. The geometry modelled is shown in Figure A3.1.

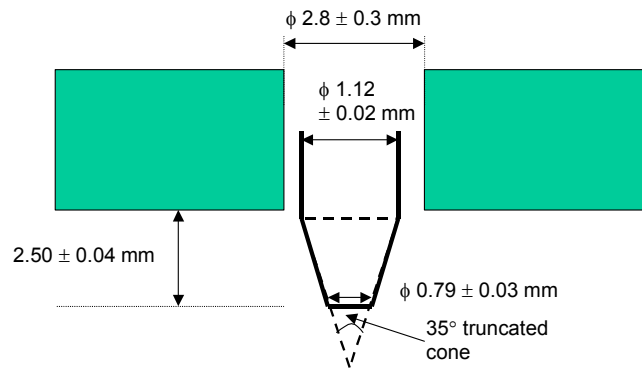


Figure A3.1: A schematic representation of the indenter used to measure hardness on the Shore A scale (Redrawn from ASTM D 2240-04)

The indenter is connected to the outer casing by a spring. The outer casing of the equipment is moved downwards until it touches the specimen surface. The indenter moves upwards by an amount that depends on the specimen material hardness. The force is calculated from the upward displacement of the indenter using the following equation:

$$F = 0.55 + 3x \text{ (N)} \quad (\text{A3.1})$$

where x is the indenter displacement (or spring displacement).

In ABAQUS/CAE the spring is modelled using an axial connector. The equation is incorporated by setting the elasticity of the spring as:

$$F = 3x \text{ (N)} \quad (\text{A3.2})$$

then setting up a reference length. The reference length is defined as the length at which the force is zero, and can be different from the actual length of the spring. In this case, the reference length is set to a value that will produce a force of 0.55 N at the starting indenter location of 2.5 mm below the casing.

A half model of the geometry was generated, and axisymmetric elements were used to mesh the geometry, making the specimen cylindrical. The mesh is shown in Figure A3.2. The steel casing and indenter were both modelled as elastic, and the hypoelastic model was used for the rubber specimen. Contact surfaces were defined between the casing and the specimen, and the indenter and the specimen. A displacement was

applied to the casing, moving it into contact with the specimen. The outputs selected were the spring relative displacement (CU1) and spring elastic force (CEF1).

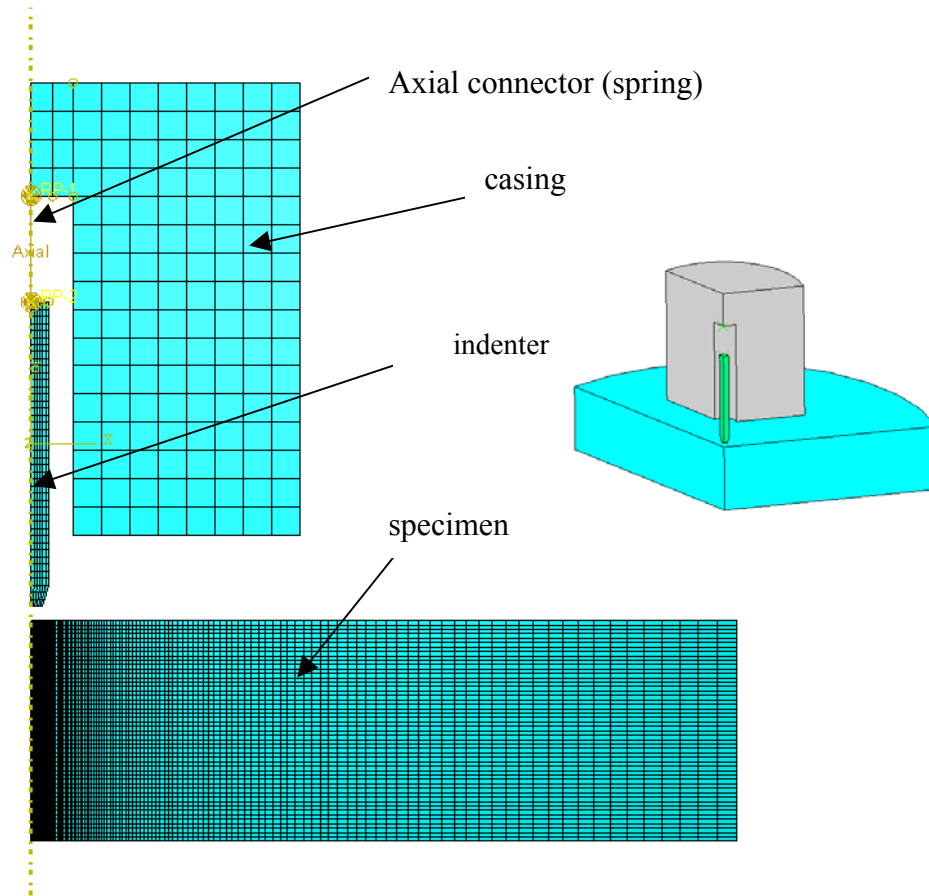


Figure A3.2: Axisymmetric finite element mesh of the Shore A hardness indenter.

The Shore A hardness, H_A , can be calculated from the FE outputs in two ways. The force output (CEF1 in mN) can be used with the following equation:

$$H_A = \frac{F - 550}{750} \quad (\text{A3.3})$$

Or by combining Equations (A3.1) and (A3.3), the relative spring displacement can be used:

$$H_A = 40 x \quad (\text{A3.4})$$

A3.2 Hypoelastic Material Model

The hypoelastic material model was used to represent the specimen material behaviour during the analysis. This model best represents the materials studied, which show non-linear behaviour at low strains. The hypoelastic model in ABAQUS/Standard is used for materials in which an increment of stress is related to an increment of strain by an elasticity matrix, which is a function of the total elastic strain. This general, nonlinear elasticity is valid for small elastic strains.

In a hypoelastic material the increment of stress is defined as a tangent modulus matrix multiplying the increment of elastic strain such that:

$$d\sigma = D^{\text{el}} : d\varepsilon^{\text{el}} \quad (\text{A3.5})$$

where $d\sigma$ is an increment of stress, D^{el} is the tangent elasticity matrix, and $d\varepsilon^{\text{el}}$ is an increment of elastic strain. The entries in D^{el} are provided by giving tangential modulus, E_T , and Poisson's ratio, ν , as functions of strain invariants. The strain invariants are defined for this purpose as:

$$\begin{aligned} I_1 &= (1 - 2\nu) \varepsilon \\ I_2 &= \nu(2 - \nu) \varepsilon^2 \\ I_3 &= \nu^2 \varepsilon^3 \end{aligned} \quad (\text{A3.6})$$

The material parameters can be defined directly on the data lines.

The data used in the analysis were obtained from an isochronous curve of stress as a function of strain at 15 seconds as this relates to the 15-second hold time of the Shore A hardness test. The data shown in Figure A3.3 are for the medium filled rubber (AAAT F004). The individual data points were obtained from the stress relaxation modulus versus time curves in Figure A2.1, by obtaining a stress value from each constant strain curve at a time of 15 seconds. A curve is fitted through the stress-strain data and the equation of this curve is used to calculate the tangential modulus at the required strains. The actual parameters obtained are presented in Appendix 2 (Table A2.2). In this case, the equation used to obtain the tangential modulus is:

$$E_T = E_0 - E_0 (m + 1) a \varepsilon^m \quad (\text{A3.7})$$

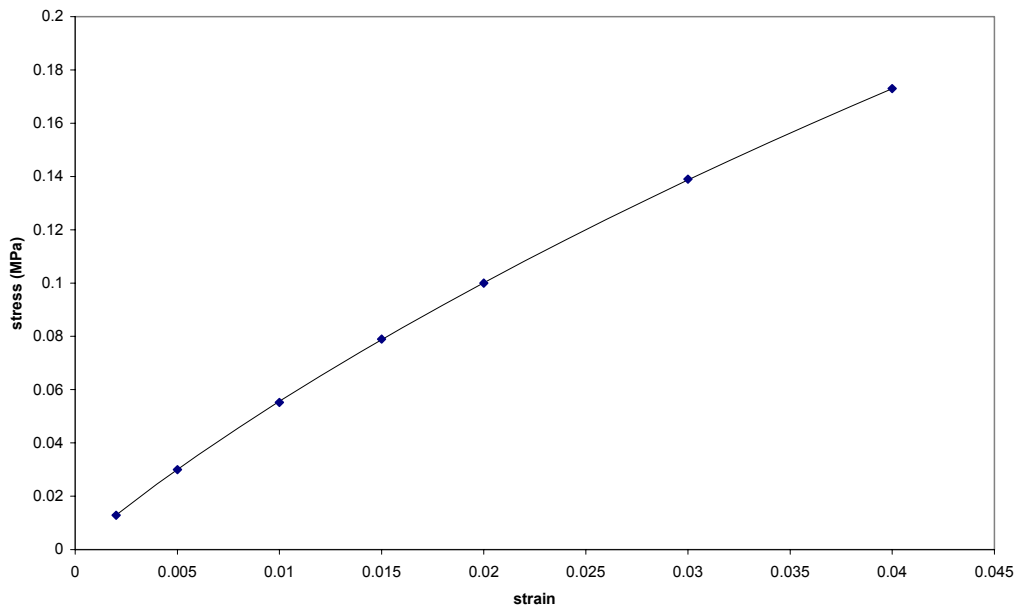


Figure A3.3: 15-second stress strain curve for the medium filled rubber (AAAT F004).