

Mechanical and rheological testing to develop thermoplastic elastomer-polyborodimethylsiloxane blends for personal impact protection

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Abstract

To claim ‘wearability’, clothing for protection against impact injury must not only act locally as a rigid shell under impact in order to satisfy drop-weight tests, but also flex freely with normal movement and offer permeability and light weight. Previous materials used carrier textiles coated with ‘dilatant’ but mechanically weak polyborodimethylsiloxane (PBDMS) compounds. We outline a procedure for developing blends of PBDMS with thermoplastic elastomers which, while minimizing the force transmitted in standard drop-weight tests on monolithic plate, can also be injection moulded into more wearable 3D shell structures. The first successful blends were developed by trial-and-error, involving the melding and testing of many plate specimens. The new procedure uses dynamic mechanical thermal analysis and time-temperature superposition to calibrate Zener-solid models for specific conditions within the service temperature and impact-speed envelope. Each model material is then subjected to a virtual drop-weight impact test to estimate the peak transmitted impact force. These results guide the selection of blends suitable for further development, correlating well with those obtained using the previous, more laborious procedure. When distributed within a suitable blend, PBDMS contributes considerably greater impact force attenuation than bulk uniaxial tests indicate.

Keywords

Impact protection; Dynamic Mechanical Analysis; Polyborodimethylsiloxane; Compression test.

1. Introduction

A variety of body-worn devices offer personal protection from impact at energy densities ranging from that of an accidental fall to that of an aimed projectile and including those from road traffic and extreme sports. When a mass m strikes any target at a relative velocity v_0 , an

interposed *protective layer* can reduce the maximum force transmitted to the target surface as it arrests the striker. If the layer is H thick and its moving mass is negligible compared to m , the minimum possible value of this peak force will be

$$F_{\text{opt}} = \frac{mv_0^2}{2H}. \quad (1)$$

To achieve this minimum, the layer must collapse onto the target at constant load, uniformly decelerating the striker to zero velocity as it ‘bottoms out’ at zero thickness. Basic personal protective devices such as cycle helmets still rely on rigid polymer or metal foams which collapse in this manner, but these foams deteriorate on cyclic loading; many will fail on the first reload (Viot *et al.* [1]). Protection layers using softer, e.g. polyolefin or polyurethane foams are generally more robust under repeated moderate impacts but less effective for protection against one at high energy.

A typical elastic-impact load trace resembles a parabola rather than this optimum, ‘top hat’ (Heaviside) function: the resisting force does not initially increase quickly enough. One remedy — the “armouring” approach — is to increase the surface stiffness of the protective layer so that the impacting mass must initially compress its core over a greater area. However, since compressive strain rates are greatest immediately after contact, another approach is to increase the high-rate stiffness *throughout* the protective layer material.

Textile-based *active* personal protection systems embody both approaches. They conform to individual wearers and allow free flexure at rates ranging from those of everyday movement to those of extreme sports, but their surface layers become *temporarily* rigid under external impact at rates which threaten injury. Dow Corning’s DeflexionTM (formerly the ‘Advanced Protection System’ of Walker *et al.* [2]) is a breathable, textile-based body Armor which owes this response to their silicone-based X3180 Dilatant Compound. X3180 is itself a development of their DC3179 Dilatant Compound, better known as the basis of Silly Putty^{TM4}. Both DC3179 and X3180 undergo a transition in behaviour, with decreasing test time, from viscous fluid to elastic solid, and both derive this transition from polyborodimethylsiloxane, PBDMS.

⁴ Now a registered trademark of Crayola Properties Inc.

Unmodified polydimethylsiloxane is a silicone oil showing little viscoelasticity at room temperature, its glass transition temperature T_g being around 150 K lower [3]. Its boronated derivatives owe their unusual rheology to dynamic crosslinks formed on reaction with boric acid. Initially identified as donor-acceptor bonds between boron and oxygen atoms on adjacent chains [4], these transient crosslinks are now attributed to hydrogen bonding between hydroxyl groups at chain ends newly formed by scission of the original siloxane chain and then re-capped by boronyl groups [3]. They place PBDMS in the class of supramolecular elastomers whose extraordinary properties, e.g. easy melt processing and self-healing of clean fractures without interpenetration of chains across the interface, attract considerable interest [5].

Because dynamic crosslinks allow local shear relaxations [6] as they migrate, they also explain the impact-mitigating properties explored here. Under low static stress (e.g. gravity) PBDMS flows at a low rate determined by their lifetime, but under impact it behaves as a rigid, densely crosslinked thermoset. At intermediate rates it exhibits the high rebound of a lightly crosslinked rubber. Fig. 1 shows DMA data for DC3179, originally published online and reproduced here by kind permission (Braithwaite [7]). Also plotted is the in-phase Newtonian viscosity, calculated as the ratio of shear loss modulus G'' to angular frequency ω [8]. At low frequencies the loss modulus dominates, and behaviour is essentially Newtonian with a high and constant viscosity. The remarkable feature of the material is the rapid (approximately 1.8th-power) increase in storage modulus G' at frequencies approaching 100 rad s⁻¹.

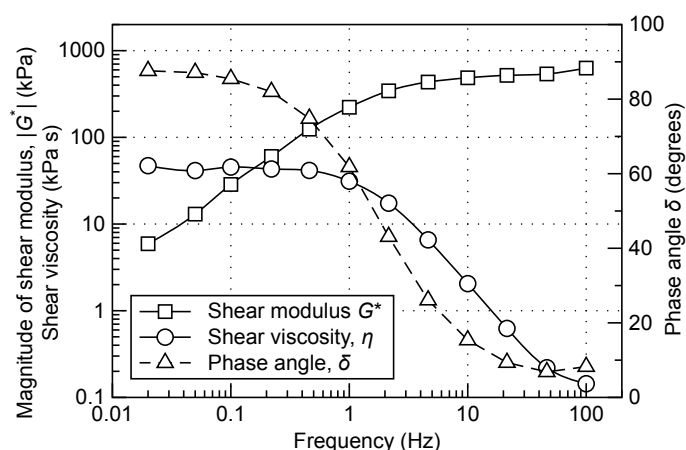


Fig. 1 Rheology of Dow Corning DC3179.

Dow Corning's PBDMS-based DeflexionTM has undergone application-specific testing to product standards such as EN 1621-1:2012 for protective layers within motorcyclists' clothing

[2]. Our objective was to develop a strategy for designing new blends of thermoplastic elastomer (TPE) and PBDMS which, when injection moulded into complex, concurrently designed layer structures, would satisfy EN 1621 tests while also providing all the other requirements of a marketable personal-protective product.

In this paper we set aside the layer design and mouldability issues and focus on the impact-attenuation performance of a *monolithic* slab of comparable thickness. There are many TPEs to choose from, and — although we have not explored this avenue — the precursor polysiloxane molecular weight, molecular weight distribution and degree of boronation could be used to tailor PBDMS properties [9, 10]. The first successful blends were designed using a trial-and-error procedure: for each promising TPE, several blends were prepared, injection moulded into plates and subjected to EN 1621 tests under a range of conditions. Much experience was gained, but at a considerable cost in time.

As the scope of the project extended to embrace a moulded product, the required balance of basic material properties became clearer and the selection process could be further refined. The more systematic procedure we demonstrate here relies on DMA data for the blend constituents and a simple analytical model of the impact test to *predict* relative performance in drop-weight tests. It set out to offer deeper insight into the TPE properties required to minimize transmitted force — ultimately, perhaps, allowing a suitable TPE to be *designed*.

After a brief introduction to the basic mechanical properties of ‘dilatant’ materials and to the standard product test method for personal protection layers, we review test methods which could support material design. Ultimately the new procedure is demonstrated using a series of blends based on two styrene-ethylene-propylene-styrene (SEPS) TPEs and a Dow Chemicals PBDMS compound.

2. Materials and method

To evaluate each candidate TPE material, we need a set of EN 1621 drop-weight test results to identify the TPE/PBDMS blend which transmits the minimum impact force across the specified product temperature range: -20 to $+40^{\circ}\text{C}$. Each of a wide range of commercially available TPEs was blended with PBDMS in volume ratios of 3:7, 1:1 and 7:3. Each blend was

compounded and pelletized on a twin-screw extruder, then injection moulded through an edge knife gate into flat, 150 mm square plaques of 2 mm and 6 mm thickness.

This section describes both the drop-weight test itself and the other methods chosen to access more basic, geometry-independent property data for a material model. It also presents results for the PBDMS component Dow Corning X3180 dilatant compound, the other component in every blend and the most challenging to test. The objective was to simulate the standard test using this data, providing deeper understanding of the TPE properties required.

2.1. The ISO EN 1621 product test

In an EN 1621 test, a 5 kg striker falls to gain a kinetic energy of (normally) 50 J before impacting a specimen of the protective layer against a fixed anvil, on which the transmitted force is measured. The protective layer, or stack of layers, must attenuate the peak transmitted force to below a specified value which comfortably exceeds F_{opt} . EN 1621 variants differ in the geometry of the striker and anvil surfaces, which are chosen to represent different anatomical features (e.g. elbow, hip) and impact sites (e.g. road surface, kerbstone). For the EN 1621-1 variant used in most tests here, the anvil surface is a dome of 50 mm radius and the striker surface a horizontal cylinder of radius 10 mm. To provide accurate and repeatable test data to current standards (and the flexibility to develop new standards) a bespoke drop-weight rig was designed and constructed.

2.2. Rheology of dilatant compounds

PBDMS presents several challenges to mechanical characterization. At rates below its Maxwell transition, the most suitable methods are viscometric. Hailemariam and Mulugeta [11] used capillary rheometry to confirm the shear thinning behaviour of Dow Corning DC3179 with rate at higher temperatures and Waffle et al. [12] used a shear disc method to represent this material (and others) using the Cross model usually associated with polymer melts. For the present work we used a TA Instruments Q800 instrument, in both cone and plate configurations.

Neither ‘dilatant’ nor ‘shear thickening’ adequately describes the reversible transition of this material, with increasing frequency, to a temporarily crosslinked rubber. A *dilatant* fluid is usually understood as one whose shear viscosity increases with applied shear rate, whereas that

of PBDMS *decreases*. Colloidal suspensions of solid flakes which agglomerate under shear can be blended with PBDMS to form compounds which *do* exhibit classical dilatancy [13]. DC3179 contains 17% silica and (probably as a pigment) 1% titanium dioxide. Amongst other interesting applications, it serves as an analogue material in tectonic models. In this context Dixon and Summers [14] noted that although the material bounced with a high coefficient of restitution, no instantaneous elastic recovery was detectable after long-term ($10^2 - 10^3$ s), constant-stress creep shear loading in an annular gap. Nevertheless, much of the creep strain was recovered over the same period. Ultimately Dixon and Summers [14] represented DC3179 as a Bingham solid with a Newtonian viscosity of 18.2 kPa s at 18°C (allowing it to model geological processes within human timescales under centrifugal ‘enhanced’ gravity) and a modest Bingham yield stress of 325 Pa (allowing tectonic models to support their own weight during setup).

The Dow Corning X3180 PBDMS tested here, however, contains no silica and is designed to be applied as a water-based emulsion to a carrier textile. After drying, the textile structure gains significant stiffness at high rates of flexure while also (unlike the open-cell foam carriers studied by Bettin [16]) maintaining its ability to transmit air and moisture: its *breathability*. Other comparable textile-carrier systems include the dilatant-impregnated Kevlar™ aramid fibre studied by Lee et al. [17]; here the dilatant effect is contributed solely by colloidal silica, which was present in DC3179 but is absent from X3180.

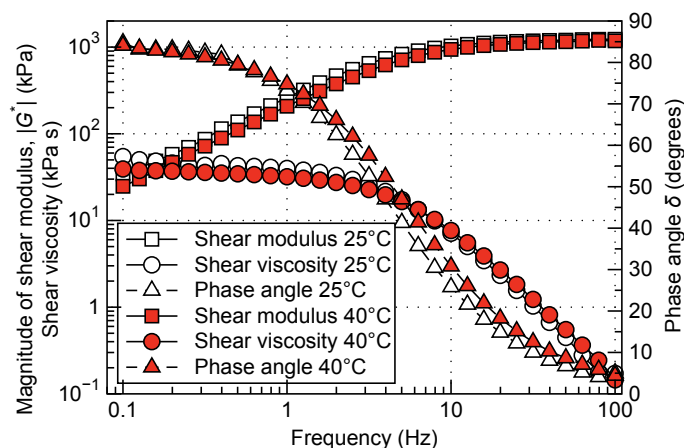


Fig. 2. Shear storage modulus, loss modulus and delta values for X3180.

The mechanical properties of X3180 (Fig. 2), like those of DC3179 (Fig. 1) are dominated by its PBDMS content. Neither its viscosity nor its modulus appears to be much affected by its lack of DC3179’s particulate content: its shear modulus even seems to be higher. We did not see the

upturn in the out-of-phase modulus at several hundred rad s^{-1} seen in DC3179 — behaviour which Seetapan [10], testing three molecular weights of which one lay below the entanglement value, attributed to the additional temporary crosslinks provided by entanglement. The PBDMS chain is very flexible and, even when the reaction with boric acid has reached gelation (after which it can achieve little more [18]), relatively long.

2.3. Compressive stress/strain testing

DMA alone cannot adequately describe materials for this high-strain application, but it can help to explain the mechanisms by which PBDMS modifies their behaviour and could, eventually, guide the development of application-specific TPEs. EN 1621 drop-weight impact tests, on the other hand, are simple enough to be defined unambiguously, but not necessarily simple enough for results to be interpreted as material properties. The various striker and anvil profiles generate varying levels of stress triaxiality during impact and, because the impact energy is limited, the deformation history depends on the material properties. To measure basic properties we used the constant-strain-rate uniaxial compression test, beginning with the most challenging material — the X3180 PBDMS, as a monolithic “solid”. The results are discussed here in some detail since we will later see very different X3180 behave very differently when dispersed in blends.

The softness of X3180 made manufacture of cylindrical compression specimens from solid difficult so they were cast to shape. To facilitate demoulding, moulds were lined with PTFE film. The viscous and opaque material was then packed in, taking great care to avoid trapping air, until the open top surface was as flat as possible. Each delicate moulding was removed while still wrapped in its PTFE sleeve. It remained wrapped until immediately before being tested.

2.3.1. Low strain rates

Cylindrical specimens of X3180 were tested to EN ISO 7124:2007 and EN ISO 7743:2008. Following Cook and Larke [18] and Singh and Padmanabhan [19], we chose 20 mm diameter and 20 mm height to minimize frictional effects. Specimens were tested between flat PTFE platens lubricated with Super Lube (the usual silicone-based lubricants stick to X3180).

An Instron 4466 machine with a ± 1 kN load cell was used to compress each specimen to 75% engineering strain at constant true strain rate. The crosshead was actively decelerated to compensate for decreasing thickness; similarly, the load response was actively converted to true

stress on the assumption of constant specimen volume. Note that similar tests by Seetapan [10] on PBDMS used constant displacement rate, perhaps complicating the comparison of their results with those from DMA.

Three repeat tests were carried out at each true strain rate, and after processing to true stress versus true strain the results were averaged.

2.3.2. High strain rates

Measuring high-rate stress/strain properties of soft solids is challenging. Given the 20 mm length of the compression specimens and the nature of their material, we cannot assume dynamic equilibrium even at the testing rates reported above. The density of DC3179 is 1177 kg m^{-3} [12], and although the absence of filler can be expected to reduce the density of X3180, the compressive wave speed is unlikely to exceed 40 m s^{-1} . Only after several wave reflections (and, therefore, only at significant strain) is equilibrium approached — but X3180 has an important transition at around 50 ms. Further problems arise from the need for load signals at small strains to reach a sufficient signal/noise ratio.

Chen et al. [20] reviewed the obstacles to interpreting Split Hopkinson Pressure Bar tests and devised methods to evade them and measure an equilibrium true-stress-true-strain curve for conventional (non- ‘dilatant’) soft silicon rubbers at a uniform, constant strain rate of 3200 s^{-1} . However, our requirements are less critical. We used two drop-weight rigs (the ISO 1621 and another of lower striker mass) to compress cylindrical specimens between flat plates, measuring the striker load and displacement by accelerometry and accepting that they would yield only indicative results.

3. Mechanical characterization of typical SEPS-PBDMS blends

SEPS (styrene–ethylene–propylene–styrene) copolymers at the softer end of the styrene content range are typical of the TPEs whose blends with PBDMS performed well in EN 1621 drop-weight tests. Two blends (SEPS-1 and SEPS-2) offered the excellent processability needed to mould large personal protection mats of intricate form. SEPS-1 is a 13% styrene grade with a Type A Vickers hardness of 36, supplied by Kuraray Europe GmbH as Septon S2063; SEPS-2 was provided as a development grade.

3.1. Dynamic spectra and time-temperature superposition

EN 1621 tests on several TPEs confirmed that X3180 content distinctly improves impact attenuation, but to different degrees and over different temperature ranges. Because many TPEs are available and more will arrive, it was important to understand their performance better so that candidates could be more rationally selected and even, perhaps, designed.

A drop-weight impact force/time trace resembles an isolated, unipolar Gaussian or sinusoidal pulse. Taking the period of the impact pulse to be twice the time for which its magnitude exceeds half the maximum locates it at $f_p \approx 200 - 500$ Hz. For an ideal, square pulse, the amplitude of the frequency content is greatest at zero and its successive maxima (at $3, 5, 7f_p$) are already less than 3% of the steady state. Since even for neat X3180 the modulus increases at less than one decade per decade, an adequate portrait of each candidate material would need dynamic mechanical spectra from 20 to 5 kHz.

For the base SEPS-1 TPE and its blends, time-temperature superposition was used to reduce spectra measured from -50°C to $+25^\circ\text{C}$ and from 1 Hz to 100 Hz — taking around 5 hours each — to a single master curve using a Williams-Landel-Ferry (WLF) shift function

$$a_T(T, T_{\text{ref}}) = \frac{\omega_{\text{ref}}}{\omega_T} \quad (2)$$

where

$$\log_{10} a_T = \frac{-C_1(T - T_{\text{ref}})}{C_2 + T - T_{\text{ref}}}. \quad (3)$$

Empirical in origin, Eq. (3) is now explained using kinetic arguments [21, 22] rather than earlier free-volume models, and the kinetics of temporary crosslinks in PBDMS differ from those of an entangled network. The consistency of data with the ‘universal’ WLF constants can provide useful insights: only C_1 values close to 16–17 rigorously characterise a glass transition [22], and to be physically rational the product $C_1 C_2$ should be independent of the choice of T_{ref} and of the order of 400–900 K [23]. In practice T_{ref} can be determined from data by regression analysis; for a $T_{\text{ref}} \neq T_g$, new constants C'_1 and C'_2 corresponding to the universal values are:

$$C'_1 = \frac{C_1 C_2}{C_2 + T_{\text{ref}} - T_g}, \quad (4)$$

$$C'_2 = C_2 + T_{\text{ref}} - T_g. \quad (5)$$

Other guidelines recommended by Ferry [23] are implemented in DMA instrument systems; we followed them using TA Instruments, Microsoft Excel and Visual Data Tools Datagraph software. Using SEPS-1 data, the WLF method (using ‘universal’ and freely fitted parameters) was compared with the least-squares [24, 25] and *closed form time-temperature superposition shifting* (“CFS”) methods [26]. For material selection and design, we found that these latter, more complicated methods added little value.

SEPS-1 was tested as ISO 6721 specimens in shear sandwich mode using a multi-frequency, strain control method with temperature steps and frequency sweep, at the very low strain amplitude of 0.05 %. After equilibration at -60°C for 5 minutes, the sample was cycled at 5 frequencies per decade from 1 Hz to 100 Hz. A 5°C temperature increment was followed by the next sweep — and so on up to 25°C .

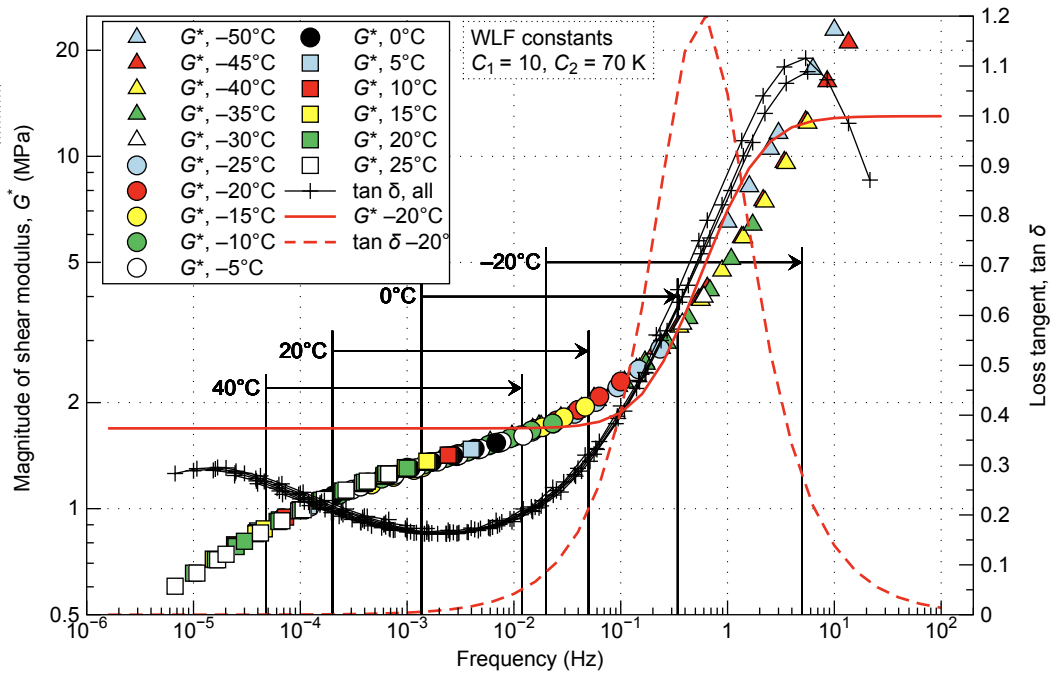


Fig. 3: Shear modulus master curve at $T_{\text{ref}} = T_g = -50^\circ\text{C}$ for SEPS-1, showing Zener fit to G^* at -20°C .

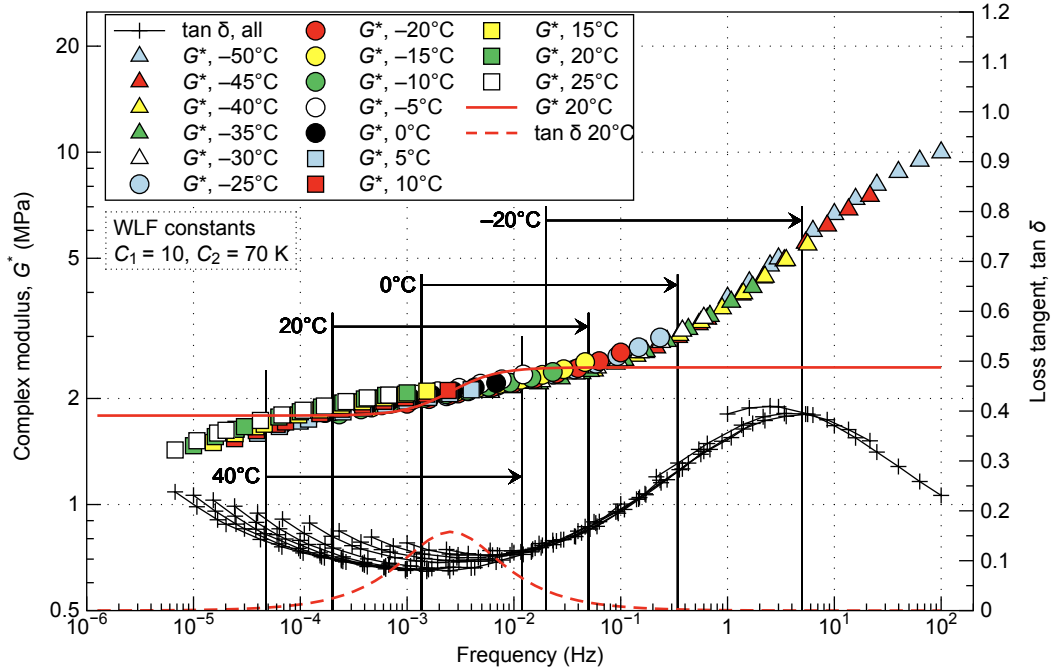


Fig. 4: Shear modulus master curve at $T_{\text{ref}} = T_g = -50^\circ\text{C}$ for SEPS-1 blended with 50% X3180, showing Zener fit to G^* at 20°C .

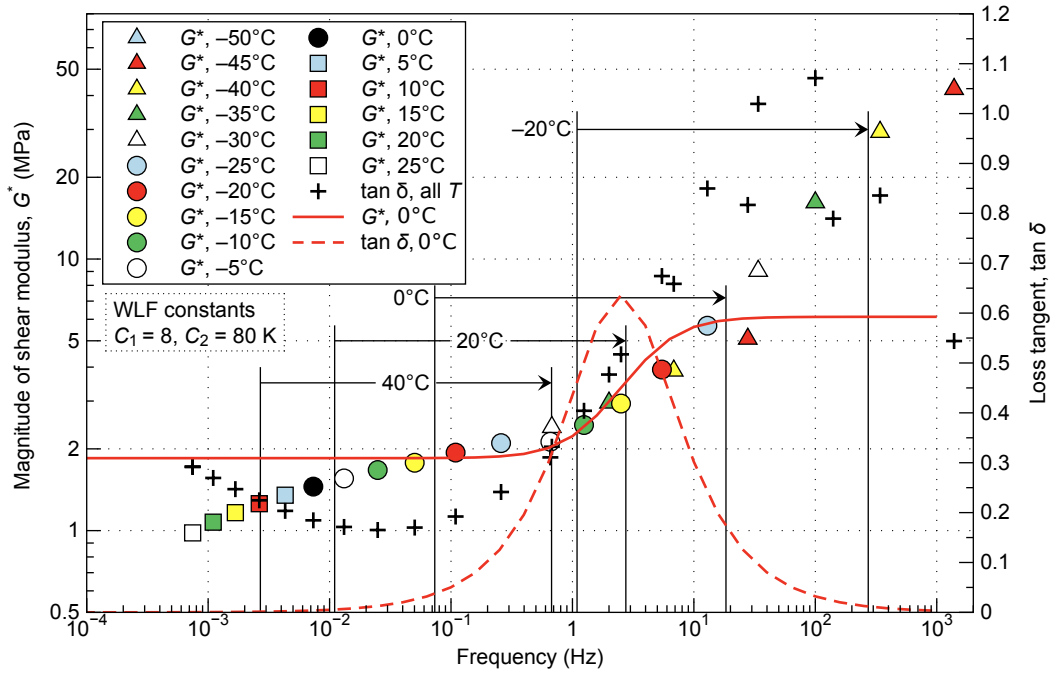


Fig. 5: Shear modulus master curve at $T_{\text{ref}} = T_g = -50^\circ\text{C}$ for SEPS-2, showing Zener fit to G^* at -20°C .
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For SEPS-1 (Fig. 3) and each of its blends with 30%, 50% (Fig. 4) and 70% PBDMS, a T_g value of -50°C and WLF coefficients $C_1 = 10$ and $C_2 = 70$ K successfully collapsed all data onto a single master curve. Neat SEPS-2 is around 50% stiffer than SEPS-1 across the frequency-

temperature range tested. For the SEPS-2 TPE and its 30% and 50% blends with X3180, values of $C_1 = 8$ and $C_2 = 80$ K were effective for minimal DMA data sets from 2 Hz and 100 Hz scans, but the 70% X3180 blend required $C_1 = 5$ and $C_2 = 140$ K. The success of WLF as an interpolation tool is notable, given that these materials are not thermo-rheologically simple. Blends with 70% X3180, however, were generally difficult to process and mechanically fragile.

4. Results and discussion

4.1. Drop-weight test results

Figure 6 shows EN 1621 drop-weight test results for SEPS-1 at 23°C. Here an X3180 concentration of 50–70%, depending on temperature, provided the greatest attenuation of peak force at ambient temperatures. Although tests at the highest concentration occasionally showed cracking which increased scatter, these results were sufficient to identify SEPS/X3180 blends around 50/50 as candidates for further evaluation.

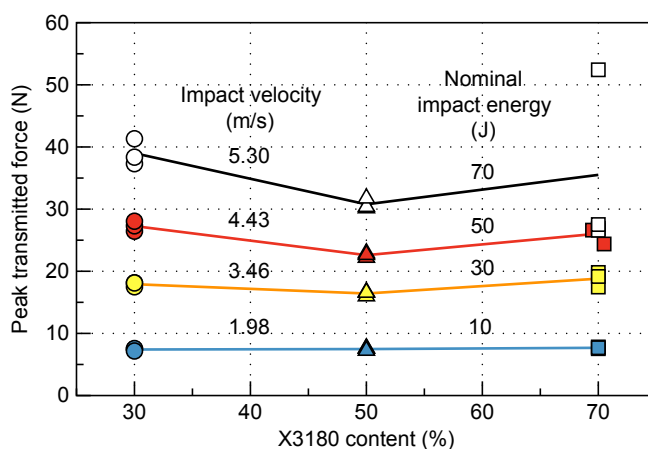


Fig. 6: EN 1621 drop-weight test results showing the effect of X3180 content on peak force transmitted through

4.2. Low rate compression of X3180

Figure 7 confirms that under these large, slowly applied strains X3180 shows no significant work-hardening, confirming the absence of a persistent network: the polymer is effectively a viscous liquid. Even without DC3179's particulate fillers, X3180 may still have a yield stress of the order measured by Dixon and Summers [15], but our results could not resolve its value.

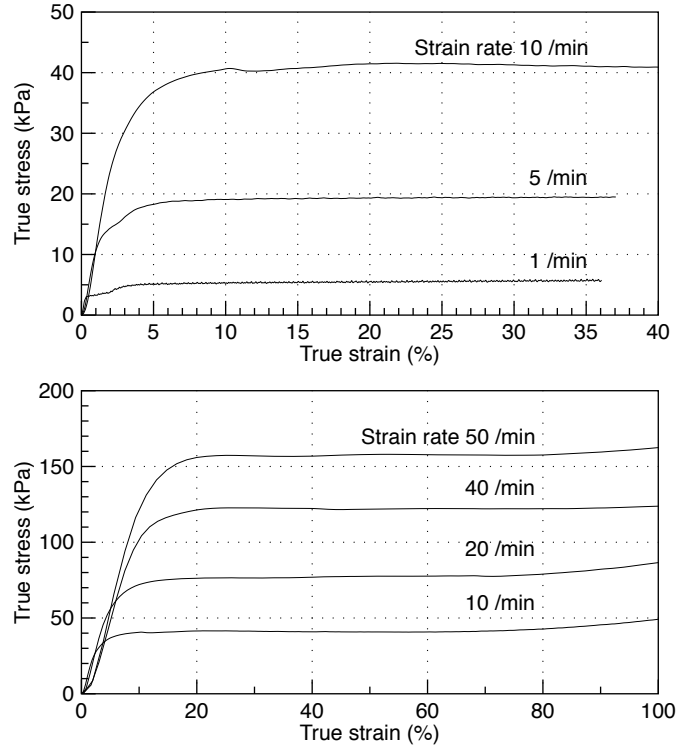


Figure 7: True stress vs. true strain curves for X3180 at constant true compressive strain rates of (above) 1–10 min^{-1} and (below) 10–50 min^{-1} .

To extract a flow stress from each test, the load was averaged for the interval from 50% strain (the maximum for which the standard for this method claims validity) back to 25% (or, for the slowest two tests, from 35% back to 10%), below which the highest rate curve is still settling. Plotted against the compressive strain rate in Fig. 8, these low-rate flow stress results indicate Newtonian behaviour with a viscosity of 230 kPa s . Viscosity results derived from our DMA data (Fig. 2) indicated some shear thinning below the transition at 20 rad s^{-1} . Indeed, the power-law exponent was about 0.2, which is not much less than a typical high-rate power-law index for shear viscosity in entangled polymer melts. This had not been apparent from DMA data for DC3179 (Fig. 1) but was again borne out by compression test results. Extrapolating the shear viscosity DMA data back to 0.2 rad s^{-1} yields 70 kPa s which, using Trouton's Law, corresponds to an extensional viscosity of $3 \times 70 = 210 \text{ kPa s}$: within 10% of the compression test result and, as expected, lower than that under hydrostatic pressure.

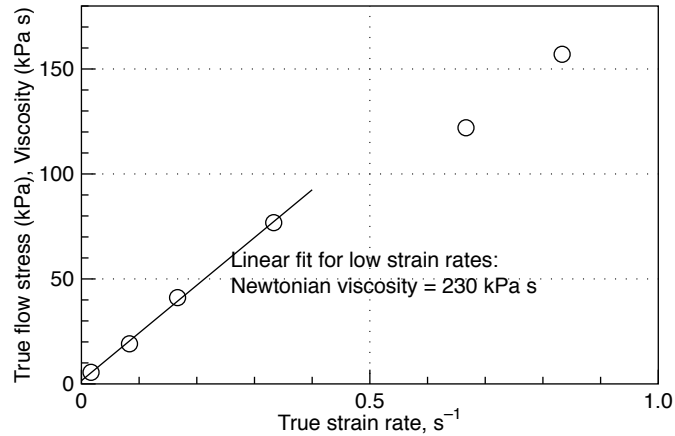


Figure 8: Steady-state true stress vs. true compressive strain rate curves for X3180 at room temperature. The linear fit indicates a low-rate Troutonian viscosity of 230 kPa s

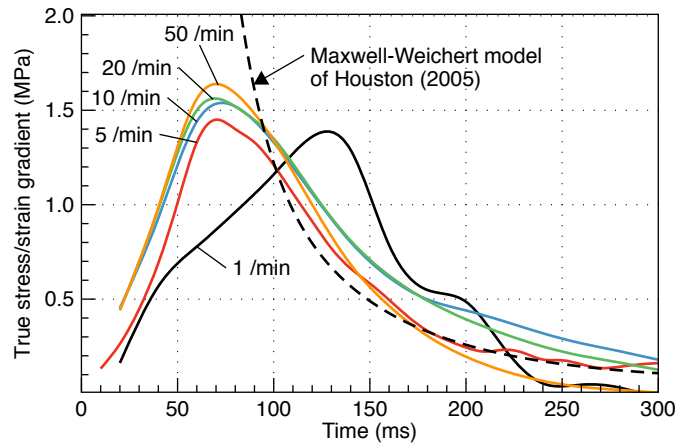


Figure 9: Local gradient of true stress vs. true strain for X3180, used to extract a modulus at each true strain rate. [Single column, width 90 mm, no colour in print, filename d_true_stress_d_strain_compression_x3180.pdf]

To extract an initial modulus, Fig. 9 plots the central true-stress/true-strain gradient from the second and subsequent non-zero data points. These data points, though logged only at 2 ms intervals, provide a consistent picture of time response over more than one and a half decades. The short-time compressive relaxation modulus emerges as 1.50 MPa at a time of 50–100 ms. Converting this to a shear modulus (assuming a Poisson ratio of 0.5) yields 500 MPa, in close agreement with the value indicated by DMA (Fig. 2) at 10–20 rad s^{-1} . The load measurement system, although fast enough to catch the principal relaxation at around 50–100 μs , was apparently not fast enough to register the true stiffness of the material at shorter times. However, that would have been difficult to correlate with DMA data even if it had been measurable: it is in the high-frequency region, i.e. $\omega \geq 20 \text{ rad s}^{-1}$, that the Cox-Merz rule is known to fail for transient-crosslinked materials, over-predicting the corresponding constant-rate viscosity [6].

Overall, measurement of the low-rate viscosity by simple compression testing was relatively straightforward, and careful treatment of the data could even extract a short-time modulus.

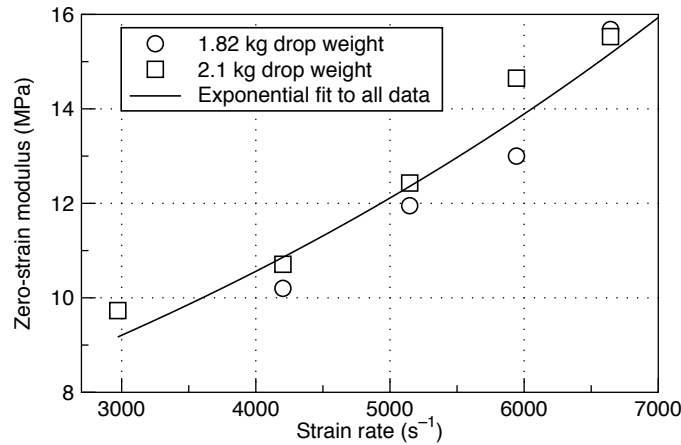


Figure 10: Zero-strain compressive modulus measured from the load-time trace from drop-weight impact tests on cylindrical X3180 specimens.

4.3. High rate compression of X3180

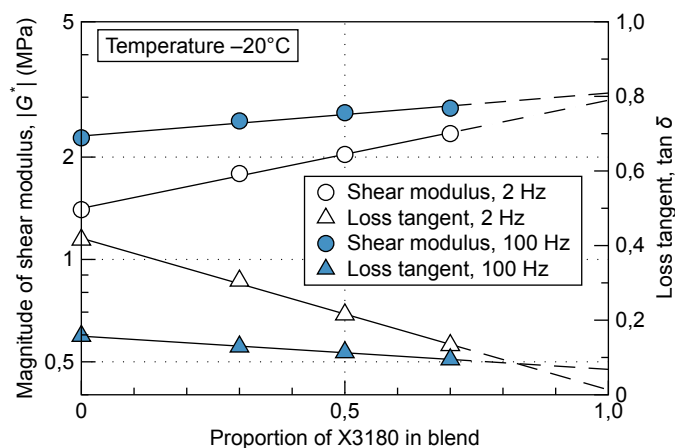
Drop-weight compression test results (Fig. 10) confirm that a lower drop-weight mass, necessarily reducing the impact duration and increasing the fundamental frequency of the loading pulse, increases the zero-strain modulus in a similar manner to increasing strain rate. They also highlight an extraordinary feature of PBDMS: under uniaxial compression between lubricated plane surfaces, which induces approximately equibiaxial strain in the cross-section, the compressive shear modulus (up to $15/2(1 + \nu) \approx 5$ MPa) largely exceeds the high-frequency elastic shear modulus from DMA (1 MPa in Fig. 2). The next section discusses the significance of this observation.

4.4. Law of mixtures for shear modulus of TPE-X3180 blends

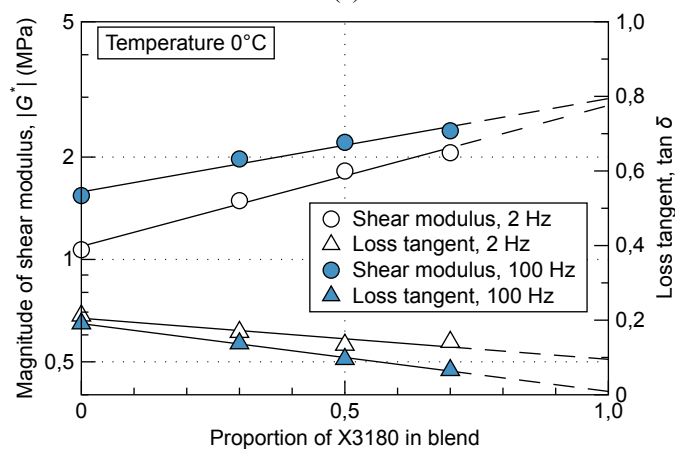
Blending increasing proportions r of relatively rigid polypropylene ('H') into relatively soft EPDM ('S'), Hoppner et al. [27] saw the logarithm of the blend modulus vary quite linearly with the weight proportion r of H, i.e.

$$G(r) = G_S \left(\frac{G_H}{G_S} \right)^r. \quad (6)$$

If these TPE-PBDMS blends followed a similar trend, the next step in their design would be straightforward. However Fig. 11, using data points either directly or (for a few) transformed back from the master curve, shows that although the linearity of Eq. 7 represents the data rather well, adding up to 70% of the soft, fluid X3180 *increases* the blend modulus and *decreases* $\tan \delta$ even at modest frequencies and at all temperatures within the operating range. The extrapolated $\tan \delta$ of neat X3180 is indeed almost zero, as expected from DMA results (Fig. 2), but its extrapolated shear modulus (Fig. 12) at 2–100 Hz in SEPS-1 is three times greater than that measured in bulk. A similar picture emerges from X3180 dispersed in the stiffer SEPS-2: indeed X3180 contributes even greater (by more than 30%) stiffness, losing it only towards the maximum service temperature.



(a)



(b)

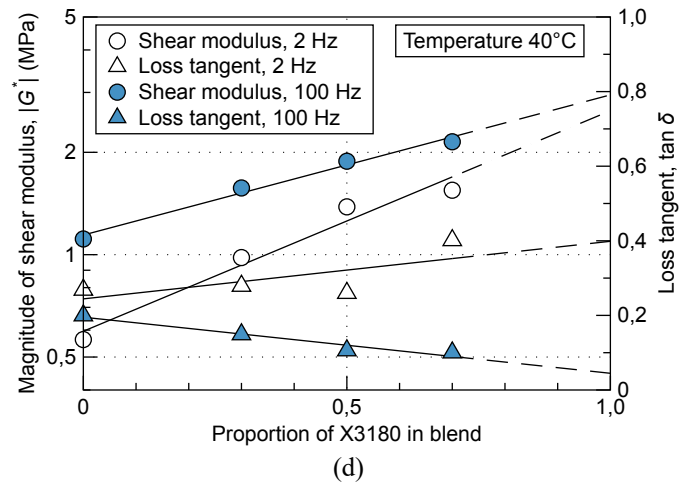
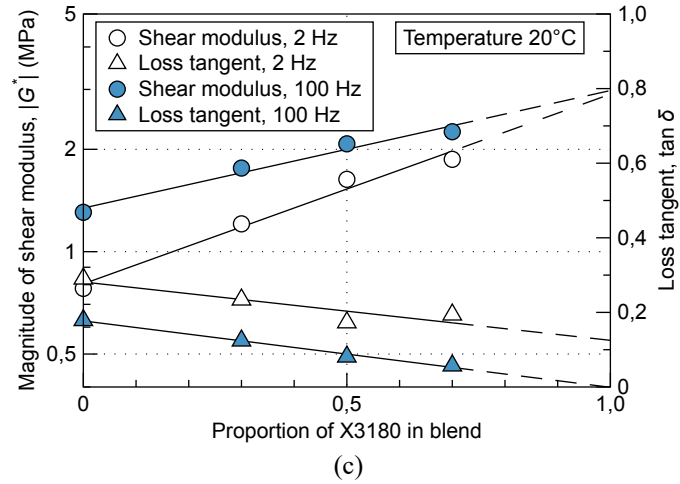


Fig. 11: Shear modulus of SEPS-1 blends with X3180 at temperatures from (a) -20°C to (d) $+40^{\circ}\text{C}$. The dashed lines illustrate extrapolation to an effective constrained shear modulus for X3180.

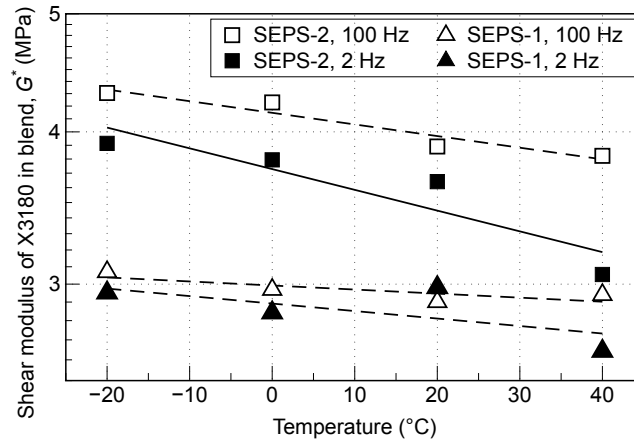


Fig. 12: Shear modulus of X3180 as dispersed in two SEPS blends, estimated as shown for SEPS-1 in Fig. 11.

with those from DMA shear modulus tests. Oscillatory tests on blends appear to confirm that X3180, confined within this TPE, exerts a disproportionately large stiffening effect which greatly enhances its value. Using low-rate compression tests similar to ours but taken to larger strains,

Seetapan [10] noted a similar, exceptionally large stiffening effect when a significant proportion of low-MW unimodal PBDMS was added to a unimodal PBDMS with an MW more than 8 times higher. This effect was attributed to the restricted extensibility of end-linked short chains. Here we see a similar effect at much smaller strains. An explanation might be found in the additional constraints imposed by bonding of PBDMS to the TPE and by frozen-in orientation of short PBDMS chains induced by injection moulding.

5. TPE-PBDMS blend design by virtual drop-weight impact testing

The framework for a model complete and tractable enough to guide selection for performance in EN-1621-type impact tests using small-strain DMA data was provided by Argatov et al. [28]. He models a flat-faced mass m striking, at incident velocity v_0 , a flat slab specimen of uniform thickness h_0 and of constant nominal area A_0 , supported on a flat, rigid surface. The specimen material is Zener solid of instantaneous elastic modulus E_0 , relaxation time τ_R and equilibrium-to-instantaneous modulus ratio $0 < \rho \leq 1$.

Since we are modelling TPE behaviour under high compressive strains stress-strain non-linearity cannot be ignored, but it can be treated generically. Argatov extends the material model using Fung's *quasilinear viscoelastic* (QLV) formulation which represents non-linearity as a multiplying factor distinct from the time-dependence of stress and evaluated in the form

$$\frac{d\sigma}{de} = E_0 \exp(Be) \quad (7)$$

where B is a material constant and e is the engineering strain.

In EN 1621 tests the anvil is spherical the striker flat (EN 1621-1) or horizontal-cylindrical (EN 1621-2). Neither offers a finite A_0 at contact nor a constant A_0 during compression; the uniaxial-stress assumption, corresponding to a contact area which increases with λ , will have to model contact area spreading until a better model (if needed) is formulated. The ability to combine separate non-linearities arising from material properties and from large-strain contact effects (evaluated experimentally or numerically) to arrive at an appropriate 'effective' value of B is a particular strength of the QLV model.

Argatov's analysis yields non-dimensional values of the peak contact force

$$F_M = \frac{AE_0}{h_0} v_0 \tau_R \mathcal{F}(\alpha, \beta, \rho), \quad (8)$$

in terms of dimensionless parameters

$$\alpha = \frac{AE_0 \tau_R^2}{mh_0}, \quad (9)$$

h_0 being the initial specimen thickness, and

$$\beta = \frac{Bv_0 \tau_R}{h_0}. \quad (10)$$

Argatov [28] computed the dimensionless function $\mathcal{F}(\alpha, \beta, \rho)$ for a representative range of conditions and with $\beta = 0.4$.

Here the striker mass $m = 5$ kg while the compressed area A is indeterminate but is modelled from imprint measurements as a disk of radius 20 mm. Argatov's model and solutions are used in a frankly heuristic manner, but they are useful both for stricter and for broader application — e.g. to higher order viscoelastic models.

5.1. Local Zener models of blends within the service temperature range

We argued in Section 3.1 that the response of a material to impact at a given temperature could be characterised by its dynamical response within a window centred at 200-500 Hz. For our target operating temperature range, the window boundaries cannot be set below 20 Hz or above 5 kHz without extrapolating the master curves (Figs. 3 to 5, on which the corresponding frequency ranges at -20 , 0 , 20 and 40°C are marked). Because we seek a preliminary ranking of materials rather than a precise characterisation, we model DMA shear modulus magnitude (G^*) data — already reduced to the master curve — as a linear Zener solid within the appropriate frequency window for each temperature. An interesting alternative is offered by Meram [29]

who, using Argatov's model to characterize the dynamic behaviour of a thermoplastic polyurethane elastomer buffer under drop weight impact loading, chose to use simpler two-parameter Maxwell and Voigt-Kelvin models but to account explicitly for their non-linearity.

Experimentation with the interactive graphing software Datagraph established a quick and efficient method to fit Zener parameters to the data points within each frequency window. Modulus data points within the frequency window were replotted on a linear scale. The Zener modulus magnitude and $\tan\delta$ functions

$$G^* = G_0 \left(1 - \frac{(1 - \rho)}{(1 + \omega^2 \tau_1^2)(1 + \tan^2 \delta)} \right), \quad (11)$$

$$\tan\delta = \frac{(1 - \rho)\omega\tau_1}{\rho + \omega^2 \tau_1^2}, \quad (12)$$

were overplotted, with adjustable G_0 , ρ and τ_R parameters, as continuous lines. A best fit was determined giving greatest weight to points nearest the centre of the frequency window, allowing G_0 and ρ to be estimated with little effort. Each of Figs. 3 to 5 illustrates one of these Zener model fits for one of the four drop-test temperatures; note that due to the logarithmic scale used here this fit may not appear to be the 'best'.

5.2. Predicted results for SEPS-1 and SEPS-2

Figure 13 shows the values computed using Eq. (9) for SEPS-1 and its three blends with X3180 at four temperatures spanning the intended service range. Because the force prediction is relative rather than absolute it does not guarantee that at the lowest service temperatures this material would reduce the peak impact force to below 35 kN, as required. However, the blend did prove to do so and even to exhibit the rather tentatively predicted minimum in transmitted force at 50% X3180 at room temperature (Fig. 13). For direct comparison with the scoping test data for SEPS-1 presented in Fig. 6, Fig. 15 shows the peak force at 20°C predicted for several impact energies.

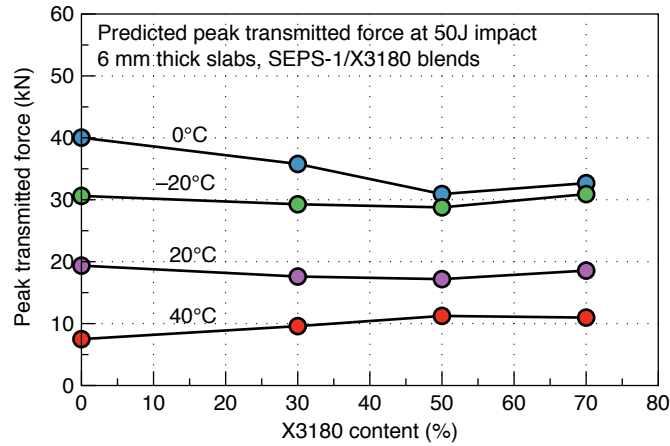


Fig. 13: Peak transmitted force from EN 1621 drop-weight tests on SEPS-1 blends at 50 J impact energy and at temperatures -20 to 20°C , as predicted from DMA data.

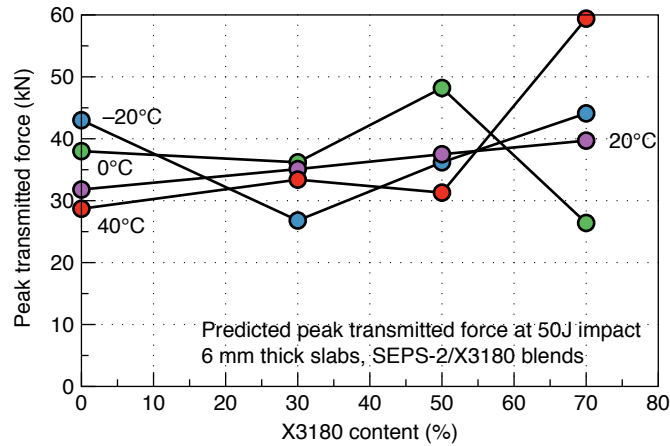


Fig. 14: Peak transmitted force from EN 1621 drop-weight tests on SEPS-2 blends at 50 J impact energy and temperatures -20 to 40°C , as predicted from DMA data.

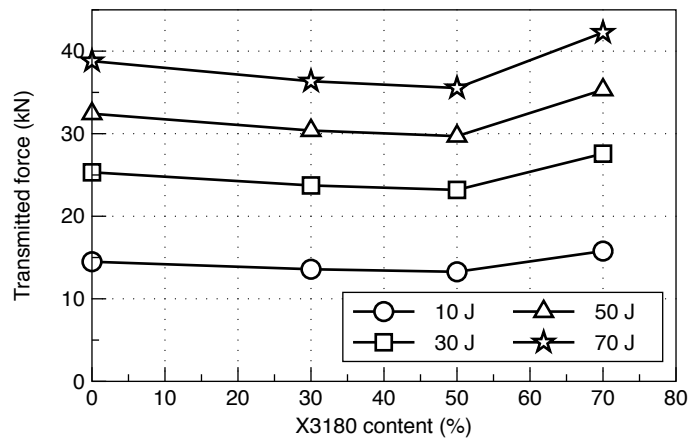


Fig. 15: Peak transmitted force from EN 1621 drop-weight tests on SEPS-1 blends at 0°C and impact energies from 10 to 70 J, as predicted from DMA data.

The predicted performance of SEPS-2 (Fig. 14) on the other hand, compares poorly with that of SEPS-1. The computed results are scattered and, although in part reflecting the relative paucity

of DMA data used to derive them, it was indeed SEPS-1 which was selected, on the basis of its performance in drop-weight tests, for the first commercial versions of a moulded TPE/PBDMS personal protection layer [31].

6. Discussion

We cannot yet definitively identify, solely on the basis of DMA data, the best TPE to blend PBDMS into for moulding into structures for personal protection against impact. As always, secondary criteria — some of them non-technical — will always weigh heavily in the choice. The model outlined here offers no warning of the fracture problems in high-PBDMS blends. Nevertheless, its results are promising. A minimum in $F_{\max}$ is only tentatively predicted by our relatively unsophisticated implementation of Argatov's model; but it is predicted, providing a fair overall evaluation.

The model also has capabilities which we have not yet used. Its use of a Fung-type QLV material model allows the force-displacement non-linearity arising from the EN 1621 test's complex anvil-striker geometry to be modelled, at least approximately. Further development of the code would also allow it to model the TPE's Mooney-Rivlin-type stress-strain curve using a strain-dependent B value, and to replace our laborious and inelegant “piecewise Zener” representation of the DMA data with a Maxwell-Weichert model.

However, the unusual response of PBDMS to mechanical constraint poses a challenge. To model TPE-PBDMS blends with arbitrary proportions, a law of mixtures is needed. Our results appear to confirm earlier work, showing that one parameter of this law — the stiffness of PBDMS — is higher when constrained within a blend morphology than in bulk.

7. Conclusions

Structured cellular mats, injection moulded from blends of thermoplastic elastomers with polyborodimethylsiloxane (PBDMS), are now available which satisfy the EN 1621 drop-weight test method for personal protection against accidental impact. The first of these blends were designed, and their base polymers selected, by trial-and-error testing — using the EN-1621

product acceptance method — of monolithic slabs moulded from experimental blends based on many commercial TPEs.

The pilot study reported here, using blends based on SEPS, has shown that DMA data for the base polymer and for PBDMS can be used to support the selection process — potentially eliminating the need to prepare, mould and test many blends. The procedure involves the measurement of a DMA master curve valid for the chosen service envelope; extraction from the master curve of Zener models for specific operating temperature and impact conditions; modelling of blend DMA data using a law of mixtures and, finally, use of a semi-analytical model to predict how effectively a slab could attenuate the impact force transmitted in a simulated EN 1621 test.

The procedure has scope for further development, specifically in the method of Zener model approximation and in the representation of non-linearities arising from anvil and striker geometry. However it has demonstrated its potential not only to more efficiently select candidate base TPEs for blending but also, based on the understanding of DMA spectra in terms of structure, to *design* them.

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