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Polyurethanes for potential use in transparent armour investigated using DSC and DMA

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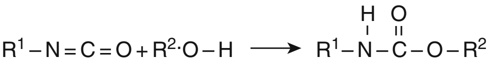
Abstract A material combination that may be applied as transparent armour is glass-clad polyurethane. These are comprised of a relatively thin glass strike face and a relatively thick (transparent) polyurethane backing layer. Three transparent polyurethane samples were investigated using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The DSC results identified the glass transitions and in some cases the melting and crystallisation processes. The DMA experiments were only performed on heating around the glass transition region to further investigate this transition. The experiments were performed at three different frequencies (1, 10 and 100 Hz); the shift of the glass transition with the frequency was clearly observed. The method of time–temperature superposition was used to extrapolate the results to higher frequencies as the magnitude of the strain-rate occurring within ballistic applications is in the order of 1000 s^{-1} or higher. Polyurethane with a rubbery behaviour at normal (low) strain rates can be stiff and brittle when used as an armour component (temperature below its dynamic T_g value).

Keywords Polyurethanes · Elastomers · Transparent armour · DSC · DMA

Introduction

Polyurethane elastomers

Polyurethanes are polymers which are formed in a reaction between monomers that contain at least two isocyanate (–N=C=O) functional groups and other monomers that contain at least two hydroxyl (–OH) groups. The reaction between the functional groups is



$$R^1{-}N{=}C{=}O + R^2{\cdot}O{-}H \longrightarrow R^1{-}\overset{\overset{\displaystyle H}{|}}{N}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}R^2 \tag{1}$$

When all monomers are diisocyanates and diols a linear chainlike polymer is obtained. Crosslinks are formed when there are monomers with three or more isocyanate and hydroxyl groups.

Linear segmented block polyurethanes are made using diisocyanates, short-chain diols (called chain extenders) and long-chain diols (also called polyols) as building blocks. The resulting polymers are composed of hard segments formed by the reaction of the diisocyanates with the short-chain diols and soft segments formed by the reaction of the diisocyanates with the long-chain diols. Because the hard segments show a significant polarity there is a relatively strong attraction between these segments. This may cause (pseudo-) crystalline phases in a soft, flexible matrix [1]. Properties of the elastomeric polyurethanes are

- high rubber-like elasticity;
- excellent abrasion resistance;
- good tear strength;
- good oil and grease resistance;
- outstanding low-temperature performance;and
- high transparency.

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The materials may show both a glass transition and (pseudo-) melting or (pseudo-) crystallisation of the hard segments. Both of these processes can be investigated using differential scanning calorimetry (DSC). The glass transition region can be investigated very well using dynamic mechanical analysis (DMA).

However, Saiani et al. [2] indicate that processes may be considerably more complex than indicated above. Different mixed phases may coexist and at higher temperatures, on heating, besides endothermic effects also exothermic effects can sometimes be observed; these effects may be caused by micro-phase mixing or demixing.

Transparent armour

The 'traditional' transparent armour, or bullet-resistant glass, is usually constructed as laminated glass in which the sheets of glass are bonded together by polyvinyl butyral, polyurethane and/or ethylene–vinyl acetate films. Layers of polycarbonate may also be used, especially on the rear face to avoid splinters from escaping from the free surface of the last glass layer. Characteristic of the construction is that the glass layers are much thicker than the polymer layers. For combat vehicles the total thickness usually is between 70 and 120 mm. Since 80–90% of the construction consists of glass, the armour is both thick and very heavy.

At the Netherlands Organisation for Applied Scientific Research (in Dutch abbreviated as 'TNO') another material was found to have potential for transparent armour applications [3]. This armour concept consists of a layer of glass backed by a single layer of a transparent elastomer. In particular the glass-clad polyurethanes showed good results in ballistic tests. A typical construction consisting of a 6-mm-thick glass layer backed by a 20-mm-thick layer of transparent polyurethane was ballistically tested using 1.1 g fragment simulating projectiles (FSP's) at impact velocities up to 1300 m s^{-1} and 9 mm full-metal jacked (FMJ) soft core (lead) bullets at 450 m s^{-1}. Both of these projectiles were stopped by the construction. After the impact the glass strike face was heavily damaged and the projectile was severely damaged by plastic deformation. The polyurethane backing, however, showed no damage and no residual deformation; see Fig. 1. The average strain rate in the polyurethane layer is estimated to be about 2000 s^{-1}.

Clearly, these materials demonstrate some significant advantages over the 'conventional' bullet-resistant glass construction:

- less weight;
- significantly less thick;
- possibility to apply to an existing window; and
- good/better residual visibility.

Fig. 1 Photograph of a glass-clad polyurethane after bullet impact

It is obvious that the ballistic performance of a specific polyurethane depends on its dynamic mechanical properties. The dependence of the mechanical properties of polyurethanes on strain rate is described in several studies, e.g. [4–6]. It is, however, not known which mechanical properties are required for a polyurethane to perform well in the transparent armour application. To initiate research on this topic, we performed the thermal and thermo-mechanical characterisation of three candidate polyurethane products: Clear Flex 75 (Smooth-on), Hyperlast 100 (Dow) and the thermoplastic polyurethane (TPU) PEARLTHANE D91F88 (Merquinsa). These materials have been used to prepare a transparent armour window which was ballistically tested. Under room temperature conditions it appeared that Clear Flex 75 and PEARLTHANE D91F88 performed very well [3], while the performance of Hyperlast 100 was significantly worse.

Differential scanning calorimetry (DSC) was performed to evaluate the position of the glass transition and to see whether (pseudo-) melting and/or crystallization of hard segments can be observed. Since the visco-elastic properties of the polyurethanes seem to be especially important, the materials were also investigated using dynamic mechanical analysis (DMA).

Experimental

Samples

A short description of the three polyurethanes that were investigated in this study is presented in Table 1. Material for the DSC measurements was delivered in the form of blocks of material from which the samples for DSC-measurements were cut. Material for the DMA-measurements was delivered in the form of sheets of material with a thickness between 3.30 and 3.85 mm from which the

Table 1 Short description of the polyurethanes investigated in this study

Polymer (manufacturer)	Short description
Clear Flex 75 (Smooth-on)	Colourless, transparent (clear), soft (Shore A Hardness: 75)
Hyperlast 100 (Dow)	White, transparent but not clear, hard (about the same hardness as PEARLTHANE D91F88)
PEARLTHANE D91F88 (Merquinsa)	Thermoplastic polyurethane (TPU); Colourless, transparent (clear), hard (Shore A Hardness: 90)

samples for the measurements were taken as described below in the paragraph "Dynamic Mechanical Analysis" section. The sheets of Clear Flex 75 and of Hyperlast 100 were cast; the sheet of PEARLTHANE D91F88 was hot-pressed (compression moulded) at 160 °C.

Differential scanning calorimetry

The DSC-measurements were performed using a Mettler Toledo DSC 822^{e}. Samples of about 10 mg were placed in standard aluminium crucibles with a volume of 40 μL. The crucibles were closed with a lid. In all cases an empty crucible was used as the reference. Nitrogen was used as a purge gas with a flow rate of about 50 mL min^{-1}. All samples were measured using a cyclic temperature program:

- heating and cooling rates: 5 K min^{-1};
- first cooling (from room temperature) to −100 °C;
- first heating to 220 °C;
- second cooling to −100 °C;
- second heating to 220 °C;
- between heating and cooling steps, the samples were kept at constant temperature (i.e. at −100 and at 220 °C) for a period of 5 min.

All results presented in this paper have been corrected for a blank measurement performed on two empty crucibles. Each material was measured twice using fresh samples.

Dynamic mechanical analysis

The DMA-measurements were performed using a Mettler Toledo DMA-SDTA 861^{e}, equipped with the shear clamp. The samples were measured during heating with a rate of 0.5 K min^{-1} from −75 to 85 °C. The force amplitude and the displacement amplitude were set not to exceed 10 N and 5 μm, respectively. Measurements were performed at three frequencies: 1, 10 and 100 Hz. The samples of Clear Flex 75 and Hyperlast 100 were taken from the sheets of material that were delivered by using two methods.

- Cylindrical samples (diameter about 14 mm) were taken from the sheets using a corer. A lot of force was necessary and samples deformed significantly during the sample preparation. The obtained samples, however, appeared undamaged.
- Block-formed samples (length and width both about 10 mm) were taken from the sheets using a diamond wire saw.

For Clear Flex 75 and for Hyperlast 100 three experiments were performed: one on cylindrical samples and two on block-formed samples. For PEARLTHANE D91F88, two experiments were performed using only block-formed samples. Each experiment was performed with freshly cut samples.

With these dimensions and experimental conditions the (shear) strain rates are up to the order of 1 s^{-1}, at least three orders of magnitude lower than the strain rates which are reached in ballistic applications.

Results and discussion

DSC-measurements

Each material was measured twice in the DSC. The DSC-curves recorded for each material showed little variation. Therefore, in Figs. 2, 3 and 4 for Clear Flex 75, Hyperlast 100 and PEARLTHANE D91F88, respectively, the recorded DSC-curves of only one of the two measurements are presented.

The evaluated glass transition temperatures are presented in Table 2. All reported DSC glass transition temperatures are evaluated from the so-called 'mid-points', i.e. the temperature at which the measured curve crosses the imaginary line that is drawn exactly in between the two extrapolated baselines.

The material Clear Flex 75 (see Fig. 2) showed a glass-transition in the temperature range from −20 to 10 °C both in the cooling and heating process. During the first heating another effect besides the glass transition was observed: an exothermic effect of 9–10 J g^{-1} between about 175 and 220 °C. It is not clear what process caused this effect. Since no effects were observed during successive cooling and reheating it was possibly caused by some (irreversible) curing or mixing/demixing process. The process probably will have changed the material, but the change apparently has no or only a very minor influence on the position of the glass transition.

The DSC-curves recorded for Hyperlast 100 (see Fig. 3) show that this material shows a glass-transition in the temperature range of −60 to −40 °C, at much lower temperatures than Clear Flex 75. Besides the glass

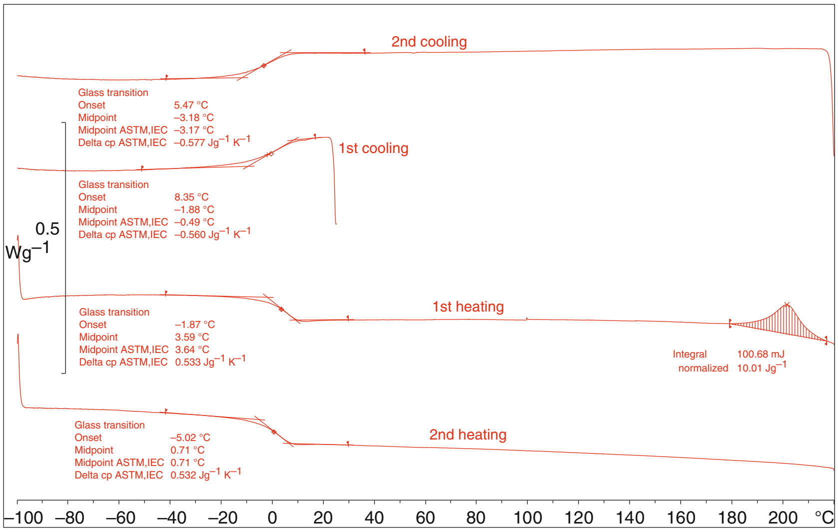

Fig. 2 DSC-curves recorded for Clear Flex 75 (endothermic effects plotted downwards)

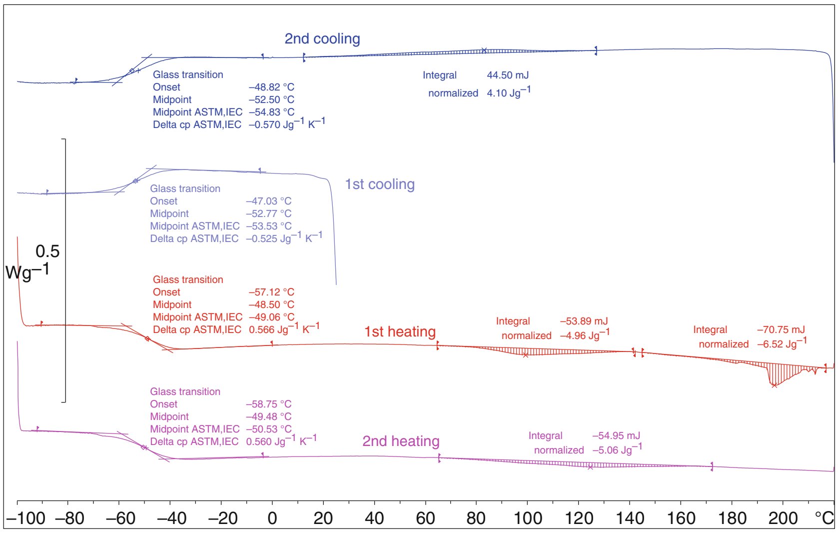

Fig. 3 DSC-curves recorded for Hyperlast 100 (endothermic effects plotted downwards)

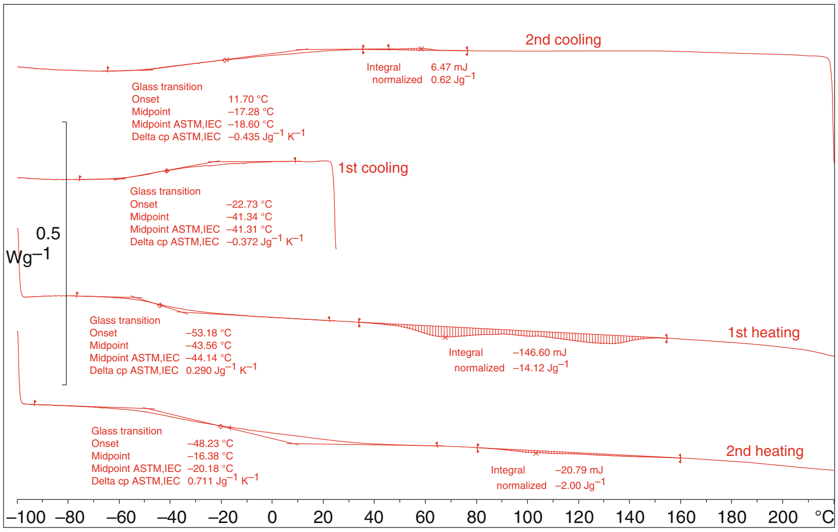

Fig. 4 DSC-curves recorded for PEARLTHANE D91F88 (endothermic effects plotted downwards)

Table 2 Glass transition temperatures evaluated from the DSC- and DMA-experiments

Experiment/method	Clear Flex 75	Hyperlast 100	PEARLTHANE D91F88
DSC	2 °C (1st and 2nd heating)	−49 °C (1st and 2nd heating)	−43 °C (1st heating) −20 °C (2nd heating)
DMA/max. G''			
1 Hz	−2 °C	−50 °C	−20 °C
10 Hz	1 °C	−47 °C	−15 °C
100 Hz	6 °C	−43 °C	−12 °C
DMA/max. tan δ			
1 Hz	11 °C	−39 °C	29 °C
10 Hz	16 °C	−33 °C	37 °C
100 Hz	24 °C	−26 °C	46 °C
DMA Time–temp superposition/max. G''			
1 kHz	13 °C	−38 °C	
10 kHz	19 °C	−33 °C	
100 kHz	27 °C	−24 °C	
DMA Time–temp superposition/max. tan δ			
1 kHz	34 °C	−16 °C	
10 kHz	48 °C	−4 °C	
100 kHz	67 °C	15 °C	

DMA glass transition temperatures extrapolated to high frequencies using the method of time–temperature superposition are also presented

transition, during the first heating two small endothermic effects were observed: the first effect (of about 5 J g^{-1}) was observed in the temperature range from 70 to 140 °C, the second effect (of about 7 J g^{-1}) between 170 and 215 °C. The first effect is probably caused by a reversible process: the cooling curve recorded after the first heating shows a small exothermic effect (about −4 J g^{-1}) between 120 and 20 °C while during successive reheating again an endothermic effect of about 5 J g^{-1} was observed between a somewhat wider temperature range between 70 and 170 °C. The reversible process possibly may be associated to (pseudo-) melting/crystallization of the hard segments. The irreversible process probably will have changed the material somewhat; the position of the glass transition, however, appears to be unchanged.

During first cooling and successive first heating, material PEARLTHANE D91F88 showed its glass-transition at low temperatures, like Hyperlast 100, but over a somewhat wider temperature range: between −60 and −10 °C (see Fig. 4). During the first heating, between 40 and 160 °C, an endothermic effect of about 14 J g^{-1} was observed. During successive cooling no significant heat effect was observed before the glass-transition started, and during the second heating step only a very small, possibly non-significant endothermic effect of 1–2 J g^{-1} was observed between 80 and 160 °C. Therefore, the endothermic effect observed during the first heating was probably caused by an irreversible process which changed the material. This change clearly had an influence on the glass transition since during the second cooling and second heating the transition occurred over a much wider temperature range (between −70 and 30 °C) than was observed for the 'fresh' material.

DMA experiments

The result of the DMA-measurements is the complex shear modulus (G^*) of the samples at three frequencies as a function of temperature. The complex modulus is usually presented in the form of the storage modulus G' and the loss modulus G''. The relation between these three quantities is

$$G^* = G' + iG'' \tag{2}$$

The ratio between the loss modulus and the storage modulus represents the so-called damping factor. The damping factor is represented by tan δ, where δ equals the phase angle between the oscillating force and the oscillating displacement.

$$\tan\delta = G''/G' \tag{3}$$

An interesting observation in comparing the measurements on cylindrical samples and on block-formed samples for the materials Clear Flex 75 and Hyperlast 100 was that the shear modulus at low temperatures (below the glass transition) of the cylindrical samples appeared to be smaller than the shear modulus of

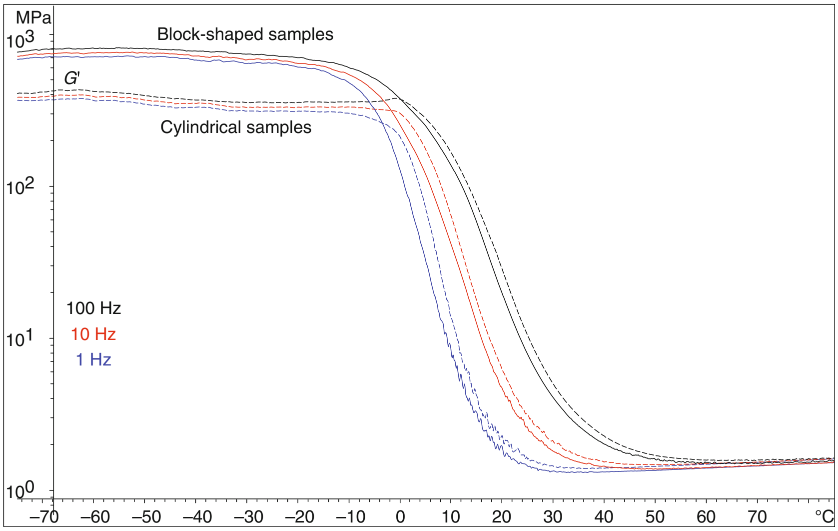

Fig. 5 Measured storage modulus of Clear Flex 75 for cylindrical and block-shaped samples

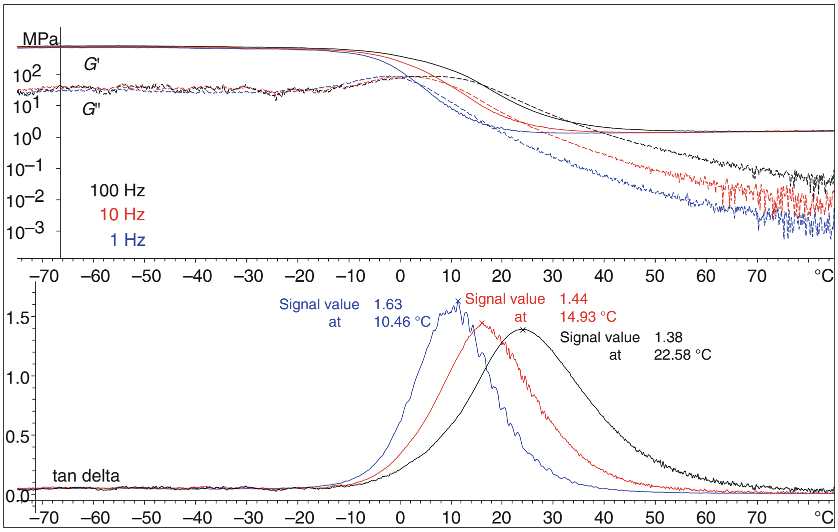

Fig. 6 Storage modulus, loss modulus and damping factor of Clear Flex 75 measured as a function of temperature at three frequencies

the block-formed samples. This is represented for Clear Flex 75 in Fig. 5. This behaviour is unexpected since the (shear) modulus is a material property and should be independent on the shape of the sample. It is believed that the difference may be caused by the method of sample preparation. Since it was observed that during the preparation of the cylindrical samples a lot of force was needed and the samples deformed significantly, it is possible that this damaged the structure of the material somewhat, resulting in the lower modulus below the glass transition. The position of the glass transition, however, was not significantly different for the measurements on cylindrical and block-shaped samples.

The results of the measurements on block-shaped samples of Clear Flex 75, Hyperlast 100 and PEARLTHANE D91F88 are presented in Figs. 6, 7 and 8, respectively. The plots show the storage and loss moduli as well as the damping factor tan δ as a function of temperature. In the glass transition range the storage modulus decreases a couple of orders of magnitude, the loss modulus first increases somewhat and then decreases considerably and the damping factor (tan δ) passes through a maximum. Glass transition temperatures are usually evaluated from DMA experiments as the temperature of the maximum of the tan δ curve; sometimes also the maximum temperatures of the loss modulus curves are used. There may be significant differences in the results obtained using these two methods [7].

The results show that the glass transitions as observed in the DMA experiments appear at higher temperatures and over wider temperature ranges than in the DSC experiments, especially for the measurements at higher frequencies. The dependence on frequency was also clearly observed. In Table 2 the glass transition temperatures evaluated from the DMA-experiments as well as those evaluated from the DSC heating curves are presented.

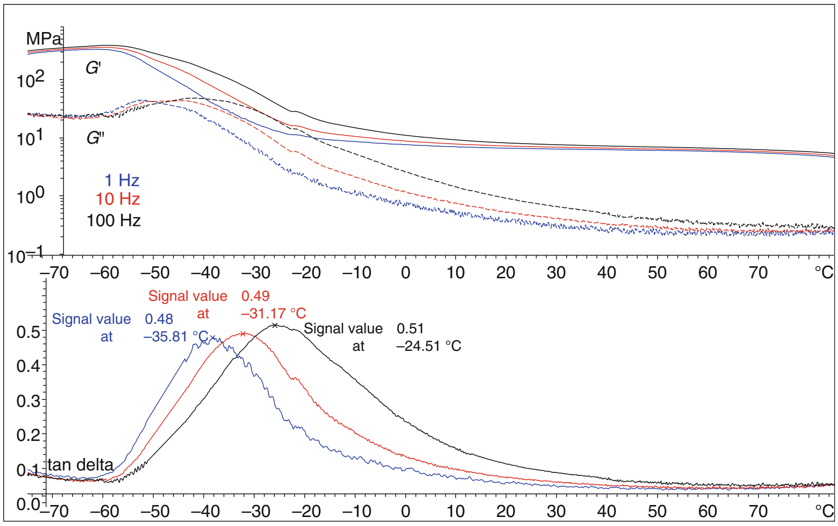

Fig. 7 Storage modulus, loss modulus and damping factor of Hyperlast 100 measured as a function of temperature at three frequencies

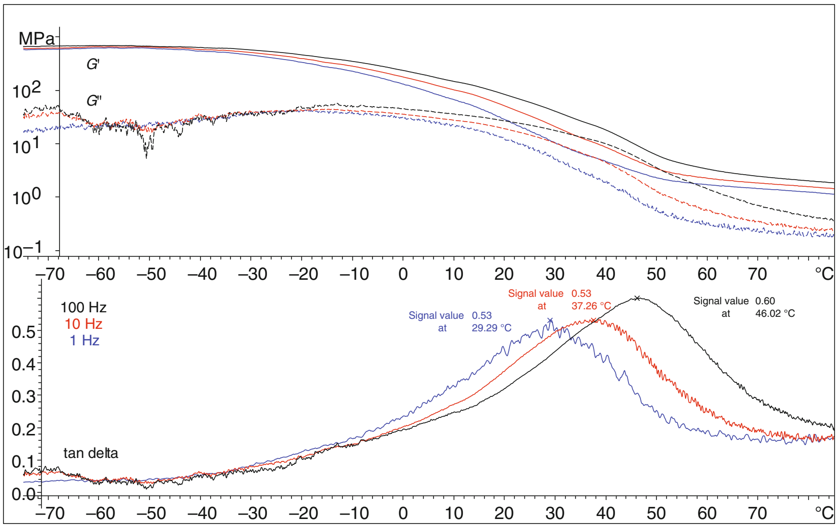

Fig. 8 Storage modulus, loss modulus and damping factor of PEARLTHANE D91F88 measured as a function of temperature at three frequencies

The DMA result for PEARLTHANE D91F88 (see Fig. 8) shows the glass transition over a wide temperature range. In this case it was concluded that the material changed during the first heating resulting in a glass transition over a much wider temperature range. Looking at the DSC-results obtained for this material (Fig. 4), it is clear that the material used for the DMA experiment resembles the (changed) material more than the original material used for the DSC-experiment. The explanation may be that the sheet of material that was used for the DMA-experiment was prepared by hot pressing, i.e. the material received a heat treatment, which resulted in (more or less) the same material change as occurred during temperature cycle during the DSC-experiment.

Since the strain rates which occur in the ballistic application are at least about three orders of magnitude higher than the strain rates in the DMA experiments, the method of time–temperature superposition [7] to extrapolate the obtained DMA results to higher frequencies was used. This method is based on the equation presented by Williams et al. [8] (the so-called WLF-equation):

$$\log(a_T) = \frac{C_1(T - T_0)}{C_2 + (T - T_0)} \quad (4)$$

This equation quantifies that a change in visco-elastic properties caused by increasing or decreasing the temperature can also be accomplished by, respectively, decreasing or increasing the frequency isothermally. The shift over the logarithm of the frequency axis is indicated by $\log(a_T)$, T is the temperature (expressed in kelvin), T_0 is a reference temperature and C_1 and C_2 are adjustable parameters.

For Clear Flex 75 and for Hyperlast 100 the obtained storage modulus curves at three frequencies, as a function of temperature, were used to fit the parameters of the WFL-equation for selected values of T_0; the result is presented in Table 3.

Table 3 Parameters of the WFL-equation evaluated from the measured storage modulus curves for selected values of T_0

Sample	T_0/K	C_1	C_2/K
Clear Flex 75	283.15	−10.1	60.4
Hyperlast 100	233.15	−10.0	49.9

With the parameters given in Table 3 the experimental DMA-results were extrapolated to higher frequencies: 1, 10 and 100 kHz. The highest of these frequencies corresponds to a (shear) strain rate of about 1000 s^{-1}, in the range of the ballistic application. The glass transition temperatures extrapolated to these higher frequencies are also presented in Table 2. It should be noted that the results are less reliable when the data are extrapolated over a larger frequency range.

As was previously indicated, in ballistic tests (performed at room temperature) on the glass-clad polyurethanes, Clear Flex 75 performed very well, while the performance of Hyperlast 100 was significantly worse. The experimental results clearly show that Clear Flex 75 shows a considerable visco-elastic behaviour under the indicated conditions as the material is in its (dynamic) glass transition range. Hyperlast 100, on the other hand, behaves significantly more elastically under these conditions; its glass transition range is at lower temperatures, even for the high frequencies. Preliminary ballistic tests performed at temperatures below 0 °C showed that the performance of Hyperlast 100 as backing material was significantly better under these conditions than at room temperature.

This supports the idea that for an elastomeric material to perform well as a backing material in transparent armour applications, the material must be in its (dynamic) glass transition range, more or less in the region in between the maximum of the loss modulus and the maximum of tan δ.

Conclusions

DMA seems to be an excellent tool to quickly characterise materials for their suitability to be used as backing material in transparent armour applications. Materials appear to perform best when they are in their glass transition range, when the behaviour is visco-elastic, more or less in the region in between the maximum of the loss modulus and the maximum of tan δ. Although the (shear) strain rates that can be applied experimentally in DMA experiments are much lower than that in the ballistic application, the method of time–temperature superposition can be used to extrapolate the results to more relevant strain rates for armour applications. Thus, the visco-elastic properties of the materials under conditions as observed in the ballistic application may be estimated.

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