Viscoelasticity of new generation thermoplastic polyurethane vibration isolators^{a)}

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This paper presents the analysis of pressure dependence of three thermoplastic polyurethane (TPU) materials on vibration isolation. The three TPU Elastollan[®] materials are: 1190A, 1175A and 1195D. Aim of this investigation was to analyze how much the performance of isolation can be enhanced using patented *Dissipative bulk and granular systems technology*. The technology uses granular polymeric materials to enhance materials properties (without changing its chemical or molecular composition) by exposing them to 'self-pressurization', which shifts material energy absorption maxima towards lower frequencies, to match the excitation frequency of dynamic loading to which a mechanical system is exposed. Relaxation experiments on materials were performed at different isobaric and isothermal states to construct mastercurves, the time-temperature-pressure interrelation was modeled using the Fillers-Moonan-Tschoegl model. Dynamic material functions, related to isolation stiffness and energy absorption, were determined with the Schwarzl approximation. An increase of stiffness and energy absorption at selected hydrostatic pressure, compared to its stiffness and energy absorption at ambient conditions, is represented with $\kappa_k(p, \omega)$, defining the increase of stiffness and $\kappa_d(p, \omega)$, defining the increase of energy absorption. The study showed that close to the glassy state, moduli of 1190A and 1195D is about 6-9 times higher compared to 1175A, whereas, their properties at ambient conditions are for all practical purposes the same. TPU 1190A turns out to be most sensitive to pressure: at 300MPa its properties are shifted for 5.5 decades, while for 1195D and 1175A this shift is only 3.5 and 1.5 decades, respectively. In conclusion, the stiffness and energy absorption of isolation may be increased with pressure for about 100 times for 1190A and 1195D, and for about 10 times for 1175A.

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I. INTRODUCTION

Negative effects of vibration and noise on people as well as on performance and reliability of machines and devices are well-known facts^{1,2}. Obviously, the best solution is to avoid vibration problem in the first place, however this is often not possible and vibration control is necessary to provide vibration protection. The role of vibration protection is to minimize the vibration transmission between the source and surrounding (receiver). The effectiveness of vibration isolation is determined by vibration parameters: mass, stiffness and damping of an isolator³.

Metals and polymers are materials most often used for this purpose. Polymers are used due to their good damping properties through viscous mechanisms, low specific density and good design and production flexibility⁴. On the other hand, also metals exhibit some damping resulting from dislocations, phase boundaries, grain boundaries³, and damping arising in structures with complex geometry, resulting from the interplay between the macroscopic vibrations and wave propagation. Comparing metallic and polymeric materials used for damping, shows that polymers exhibit far better damping, however they suffer from low stiffness⁵. This is one of the reasons why metals are still often used for vibration protection, for example in foundation of heavy machinery that operates at constant excitation frequency.

However, for systems that function at or near resonance we need damping elements that exhibits as high energy dissipation (absorption) as possible. In such applications using polymeric materials is the only option.

The selection of a particular polymeric material for vibration control will depend on vibrating system, operating conditions and environment, particularly temperature, where vibrating system is located, as well as on allowable/desired vibration levels. Comparing the stiffness and damping of different polymeric materials, shows that the two properties are contradictory. Hence, polymers with high damping (energy absorption capability), typically elastomeric materials, have lower stiffness compared to polymers with lower damping, typically thermoplastic polymers^{6,7}.

Due to their lower stiffness, polymers with higher damping are usually not used for vibration isolation. In addition, these materials exhibit maximal values of damping (energy absorption) at high frequencies, often at frequencies far away from working range of machines and devices. It becomes clear that, at present, we do not have available solutions allowing

us to utilize the full damping potential that especially elastomeric materials offer. In order to overcome these drawbacks of polymeric materials (limited stiffness and maximal damping at high frequencies), two main challenges need to be addressed: (i) stiffness of a material should be increased and (ii) its maximal values of damping have to be shifted towards lower frequencies.

Combining high stiffness with high damping can be achieved in several ways using different combinations of layered and/or composite structures combining either: (i) metal layers⁸⁻¹¹ or metal structures¹² with polymers; (ii) carbon (or other) fibers with polymers¹³⁻¹⁷ and (iii) mixing different materials or adding (nano) particles to the matrix polymeric material^{7,18-21}.

Our approach on the other hand, utilizes pure polymeric materials without any modifications to it (no reinforcements or additives) and combines the effect of hydrostatic pressure on polymeric materials and properties of granular materials to obtain desirable stiffness and increased damping.

A. Granular Damping Elements

The answer to the two challenges are a new generation damping elements which we call Granular damping elements (GDE) which are based on a patented *Dissipative bulk and granular systems technology*²². Patented research-based invention utilizes two scientific findings:

1. *Hydrostatic pressure allows for frequency adjustment of the material damping properties.*

Using our unique high-pressure apparatus²³⁻²⁵ we have shown that exposing polymeric materials to selected hydrostatic pressure causes a shift of mechanical properties to lower frequencies. In other words, high values of damping (that are usually located at higher frequencies) are shifted towards lower frequencies without hampering materials damping (energy absorption) properties. Hence, by selecting a proper (elastomeric) material with high damping properties and exposing it to a selected hydrostatic pressure, we can match the frequency range where material exhibits its maximal dissipation properties with the excitation (resonance) frequency range of a vibrating structure.

Using this principle, the material energy dissipation properties can be enhanced for several orders of magnitude.

Unfortunately, pressures required for substantial change of damping properties may be quite high i.e., from $50 - 100\text{MPa}$ or even higher^{24,26–28}. Exposing bulk materials to such pressure levels in uniaxial compression will inevitably lead to appearance of cracks due to excessive accompanying shear stresses, and eventually to material failure.

We have solved this problem with an inventive solution described below.

2. *Improving granular material flow properties for their self-pressurization.*

We have realized that granular materials with proper particle size-distribution may exhibit a flow-like behavior while maintaining all properties of a bulk material. To study the flowability of granular materials we have developed GFA apparatus (Granular Friction Analyzer)²⁹. The apparatus allows studying the ability of granular materials to flow in case when driving force is high (hydrostatic) pressure. The GFA is composed of a hollow cylinder (with one of its ends closed) that is loaded with granular material. Once the cylinder is filled with particles, a force is applied by means of a piston; such force will induce a pressure inside the cylinder that induces elastic deformations in the axial and tangential directions of the external wall of the cylinder. The strain in the external face of the cylinder can be measured experimentally, e.g., by means of a strain gages setup, or optically. From the measured strains, we can determine the pressure profile along the length of the cylinder and relate such profile with the flowability of granular materials. If the cylinder would be filled with a Newtonian fluid the internal pressure throughout the cylinder would be uniform and the strain in the external face of the cylinder would be the same along the length of the cylinder. In this context, one expects that depending on the flow properties of granular materials, the pressure will be transmitted in a different way along the cylinder, thus allowing us to obtain a method for flowability characterization²⁹.

Based on the studies of granular materials flowability we have concluded that polymeric granular materials with proper particles size-distribution may be used as a pressurizing media (similar as air in tires) to impose hydrostatic pressure on themselves (i.e., self-pressurization) and, as a result, change frequency dependence of their own damping properties. With

FIG. 1. Schematic presentation of Granular damping element (GDE).

a proper adjustment of the hydrostatic pressure, we can also adjust the stiffness of the damping element (again, similar as with air in tires). Since energy dissipation of a damping element is proportional to the volume of used granular materials, whereas the stiffness in addition depends on geometry of a damping element, the two parameters (damping and stiffness) may be adjusted independently.

Considering this, polymeric Granular damping elements (GDE), were developed. GDE consists of a container, made of woven basalt, carbon or glass fibers, which is filled and pressurized with polymeric granular materials with multi-modal particles size-distribution. Due to the flow-like behavior of granulated polymers, the generated pressure within the container will be hydrostatic and will act on polymeric particles themselves, and consequently modify frequency dependence of their energy absorption properties. Hence, with a proper pressurization we may shift the material energy absorption maximum to any desired frequency. A sketch of such Granular damping element (GDE) is shown Fig.1, whereas Fig.2 schematically presents its working principle. Described GDE elements differ from the similar elements, devices and patents^{30–33} that use sand^{34,35}, granulated polymers^{36–39} or metals^{40–45} for enhanced damping, since in our case enhanced damping is not only the result of friction between particles but also result of changed material properties.

Let us assume that a vibrating structure is equipped with a damping element made

FIG. 2. Working principle behind GDE elements.

of a polymeric material of which its frequency dependent damping properties at ambient pressure p_0 , expressed with the loss modulus $G''(\omega)$, are shown in Fig.2(a) as a dashed line. In the frequency range where the structure is in resonance, indicated as a shadowed area, the damping properties of this material are low. Consequently, the structure vibration amplitudes in the resonance frequency range will be large, as shown with a dashed line in Fig.2(b). Now, if we take the very same material in a granular form with a proper particles-size distribution and self-pressurize it within a woven container, we obtain the new GDE damping element with the ultimate damping properties. This is achieved by selecting a proper hydrostatic pressure p_1 within the container that shifts the loss modulus maximum to the resonance frequency range of the structure, as shown in Fig.2(a) with a solid line. As a result, the vibration amplitudes of the structure will substantially diminish, as shown as a solid line in Fig.2(b).

To summarize, for vibration and/or impact control, where high damping is necessary, high values of the loss modulus $G''(\omega)$ are needed since the loss modulus is related to dissipated energy. To fully utilize the damping properties of a polymeric material, the frequency range of its loss modulus maximum $G''_{max}(\omega)$ should be matched with an excitation frequency or an impact rate imposed to a mechanical system. As mentioned before, this may be achieved

by exposing the elastomeric granular material to a properly selected hydrostatic pressure and adjust the frequency at which the material exhibits maximum energy dissipation i.e., $G''_{max}(\omega)$ such that it matches the resonance frequency of the vibrating structure. The described approach allows ultimate utilization of damping properties of all existing and/or newly developed polymeric materials of which its maximum damping frequency is located at higher frequencies than the resonance frequency range of an observed dynamic system.

To this end, the goal of this paper is to examine the pressure and frequency dependence of three polyether-based thermoplastic polyurethane (TPU) materials on vibration isolation. The investigated materials are from the Elastollan[®] 11 series⁴⁶ i.e., (i) 1190A, (ii) 1175A, and (iii) 1195D, manufactured by BASF. Within this paper, properties of TPU materials in solid state are investigated, which after granulation are potential candidates for producing the new generation GDE damping elements.

II. BACKGROUND

The background section reviews the underlying knowledge relevant for the experimental investigation of the three materials to be used in a new generation vibration isolation systems. It is sub-divided into several sections, starting with a brief review of the effect of pressure, followed by the description of high-pressure CMS apparatus⁴⁷, the new standardized procedure for generating unique master curves and selected methodology for interconverting material functions between the time and frequency domain. The latter is needed because the shear relaxation experiments under pressure have been performed in time-domain and had to be converted into the frequency domain to obtain information on the storage modulus $G'(\omega)$, responsible for vibration isolation stiffness, and information on the loss modulus $G''(\omega)$ which represents the material's capability to dissipate mechanical energy.

A. The effect of pressure

A comprehensive review of the effect of pressure and temperature on time-dependent behavior of polymeric materials is given in Tschoegl, et. al⁴⁸, here we will briefly review only those facts that are relevant to the present paper.

The effect of pressure on macroscopic time-dependent behavior of polymeric materials is,

in principle, analogous but opposite to that of temperature. As it is well known, exposing viscoelastic materials to lower temperatures (compared to a reference temperature) hinders the mobility of molecular chains in the amorphous phase, which is exhibited through the extension of the material creep and relaxation time scales^{25,49}. On the other hand, exposing viscoelastic material to higher temperatures (compared to a reference temperature) increases the mobility of the molecular chains, which is now exhibited as reduction of the material relaxation (and creep) time scales. Pressure has similar, though opposite effect on material macroscopic time-dependent mechanical properties as temperature. When viscoelastic materials are exposed to high (hydrostatic) pressures the mobility of polymer chains is hindered (similarly as exposing material to low temperatures). On the macro scale, this is exhibited through the extension of the material relaxation (and creep) time scales. Hence, under hydrostatic pressure the viscoelastic relaxation and retardation times of solid polymers increase. The opposite happens when material is exposed to decreased pressure (relative to a higher reference pressure), viscoelastic relaxation and retardation times of polymers decrease^{25,48}. Of course, it is obvious that the ambient pressure is essentially the lowest pressure to which material may be exposed.

Since frequency and time domain are interrelated, pressure also affects dynamic material properties i.e., storage modulus $G'(\omega)$, loss modulus $G''(\omega)$ and damping ratio $\delta(\omega)$. Due to the same molecular mechanisms, increased pressure causes the dynamic properties to shift towards lower frequencies (compared to reference values) and vice-versa; decreased pressure, relative to a higher reference pressure, causes properties to shift towards higher frequencies.

There are several different models for mathematical description of the effect of pressure and temperature⁴⁸, in our case we have used the so called FMT model, proposed by Fillers, Moonan and Tschoegl²⁶⁻²⁸. The FMT model can be viewed as an extension of the WLF equation to account for the effect of pressure in addition to that of temperature. The shift factor as function of temperature and pressure is given in the form:

$$\log a_{T,p} = -\frac{c_1^{00}[T - T_0 - \theta(p)]}{c_2^{00}(p) + T - T_0 - \theta(p)}, \quad (1)$$

where

$$\theta(p) = c_3^0(p) \ln \left(\frac{1 + c_4^0 p}{1 + c_4^0 p_0} \right) - c_5^0(p) \ln \left(\frac{1 + c_6^0 p}{1 + c_6^0 p_0} \right), \quad (2)$$

and c 's follow as

$$c_1^{00} = B/2.303f_0, \quad (3)$$

$$c_2^{00} = f_0/\alpha_f(p), \quad (4)$$

$$c_3^0(p) = 1/k_e\alpha_f(p), \quad (5)$$

$$c_4^0 = k_e/K_e^*, \quad (6)$$

$$c_5^0(p) = 1/k_\phi\alpha_f(p), \quad (7)$$

$$c_6^0 = k_\phi/K_\phi^*, \quad (8)$$

The 00 superscript indicates that the parameter is referred to the reference temperature T_0 (first place) and to the reference pressure p_0 (second place). A single 0 superscript refers to the reference temperature only. The * superscript refers to zero (in practice, atmospheric) pressure, while subscripts e and f stand for entire- and free- volume, respectively.

Eq.1 is the Fillers-Moonan-Tschoegl (FMT) equation. K_e^* and k_e , and thus c_4^0 , can be determined from separate volume-pressure measurements through a fit to the the Murnughan equation of state⁵⁰

$$\ln \frac{V}{V_0} = -\frac{1}{k_e} \ln \left[\frac{K_e^*(T) + k_e p}{K_e^*(T) + k_e p_0} \right], \quad (9)$$

by a non-linear least-squares procedure. In Eqs.1-9, α_f denotes expansivity (i.e., the isobaric cubic thermal expansion coefficient) of the fractional free volume, $f_0 = f(p_0)$ is fractional free volume at reference pressure, $K_e^*(T) = K_e(T)|_{p=0}$ is the bulk modulus at atmospheric pressure and k_e is a proportionality constant deemed independent of either pressure or temperature.

Described facts on the effect of pressure demonstrate that hydrostatic pressure may be used for adjustments of the energy absorption maximum to a desired frequency. However, since vibration isolation usually operates at ambient conditions, pressure may be only increased. The pressure induced shifting is therefore possible from higher toward the lower frequencies only. Hence, for the GDE damping elements we may use only those polymeric materials which energy absorption maxima are located at frequencies that are much higher than the frequency at which vibrations take place. The three materials analyzed here fulfill this condition.

FIG. 3. Schematic representation of CMS apparatus. Reproduced from *Experimental mechanics*, A measuring system for bulk and shear characterization of polymers, 46, 2006, 429, I. Emri and T. Prodan, Society for Experimental Mechanics 2006. With permission of Springer.

B. High-pressure CMS apparatus

All experiments were performed on a CMS apparatus^{23–25}. CMS allows measurements of shear relaxation and bulk creep compliance properties of polymers in solid state, simultaneously subjected to temperatures ranging from -40°C to $+120^{\circ}\text{C}$, and hydrostatic pressures ranging from atmospheric to 500MPa . The apparatus is shown schematically in Fig.3. The pressure is generated by the *pressurizing system* using silicone oil. The *pressure vessel* is contained within the *thermal bath*, where another silicone oil circulates from the *circulator*, used for precise temperature control. The apparatus utilizes two separate *measuring inserts*, which can be inserted into the *pressure vessel*, the *relaxometer* and the *dilatometer*, both shown in Fig.4. Signals from the measuring inserts pass through the *carrier amplifier* prior to being collected in digital format by the *data acquisition system*.

The *magnet* and *motor charger* supplies current to the *electromagnet*, which activates the measurement. The same charger also supplies current to the *electric motor* of the *relaxometer*, shown in Fig.4(a), which pre-loads the spring that then applies the desired torsional deformation (angular displacement), to the specimen. Specimens can be simultaneously subjected to pressures of up to 500MPa with a precision of $\pm 0.1\text{MPa}$, and to temperatures ranging from -40°C to $+120^{\circ}\text{C}$ with a precision of $\pm 0.01^{\circ}\text{C}$.

The *relaxometer* insert, shown in Fig.4(a), measures the shear relaxation modulus by applying a constant torsional strain to a cylindrical specimen, and by monitoring the induced moment as a function of time. The specimen diameter can range from 2mm to 12mm , while its length may vary from 38mm to 60mm . The two main parts of the insert are the *loading device*, and the *load cell*. The *loading device* applies a torsional strain by twisting the

FIG. 4. Relaxometer (a) and dilatometer (b) inserts with main components. Reproduced from Experimental mechanics, A measuring system for bulk and shear characterization of polymers, 46, 2006, 429, I. Emri and T. Prodan, Society for Experimental Mechanics 2006. With permission of Springer.

specimen for a few degrees in approximately 0.01 seconds (depending on the initial stiffness of the specimen). To induce the deformation of the specimen, the *electric motor* is used to first pre-load an Archimedes spring. Once twisted, the spring is kept in its pre-loaded position by a rack-and-pawl mechanism, which is activated with the *electromagnet*, mounted outside the pressure vessel (see Fig.3). The latter pulls the pawl out of the rack, and the energy of the spring deforms the specimen to a pre-determined angle, which is typically around 2 degrees. The induced moment is then measured by the *load cell*, which is attached to the *slider mechanism* to compensate for possible changes in the length of the specimen resulting from various temperature and pressure conditions, as well as from the pointing effect (shortening of the specimen caused by a torsional deformation). After the shear relaxation measurement is complete, the *electric motor* brings the specimen to its original un-deformed state, while maintaining the pressure vessel fully pressurized. The *relaxometer* can measure shear relaxation moduli in the range of $10^{-2} - 10^4 MPa$.

The shear relaxation modulus $G(t)$ is the ratio of the time-dependent shear stress $\tau(t)$ over a fixed and constant shear strain γ_0 :

$$G(t) = \frac{\tau(t)}{\gamma_0} = \frac{32L_0M(t)}{\pi D_0^4\theta_0}. \quad (10)$$

Here $M(t)$ is a decaying moment measured over time with a load cell, θ_0 is an initial angular deformation of the specimen induced by the spring, as described above, and D_0 and L_0 are the specimen diameter and effective length (distance between the two grips) respectively.

The *dilatometer* insert, shown in Fig.4(b), is used to measure bulk properties such as the: bulk creep compliance, $B(t, T, p)$; equilibrium bulk creep compliance, $B(T, p) = B(t \rightarrow \infty, T, p)$; equilibrium bulk modulus, $K(T, p) = K(t \rightarrow \infty, T, p) = 1/B(T, p)$; specific volume $v(T, p) = v(t \rightarrow \infty, T, p)$, and thermal (equilibrium) expansion coefficient, $\beta(T, p) = \beta(t \rightarrow \infty, T, p)$. The measurements are performed by monitoring the volume change of the specimen, which results from the imposed changes in pressure and/or temperature, by measuring the change in length of the specimen, $L(t, T, p)$, with the aid of a built in Linear Variable Differential Transformer (LVDT). The volume estimate can be considered accurate if the change in volume is small (up to a few percent) and the material is isotropic. Specimens for the *dilatometer* can be up to 16mm in diameter and from 40 to 60mm in length. The absolute volume measurement error is about 0.1%, while the relative error is 0.05%.

Within this research the specific volume $v(T, p)$, measurements were needed for determination of FMT constants (non-linear least-squares fitting of Eq.9). The specific volume is defined as a ratio between the specimen volume V and its mass m :

$$v(T, p) = \frac{V(t_\infty, T, p)}{m} = \frac{\pi D_0^2}{4mL_0^2}(L_0 + \Delta L)^3, \quad (11)$$

where L_0 and D_0 are the initial length and diameter of a specimen and ΔL is the change of the length of the specimen induced by temperature/pressure changes. Since the change of volume is small we assumed that the relative change in length L , equals the relative change in diameter

$$\frac{D}{D_0} \approx \frac{L}{L_0} \approx \frac{L_0 + \Delta L}{L_0} \rightarrow D = \frac{(L_0 + \Delta L)D_0}{L_0}. \quad (12)$$

Similarly, we find for the volume of a cylindrical specimen:

$$V = \frac{\pi D_0^2}{4L_0^2}(L_0 + \Delta L)^3. \quad (13)$$

C. Construction of mastercurves using CFS methodology

As will be explained in the experimental section, the experiments were performed at several different temperatures and pressures within an experimental window of 10^3 seconds to obtain the response function segments, which had to be shifted according to the time-

FIG. 5. Schematics of the shifting procedure. Reproduced from M. Gergesova, B. Zupancic, I. Saprunov, and I. Emri, *Journal of Rheology*, Vol. 55, 1, (2011); used in accordance with the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

temperature-pressure superposition principle⁴⁸ to obtain the corresponding mastercurve. Instead of commonly used hand shifting, the shifting was done by using the close-form-shifting (CFS)^{51,52} algorithm, which leads to a unique objective mastercurve. The CFS shifting procedure, which is becoming the new ISO standard (ISO/DIS 18437-6:2017), is briefly summarized below.

Let the temperature T_k be the reference temperature, and the corresponding data measured at these conditions the reference segment of the master curve,

$$G(T_k, t) = \{\log G_{k,i}, \log t_{k,i}; i = 1, 2, \dots, N_k\}. \quad (14)$$

To construct the master curve at the selected temperature T_k we need to shift all segments measured at $T_j > T_k$ to the right, and the remaining segments, measured at $T_j < T_k$ to the left along the logarithmic time-axis, so as to obtain a smooth mastercurve, as schematically shown in Fig.5. The shifting must be executed sequentially, starting with segments measured at $T_{k+1} > T_k$, and $T_{k-1} < T_k$, until all the segments are brought together.

The set of temperatures, $\{T_j, j = 1, 2, \dots, M\}$, at which relaxation experiments were performed should be selected such that segments measured at two consecutive temperatures, e.g., T_k , and T_{k+1} will overlap sufficiently to allow effective construction of the master curve. The common rule of thumb is that this overlapping should be at least one logarithmic decade

of time.

The first datum point of the segment $(k+1)$ i.e., $\log G_{k+1,1}$, and the last datum point of the segment (k) i.e., $\log G_{k,N_k}$ represent strengths of the first and the last datum points in the window where the two segments overlap, as shown in Fig.5.

The overlapping sets of two segments we denote as

$$U_{k+1} = \{\log G_{k+1,n}, \log t_{k+1,n}; n = 1, 2, \dots, U_{k+1}\}, \quad (15)$$

and

$$L_k = \{\log G_{k,n}, \log t_{k,n}; n = L_k, L_k + 1, \dots, N_k\}. \quad (16)$$

The location of the last datum point of the set U_{k+1} i.e., $\log G_{k+1,U_{k+1}} = \log G_{k,N_k}$, may be expressed as

$$\begin{aligned} \log t_{k+1,U_{k+1}} &= \log t_{k+1,u} + (\log G_{k+1,u} - \log G_{k+1,U_{k+1}}) \\ &\times \frac{\log t_{k+1,u+1} - \log t_{k+1,u}}{\log G_{k+1,u} - \log G_{k+1,u+1}}. \end{aligned} \quad (17)$$

Whereas the location of the first datum point of the set L_k i.e., $\log G_{k,L_k} = \log G_{k+1,1}$, is given in the form,

$$\begin{aligned} \log t_{k,L_k} &= \log t_{k,l} + (\log G_{k,l} - \log G_{k,L_k}) \\ &\times \frac{\log t_{k,l+1} - \log t_{k,l}}{\log G_{k,l} - \log G_{k,l+1}}. \end{aligned} \quad (18)$$

To construct the master curve at the selected temperature T_k we need to shift the segment measured at T_{k+1} to the right along the logarithmic time-axis, to obtain the smooth mastercurve. Thus, in the ideal case, for all data within the Overlapping Window the condition

$$G_k(t) = G_{k+1}(t \cdot a_{k+1}). \quad (19)$$

must be fulfilled. Here a_{k+1} denotes time-temperature-pressure shift factor corresponding to the temperature T_{k+1} . We may intuitively see that an optimal overlapping of the two curves is obtained when the shaded area between the two curves is equal to zero, see Fig.5.

Hence,

$$A = A_k - A_{k+1} = 0, \quad (20)$$

where

$$A_{k+1} = \sum_{n=1}^{U_{k+1}-1} \left[\left(\frac{(\log t_{k+1,n+1} + \log a_{k+1})}{2} \right. \right. \\ \left. \left. \times \frac{(\log t_{k+1,n} + \log a_{k+1})}{2} \right) \right. \\ \left. \times (\log G_{k+1,n+1} - \log G_{k+1,n}) \right], \quad (21)$$

and

$$A_k = \sum_{n=L_k}^{N_k-1} \left[\frac{\log t_{k,n+1} + \log t_{k,n}}{2} (\log G_{k,n+1} - \log G_{k,n}) \right]. \quad (22)$$

Combining equations (17) - (22), we may calculate the shift factor belonging to the segment measured at t_{k+1}

$$\log a_{k+1} = \frac{A_k - \sum_{n=1}^{U_{k+1}-1} \left[\frac{\log t_{k+1,n+1} + \log t_{k+1,n}}{2} \right. \\ \left. (\log G_{k+1,n+1} - \log G_{k+1,n}) \right]}{\log G_{k,N_k} - \log G_{k+1,1}} \\ \times \frac{(\log G_{k+1,n+1} - \log G_{k+1,n})}{\log G_{k,N_k} - \log G_{k+1,1}}. \quad (23)$$

This algorithm is valid for shifting the segments measured at $T_j > T_k$. For shifting those segments that were measured at $T_j < T_k$ we need to modify the algorithm as follows,

$$\log a_{k-1} = \frac{A_k - \sum_{n=L_k-1}^{N_{k-1}-1} \left[\frac{\log t_{k-1,n+1} + \log t_{k-1,n}}{2} \right. \\ \left. (\log G_{k-1,n+1} - \log G_{k-1,n}) \right]}{\log G_{k-1,N_{k-1}} - \log G_{k,1}} \\ \times \frac{(\log G_{k-1,n+1} - \log G_{k-1,n})}{\log G_{k-1,N_{k-1}} - \log G_{k,1}}, \quad (24)$$

where

$$A_k = \sum_{n=L_k-1}^{N_{k-1}-1} \left[\frac{\log t_{k,n+1} + \log t_{k,n}}{2} \cdot (\log G_{k,n+1} - \log G_{k,n}) \right]. \quad (25)$$

We have used the above CFS approach to generate the unique, person-independent master curves presented in this paper. The CFS software may be freely downloaded at: <http://standards.iso.org/iso/18437/-6/ed-1/en>.

D. Interconversion between time- and frequency-domain material functions

Pressure dependence characterization was performed in time-domain as relaxation experiments. Details are presented in experimental section (Section III). The frequency dependent material functions i.e., the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$, were then obtained via the interconversion. For the case of shear relaxation $G(t)$, and storage $G'(\omega)$ and loss $G''(\omega)$ modulus, the interrelation is given through the inverse Fourier transform⁵³ as:

$$\begin{aligned} G(t) &= \mathcal{F}^{-1}[G^*(\omega)/i\omega; t] \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{G^*(\omega)}{i\omega} \exp(i\omega t) d\omega, \end{aligned} \quad (26)$$

where $i = \sqrt{-1}$, and $G^*(\omega)$ is the complex modulus, composed of storage and loss modulus:

$$G^*(\omega) = G'(\omega) + iG''(\omega). \quad (27)$$

However, there are several other possible ways to interconvert material functions from the time to frequency domain and vice versa⁵⁴. In our case we have used an approximate method proposed by Schwarzl⁵⁵. In this case the interrelation between the storage $G'(\omega)$ and the loss $G''(\omega)$ modulus and the shear relaxation $G(t)$ is given as:

$$\begin{aligned} G'(\omega) &\cong 0.143G(8t) - 0.86G(4t) + 0.674G(2t) \\ &\quad + 0.842G(t) + 0.001G(t/2) + 0.101G(t/4) \\ &\quad - 0.00855G(t/8) + 0.00855G(t/16)|_{t=1/\omega}, \end{aligned} \quad (28)$$

and

$$\begin{aligned} G''(\omega) &\cong 0.470G(4t) - 2.144G(2t) + 1.476G(t) \\ &\quad - 0.422G(t/2) + 0.608G(t/4) \\ &\quad - 0.160G(t/8) + 0.1722G(t/16)|_{t=1/\omega}. \end{aligned} \quad (29)$$

TABLE I. Extrusion parameters for TPU's on PolyLab HAAKE Rheomex PTW 16 extruder.

Type	Sample diam.	Temperature in heating zones [$^{\circ}C$]											Screw speed	Meetering feeder
		1	2	3	4	5	6	7	8	9	10	Die		
1190A	4mm	160	160	170	170	180	180	180	190	190	185	180	50	120
	6 & 11mm	160	160	170	170	180	180	180	190	200	200	200	55	45
1175A	6mm	140	140	140	150	150	160	160	160	180	190	195	50	30
	11mm	140	140	140	150	150	160	160	160	180	180	180	50	65
1195D	3 – 4mm	170	170	180	180	190	190	190	200	210	210	200	50	35 - 75
	6 & 11mm	170	170	180	180	190	190	190	200	210	210	210	50	30

The error analysis which we have performed in the past⁵⁴ showed that this approximate method brings in an error smaller than 2%, which we considered sufficient for the purpose of current investigation.

III. CHARACTERIZATION OF SELECTED MATERIALS

We have investigated three polyether-based thermoplastic polyurethane (TPU) materials in solid state from the BASF Elastollan[®] 11 series⁴⁶ i.e., (i) 1190A, (ii) 1175A, and (iii) 1195D, that are already used for vibration isolation applications. Since Elastollan[®] is hygroscopic material, all materials were dried at 100 $^{\circ}C$ for 3 hours in a commercial dryer (SP105-C, Kambič, Slovenia), to avoid bubble formation during the extrusion process, which was used for sample preparation.

A. Bulk sample preparation

Due to measuring limitations of the CMS apparatus (see Section II B), we had to prepare samples with different diameters for measurements at different pressure-temperature boundary conditions. Samples were prepared with a PolyLab HAAKE Rheomex PTW 16 extruder (Thermo Haake, Germany) equipped with two co-rotating 16mm screws. Its extruder barrel is divided into ten independent heating zones and a separate die temperature control. Based on experience, we have used the temperature profiles summarized in Tab.I.

Thicker samples ($\sim \phi 6mm$ and $\phi 11mm$) were prepared by extrusion into glass tubes that were coated from the inside with a silicon rubber (Tesacoma, silicone pastry board), to prevent the extruded melt from sticking to the glass. Coated glass tubes were pre-heated

to 100°C before they were filled with materials, and afterwards naturally cooled to ambient conditions. Thinner samples ($\sim \phi 2 - 4.5\text{mm}$) were prepared by continuous extrusion into a water bath. The speed of a subsequent conveyor belt together with the screw speed enabled us to alter diameters of thin samples. After extrusion, the thin samples were let to free hang under their own weight for about 12 hours at ambient conditions, to make them straight.

After extrusion, materials were cut with a razor blade to the specified length and the cut surfaces were finished with a sand paper (using very fine P220 and super fine P1200 sand paper). Diameter of each sample was measured 10 times along its diameter, and its length 5 times, using a digital caliper (Digimatic Caliper Series 500, Mitutoyo, USA). The weight of samples for bulk properties was measured 5 times using a laboratory scale (Mettler Toledo AG245, USA). The averaged values of diameter and length were used to calculate shear relaxation $G(t)$, according to Eq.10, while for bulk measurements also the average weight of samples was taken into account and used for calculating K_e^* and k_e , and thus c_4^0 through the Eq.9. Samples were afterwards glued to the metallic sample holders using two component epoxy glue (UHU plus schnellfest 2-K-Epoxidharzkleber, UHU GmbH & Co KG, Germany), so that they could be placed into the relaxometer insert (Fig.4(a)) or dilatometer insert (Fig.4(b)). The averaged lengths and diameters of samples used for relaxometer measurements are presented in Tab.II, the sample dimensions and mass used for dilatometer measurements are presented in Tab.III.

To remove residual stresses in samples from extrusion, cutting and gluing, all samples were annealed prior to the measurements (this is indicated in Figs.7 and 8 in the following section). The start of this procedure was raising the temperature in the commercial dryer (SP105-C, Kambič SP105-C, Slovenia) from ambient conditions to 90°C . The temperature was held constant for three hours, followed by slow cooling. Cooling was done in two stages, first stage was done inside the oven to ambient conditions, around 20°C , and in second stage samples were removed from the oven and placed inside an insulation box (to assure required rate of cooling) that was placed inside a freezer. Using this procedure temperature of -20°C was achieved. During the cooling the average cooling rate was approximately $-0.15^{\circ}\text{C}/\text{min}$ (assuring slow cooling is important in order to minimize the effect of physical aging⁵⁶).

TABLE II. Averaged values of sample dimensions for shear relaxation measurements.

Type	dimensions, $d \times l$ [mm]	boundary conditions
1190A	6.400×57.703	$T = -20 - 30^\circ C,$ $p = 0.1 MPa$
	5.921×57.854	
	5.528×59.012	
	4.160×56.966	$T = -20^\circ C,$ $p = 0.1 - 300 MPa$
	3.915×42.586	
	3.748×39.714	
1175A	6.050×53.934	$T = -20^\circ C,$ $p = 0.1 - 300 MPa$
	6.111×54.031	
	6.117×53.854	
	11.854×58.708	$T = -20 - 60^\circ C,$ $p = 0.1 MPa$
	11.479×58.613	
	11.563×58.21	
1195D	3.054×57.468	$T = -20 - 10^\circ C,$ $p = 0.1 MPa$
	3.018×59.962	
	4.778×59.783	
	6.592×60.005	$T = 20 - 60^\circ C,$ $p = 0.1 MPa$
	6.864×58.950	
	6.773×58.920	
	4.629×59.258	$T = -20^\circ C,$ $p = 0.1 - 300 MPa$
	4.592×57.748	

TABLE III. Averaged values of sample dimensions and mass for bulk measurements.

Type	dimensions, $d \times l$ [mm]	mass [g]
1190A	11.831×42.952	5.2848
	11.590×46.451	5.4939
	11.743×47.533	5.7628
1175A	11.717×49.552	6.4141
	11.788×48.643	6.2434
	11.876×49.630	6.1127
1195D	11.708×49.085	6.1012
	11.645×49.620	6.1127
	11.799×49.314	6.2232

B. Loading profiles for shear relaxation and dilatometry experiments

After the sample preparation phase, samples were tested using the previously described CMS apparatus, using relaxometer and dilatometer insert (Figs.4(a) and 4(b))

For obtaining the shear relaxation properties, experiments were performed at two dif-

FIG. 6. Boundary conditions for determining shear relaxation properties and pressure sensitivity of selected materials.

ferent sets of boundary conditions. The 1st Set of experiments was performed at isobaric conditions (at constant pressure) at $p = 0.1 \text{ MPa}$, at different constant temperatures between -20 to 60°C . The exact temperatures are provided within diagrams (Fig.7). For obtaining the pressure sensitivity of measured materials and to expand the measuring range of shear relaxation $G(t)$, the 2nd Set of experiments was performed at isothermal conditions (at constant temperature) at $T = -20^\circ\text{C}$, at different constant pressures ranging between 0.1 and 300 MPa . Fig.6 schematically shows boundary conditions of both sets of experiments, while the corresponding temperature and the pressure loading profiles for each of the three TPU's is presented in Fig.7. In all experiments, each loading step consists of 3 hours stabilization time and 1000 s ($\sim 15 \text{ min}$) measuring time. All experiments started at conditions where the material is closer to glassy state i.e., at lowest temperature for the 1st Set and at highest pressure for the 2nd Set of experiments.

In all cases at least three repetitions of measurements were performed, where for each repetition different samples was used. After averaging segments measured at the same boundary conditions, we have applied the Closed Form Shifting (CFS) algorithm, described in Section II C, to create the shear relaxation $G(t)$ mastercurves. The latter were then interconverted into the frequency domain, as described in Section II D, to obtain the storage $G'(\omega)$, and the loss $G''(\omega)$, moduli for the three examined materials.

Dilatometry measurements were needed for determining constants of the FMT model, described in Section II A. Measurements were again performed with the CMS apparatus using the *dilatometer insert*, described in Section II B. In this case, the pressure profile was the

FIG. 7. Temperature/pressure loading profiles for individual materials used in shear relaxation experiments.

same for all three materials, starting at the highest pressure, which was stepwise decreased, as shown in Fig.8. Each loading step consisted of 30min stabilization time followed by 2min measuring time of specimen length. For each material, we performed three experiments, always using different fresh samples. After averaging the obtained results, we have calculated the specific volume, using Eq.11, that was needed in calculation of the FMT parameters. The results of the FMT model parameters are displayed in Table IV.

FIG. 8. Pressure loading profile for bulk measurements, performed at 20°C for all materials.

IV. RESULTS AND DISCUSSION

A. Shear relaxation segments and mastercurves

Following the experimental procedure described in previous section, Section III B, we have performed two sets of shear relaxation experiments on three TPU materials: 1190A, 1175A and 1195D. Both sets of results are shown together in Fig.9(a) - Fig.11(a). The 1st Set of measurements were performed at different temperatures, ranging from about -20°C to $+60^{\circ}\text{C}$, while the pressure was kept constant at $p = 0.1\text{MPa}$. These results are shown in Fig.9(a) - Fig.11(a) at the bottom of figures. The 2nd Set of measurements were performed at different pressures, ranging from about 50MPa to 300MPa , at constant temperature at about $T = -20^{\circ}\text{C}$. The results are shown in the same diagrams at the top. The exact, measured temperatures and pressures are indicated in each diagram. The error bars in all diagrams indicate maximal difference between averaged and measured values.

As a next step, we have used the CFS algorithm to construct the three mastercurves at the reference temperature 20°C and the reference pressure 0.1MPa , shown in Fig.9(b) - Fig.11(b). It is important to note that combining temperature and pressure boundary conditions allows substantial widening of the experimental time-window in determination of material functions, in our case the relaxation mastercurves. It is evident from Fig.9(b) - Fig.11(b), cf. segments measured at -20°C and 0.1MPa , that performing experiments just at different temperatures and constant ambient pressure would allow determination of approximately half of the mastercurve only.

For the FMT model the c_1 and c_2 constants were obtained through time-temperature superposition using previously described CFS software. Volumetric measurements, described in Section III were used to determine material parameters K_e^* and k_e (and thus c_4 using Eq.6)

FIG. 9. (a) Segments at different temperature and pressure conditions and (b) mastercurve of bulk material 1190A at $T_{ref} = 20^\circ\text{C}$ and $p_{ref} = 0.1\text{ MPa}$.

TABLE IV. FMT parameters.

Mater.	c_1	c_2 [°C]	$\alpha_f \times 10^{-4}$ [°C ⁻¹]	K_e [MPa]	k_e	K_ϕ [MPa]	k_ϕ
1190A	31.24	202.43	1.26	2763	12.54	3092.74	12.59
1175A	11.46	52.35	1.87	2434	12.89	2494.02	13.97
1195D	24.92	105.19	1.98	2762	13.44	2877.39	15.21

fitting the Eq.9. For the calculation of the remaining constants c_3 , c_5 and c_6 , experimental shift factors obtained from measurements at constant temperature ($T = -20^\circ\text{C}$) and varying pressures, were fitted to Eq.1 using the Levenberg-Marquardt algorithm (MATLAB R2015a). Table IV shows material parameters for all three materials.

Mastercurves for the three materials are compared in double-logarithmic Fig.12(a) and semi-logarithmic Fig.12(b) diagrams. The third figure, Fig.12(c) shows their sensitivity to hydrostatic pressure. From the first, double logarithmic diagram, we observe that the ratio of moduli of the three materials remains fairly constant along the complete time-scale. In this case, the ratio is displayed as a distance between the curves. On the other hand, the

FIG. 10. (a) Segments at different temperature and pressure conditions and (b) mastercurve of bulk material 1175A at $T_{ref} = 20^\circ\text{C}$ and $p_{ref} = 0.1 \text{ MPa}$.

semi-logarithmic diagram allows better comparison of material functions absolute values.

We see that close to the glassy state i.e., at short times, the values of the shear moduli are quite high for 1190A and 1195D and about 6-9 times smaller for 1175A, whereas their moduli become very small and almost indistinguishable at longer times i.e., this is where the materials are used at conditions. Hence, their properties at ambient conditions are for all practical purposes the same. Double logarithmic diagram reveals another interesting feature of the material 1175A, indicated with the two dashed lines in Fig.12(a) i.e., material 1175A exhibits an abrupt change in its behavior at a critical time scale which may be adjusted with pressure and temperature boundary conditions. At this point in time material essentially enters its rubbery state. For the other two TPU materials, this transition is much more gradual.

From Fig.12(c), we see that all three materials are quite sensitive to pressure, the main difference in their pressure sensitivity is visible within the first 100 MPa , where 1190A proves to be most sensitive of the three materials. At the highest pressure (300 MPa), properties of 1190A are shifted for around 5.5 decades along the logarithmic time-, and/or

FIG. 11. (a) Segments at different temperature and pressure conditions and (b) mastercurve of bulk material 1195D at $T_{ref} = 20^\circ\text{C}$ and $p_{ref} = 0.1 \text{ MPa}$.

FIG. 12. Mastercurves at $T_{ref} = 20^\circ\text{C}$ and $p_{ref} = 0.1 \text{ MPa}$ in (a) double-logarithmic, and (b) semi-logarithmic coordinate system, and (c) pressure shift factors $\log a_p(p)$ of three bulk TPU materials.

frequency scale. For 1195D, this shift is about 3.5, whereas for 1175A properties are shifted along the logarithmic time/frequency-scale for about 1.5 decades only.

B. Dynamic material functions

Using the approximate interrelations Eq.28 and Eq.29, we have calculated the storage $G'(\omega)$, and the loss $G''(\omega)$, moduli for the three examined materials. The results are shown in Fig.13, again in double logarithmic and semi-logarithmic coordinate systems. Figs.13(a) and (c) show the storage modulus $G'(\omega)$, whereas Figs.13(b) and (d) the loss modulus $G''(\omega)$. The difference between materials in time domain (Fig.12) is also reflected in the frequency domain.

The storage modulus $G'(\omega)$, which defines the vibro-isolation stiffness, increases with excitation frequency for about 100 times for 1190A and 1195D, and for about 10 times for 1175A. However, as seen from the semi-logarithmic diagrams, within the frequency range indicated as shaded area, which is of interest for engineering applications, their stiffness is quite low. In the case of 1175A we may see that it behaves elastically i.e., its storage modulus is almost constant (up to $10^4 Hz$), whereas, within the same frequency range, the stiffness of other two materials exhibit quite strong frequency dependence. From the double logarithmic diagram, we see that 1175A exhibits an abrupt transition at $10^4 Hz$, while for the other two materials the transition is more gradual.

The loss modulus $G''(\omega)$, also increases with excitation frequency for all three materials, again for about 100 times for 1190A and 1195D, and for about 10 times for 1175A. Since the loss modulus $G''(\omega)$, defines the damping ability of a vibro-isolator, the higher values mean better damping. However, from the Figs.13(b) and (d) we may see that the maximal measured values in all three cases are located at very high frequencies, between $10^8 - 10^{12} Hz$. In addition to this, it may also be seen that the values of the loss modulus $G''(\omega)$, in the frequency range of interest in most engineering applications, are relatively low i.e. in the range between 0.1 to 25MPa, which is not bad in comparison to metals, however far away from real potentials of TPU materials.

Comparing the three TPUs shows that the material 1175A has the lowest loss modulus $G''(\omega)$ through the whole frequency range. As in the case of storage modulus $G'(\omega)$, 1175A abruptly enters the transition state at about $10^3 Hz$ where its energy absorption properties

FIG. 13. Shear storage modulus $G'(\omega)$ in (a) double logarithmic and (b) semi-logarithmic coordinate systems; and shear loss modulus $G''(\omega)$ in (c) double logarithmic and (d) semi-logarithmic coordinate systems. All figures are shown for bulk materials at $T_{ref} = 20^\circ\text{C}$ and $p_{ref} = 0.1\text{MPa}$.

are strongly excitation frequency dependent, before that its dissipation properties are more or less constant, see Fig.13(b). The transition is much more gradual for 1190A and 1195D.

C. Analysis of GDE potential

Combining the information on dynamic viscoelastic material functions presented in Figs.13 with materials hydrostatic pressure sensitivity, presented in Fig.12, we may construct 3D diagrams showing interrelation between the storage $G'(\omega)$, and the loss $G''(\omega)$, modulus, and excitation frequency and hydrostatic pressure to which material is exposed.

FIG. 14. Frequency dependent shear storage modulus $G'(\omega)$ in dependence of hydrostatic pressure for (a) 1190A, (b) 1175A and (c) 1195D at $T_{ref} = 20^\circ C$.

The results are shown in Fig.14 for the storage modulus $G'(\omega)$, and in Fig.15 for the loss modulus $G''(\omega)$.

The 3D diagrams provide a general inside how the two material functions depend on hydrostatic pressure and excitation frequency. The differences between the three materials are obvious, particularly when comparing their loss moduli. However, for more precise analysis of how hydrostatic pressure affects the storage $G'(\omega)$ and loss $G''(\omega)$, moduli within the vibro-isolation range 1 - 10000 Hz that is of interest, we need to perform some further analysis. Specifically, we are interested how much one can increase the storage $G'(\omega)$ modulus (related to stiffness) and loss $G''(\omega)$ modulus (related to energy absorption) of a vibro-isolation by exposing the material to selected hydrostatic pressure.

Stiffness of an vibro-isolator depends on its geometry and the storage modulus of a material from which it is built, whereas, its energy absorption capability is defined by the isolator total volume and material loss modulus. Hence, if we keep the geometry and volume of an isolation constant, its stiffness and its energy absorption capability will depend on material storage and loss modulus only. In fact, our main interest is to understand to what

FIG. 15. Frequency dependent shear loss modulus $G''(\omega)$ in dependence of hydrostatic pressure for (a) 1190A, (b) 1175A and (c) 1195D at $T_{ref} = 20^\circ C$.

extent (how many times) we can increase stiffness and energy absorption of an isolation by exposing the material from which it is made of to a selected hydrostatic pressure. Therefore, we introduce two parameters, first, defining the increase of vibro-isolator stiffness by exposing it to a selected hydrostatic pressure p , relative to the vibro-isolator stiffness at the ambient pressure $p_0 = 0.1MPa$:

$$\kappa_k(p, \omega) = \frac{G'(p, \omega)}{G'(p_0, \omega)}, \quad (30)$$

and the second

$$\kappa_d(p, \omega) = \frac{G''(p, \omega)}{G''(p_0, \omega)}, \quad (31)$$

which defines an increase of isolation energy absorption (damping) obtained by exposing the analyzed TPUs to a selected hydrostatic pressure.

All comparisons are made within the frequency range $(1 - 10000Hz)$, which is of interest for impact and vibration isolation. The results are shown in two different forms: (i) $\kappa_k(p, \omega)$ and $\kappa_d(p, \omega)$ as functions of excitation frequency, for four selected pressures; and (ii) $\kappa_k(p, \omega)$ and $\kappa_d(p, \omega)$ as functions of hydrostatic pressure, for four selected excitation

frequencies. In fact, both mentioned diagrams present the same information i.e., how much hydrostatic pressure we need at a given excitation frequency to obtain a desired increase of isolation energy absorption and/or stiffness. However, they present this information from a different point of views which is important for designing an vibro-isolator for a specific engineering application. In our discussion in Section IV B we have pointed out that energy absorption and stiffness of an vibro-isolator made from any of the three materials are within the excitation frequency range of interest i.e., $1 - 10^4 Hz$ approximately constant. As demonstrated in continuation, this is not necessarily so when we use hydrostatic pressure to modify vibro-isolator characteristics. In this case, both, stiffness and energy absorption characteristics of an vibro-isolator may become (strongly) excitation frequency dependent.

1. $\kappa_k(p, \omega)$ and $\kappa_d(p, \omega)$ as functions of frequency

Figs.16 and 17 show isolation excitation-frequency dependence, which stiffness and energy absorption characteristics were modified by exposing materials to selected hydrostatic pressures i.e., 50, 100, 200 and 300MPa. In Fig.16 we first show frequency dependence of the ratio $\kappa_k(p,)$ for (a) 1190A, (b) 1175A, and (c) 1195D, for the four selected pressures, which demonstrates improvement of isolation stiffness.

Comparing the three diagrams we clearly see the significant difference between the three materials in the effect of pressure on improvement of isolation stiffness. Within the frequency range of interest, TPU 1190A is very sensitive to pressure and excitation frequency to which the material (isolation) is exposed. Depending on the excitation frequency its stiffness may be increased between 3.5 and 9.5 times by exposing it to hydrostatic pressure of 300MPa. Hence, TPU 1190A is a good material for the new generation GDE damping elements, though its stiffness will be quite sensitive to excitation frequency.

This paper is not the place to discuss this in detail, but let us just mention that this feature may be cleverly utilized in vibration isolation solutions. For example, if a mechanical system with one of the currently existing isolations operates below the resonance frequency, an increase of excitation frequency will bring it closer to (or even into) its resonance, possibly causing its failure. However, if one uses GDE vibro-isolator made of TPU 1190A instead an increase of excitation frequency will cause an increase of isolation stiffness, as indicated with two arrows in Fig.16(a). As a result, the resonance frequency of such mechanical

FIG. 16. $\kappa_k(p, \omega)$ as functions of frequency for four selected pressures and materials (a) 1190A, (b) 1175A and (c) 1195D. Arrows in (a) indicating an increase of isolation stiffness with excitation frequency in selected frequency range.

system will be automatically moved to higher frequencies, hence, the system will not enter its resonance. In fact, GDE vibro-isolator allows building mechanical systems that in real engineering situations will never experience problems related to resonance.

Material TPU 1175A, Fig.16(b), in comparison to 1190A, exhibits diametric properties, stiffness of an isolation made from such material will be up to 300MPa pressure and excitation frequency (almost) independent. Hence, one cannot utilize hydrostatic pressure to improve/modify stiffness of isolations made from TPU 1175A. Finally, TPU 1195D based isolation will exhibit characteristics that are combination of the two previous materials, Fig.16(c). Its stiffness is pressure dependent, not as strongly as 1190A, however, it remains practically constant within the complete excitation-frequency range of interest. With a pressure of 300MPa one may increase the stiffness of an isolation for about 3 times.

Let us now turn to isolation energy absorption properties, displayed in Fig.17, which shows $\kappa_d(p, \omega)$ as function of excitation frequency for the four selected hydrostatic pressures i.e., 50, 100, 200 and 300MPa. The results for the three materials are shown in the same order as before. Comparing the three diagrams we again observe strong difference between the three materials, however, the effect of pressure is in this case even stronger and different

FIG. 17. $\kappa_d(p, \omega)$ as functions of frequency for four selected pressures and materials (a) 1190A, (b) 1175A and (c) 1195D.

than in the case of isolator stiffness. In case of 1190A, Fig.17(a), when exposed to 300MPa, the improvement of its energy absorption capability is about 16 times. In addition, within the range 10Hz to 1000Hz material energy-absorption is excitation-frequency independent. In fact, at 100MPa one observes an improvement of 4 times, for excitation-frequencies above 20Hz, whereas, when material is exposed to 50MPa one observes improvement of two times within the complete frequency range of interest. High energy absorption and an increase of isolation stiffness caused by excitation frequency makes TPU 1190A a very attractive material for the new generation GDE damping elements. The two characteristics work hand-in-hand, high energy absorption diminishes vibrations per se, in addition an increase of isolation stiffness will move away mechanical system resonance frequency causing additional reduction of vibrations.

Material 1175A, Fig.17(b), which its stiffness was pressure independent (Fig.16(b)), exhibits sensitivity to pressure within the complete frequency range. It is interesting that up to 30Hz an improvement of about 1.5 times is observed at all four selected pressures, however, at higher excitation-frequencies 1175A becomes more sensitive to pressure. At 300MPa the energy absorption capability may increase more than 4 times, however the improvement is observed only at excitation-frequencies larger than 100Hz. Hence, we may conclude that

1175A should be used when excitation-frequencies are larger than $100Hz$.

Material 1195D, Fig.17(c), at pressures up to $100MPa$ exhibits similar energy absorption properties as 1175A i.e., its performance improvement is about 1.5 times, and it is approximately constant throughout the frequency range of interest. In contrast to 1175A, 1195D exhibits, at pressures above $200MPa$, the largest increase of energy absorption capability at low excitation frequencies. The improvement of energy absorption at $300MPa$ increases up to 4 times.

One may conclude that energy absorption properties of 1175A and 1195D (within the frequency range of interest) mirror each other, TPU 1175A exhibits high pressure induced energy absorption at high excitation-frequencies, whereas TPU 1195D does so at low frequencies. Hence, an isolation made of two types of materials, one from 1175A and the other from 1195A, will exhibit high energy absorption through the complete frequency range of interest.

2. $\kappa_k(p, \omega)$ and $\kappa_d(p, \omega)$ as functions of hydrostatic pressure

In this section we analyze the three materials from different perspective, we examine pressure dependence of isolation stiffness, represented by $\kappa_k(p, \omega)$, shown in Fig.18, and of isolation energy absorption, represented by $\kappa_d(p, \omega)$, shown in Fig.19, at four selected excitation frequencies i.e., 1, 100, 1000 and $10000Hz$.

We will again start with analyzing pressure induced increase of vibro-isolator stiffness. Fig.18(a) shows $\kappa_k(p, \omega)$ for material 1190A at four selected frequencies, Fig.18(b) shows $\kappa_k(p, \omega)$ for material 1175A, where the results are also shown in a close-up diagram in the upper right corner, and Fig.18(c) shows $\kappa_k(p, \omega)$ for material 1195D.

The three diagrams in Fig.18 show essentially the same information as that in Fig.16, however, this time $\kappa_k(p, \omega)$ is presented as function of pressure to which materials are exposed. We see that for all three materials pressure sensitivity represented with the slope $\lambda_k(p, \omega) = (d\kappa_k(p, \omega))/dp$, increases with pressure and excitation frequency. This is most pronounced for 1190A, where for excitation frequency of $1Hz$ $\lambda_k(p > 100MPa, \omega = 1Hz) \cong 1$, and for 10^4Hz $\lambda_k(p > 100MPa, \omega = 10^4Hz) \cong 3.5/(100MPa)$. As we have already discussed, material 1175A is within the frequency range of interest practically pressure independent i.e., $\lambda_k(p, \omega) \approx 0$, except for frequencies close to $10000Hz$. Whereas, material

FIG. 18. $\kappa_k(p, \omega)$ as functions of hydrostatic pressure at selected frequencies for (a) 1190A, (b) 1175A and (c) 1195D.

1195D exhibits approximately the same pressure sensitivity for all excitation frequencies i.e., $\lambda_k(p, \omega) = 0.6/(100 \text{ MPa})$. Hence, regarding the modification of DGE isolation stiffness TPU 1190A appears to be the best material, and to a certain degree 1195D, where one can achieve improvements up to 3 times.

Capability of improving energy absorption with hydrostatic pressure, $\kappa_d(p, \omega)$, for the three materials is shown in Fig.19, again for four selected excitation frequencies i.e., 1, 100, 1000 and 10000 Hz. Materials pressure sensitivity may be again represented as $\lambda_d(p, \omega) = (d\lambda_d(p, \omega))/dp$ i.e., with the slope of $\kappa_d(p, \omega)$. From Fig.19 we observe that energy absorption of all three materials is pressure dependent and it varies with excitation frequency.

The strongest pressure dependence is found with 1190A, where the improvement can be as high as 16 times, whereas the other two materials, 1175A and 1195D, are to a large extent similar, for both the improvement is about 4 times. However, their frequency dependence is quite different, this is particularly true for 1175A and 1195D, as we have already discussed in previous section.

FIG. 19. $\kappa_d(p, \omega)$ as functions of hydrostatic pressure at selected frequencies for (a) 1190A, (b) 1175A and (c) 1195D.

V. SUMMARY AND CONCLUSIONS

This paper presents an analysis of the pressure dependence of three BASF Elastollan[®] materials i.e., (i) 1190A, (ii) 1175A, and (iii) 1195D in time and frequency domain, that are used in manufacturing of isolation systems. The aim of the characterization was to analyze how much one can enhance performance of an isolation by using these materials in Granular damping elements (GDE), that are based on a patented *Dissipative bulk and granular systems technology*. DGE isolation uses polymeric materials in granular form to enhance their dynamic properties by exposing them to hydrostatic pressure, which shifts material energy absorptions maxima towards lower frequencies, to match the excitation frequency of dynamic loading to which a mechanical system is exposed.

Pressure dependence of the three materials were characterized in time domain using a self-built high-pressure apparatus for shear-relaxation and volumetric measurements. All samples were prepared under good care and annealed to avoid effects of physical aging. Relaxation experiments were performed in isobaric state (at constant pressure) at several different constant temperatures, and in isothermal state (at constant temperature) at several different constant pressures. Following the time-temperature-pressure superposition

principle the measured segments were then shifted along the logarithmic time-scale, using the close-from-shifting (CFS) algorithm, to obtain the unique, person-independent, mastercurves, shown in Figs.9-11. Time-temperature-pressure superposition was modeled with the FMT (Fillers-Moonan-Tschoegl) model, for which additional volumetric compressibility measurements were performed. For the three materials, the parameters of FMT model are given in Table IV.

Frequency dependent material functions i.e., shear storage $G'(\omega)$ (related to isolation stiffness) and loss modulus $G''(\omega)$ (related to isolation energy absorption), were calculated through interconversion, using an approximate method proposed by Schwarzl. The obtained frequency domain material functions, $G'(\omega)$ and $G''(\omega)$, for the three materials are shown in Figs.13-15.

To study and understand to what extent (how many times) one can increase stiffness and energy absorption of a vibro-isolators we have introduced two parameters i.e., $\kappa_k(p, \omega)$ and $\kappa_d(p, \omega)$. The first defines the increase of stiffness, and the second the increase of energy absorption. These comparisons were made within the frequency range $(1 - 10000 Hz)$, which is of interest for impact and vibration isolation.

From the obtained results one may draw the following conclusions:

1. The three polyether-based thermoplastic polyurethane (TPU) materials from the Elastollan® 11 series i.e., (i) 1190A, (ii) 1175A, and (iii) 1195D, with similar chemical structure, exhibit significantly different time- and frequency-dependent properties.
2. In time domain, the strength of the shear moduli of 1190A and 1195D is about 6-9 times higher than that of 1175A, whereas, their moduli become very small and almost indistinguishable at longer times i.e., their properties at ambient conditions are for all practical purposes the same.
3. All three materials are quite sensitive to pressure, and 1190A proves to be the most sensitive of the three materials. At $300 MPa$, properties of 1190A are shifted along the logarithmic time-, and/or frequency scale for around 5.5 decades, for 1195D and 1175A this shift is only about 3.5 and 1.5 decades, respectively. These shifts may be achieved by exposing materials to selected hydrostatic pressure.
4. The storage modulus $G'(\omega)$, which defines the vibro-isolation stiffness within the fre-

quency range of interest, may be increased with pressure for about 100 times for 1190A and 1195D, and for about 10 times for 1175A.

5. The loss modulus $G''(\omega)$, which defines the vibro-isolation energy absorption capability within the frequency range of interest, may be increased with pressure for again about 100 times for 1190A and 1195D, and for about 10 times for 1175A.

In conclusion, among the three measured materials it was shown that material 1190A seems to be the most promising for the use in Granular damping elements. Besides having the largest values of loss modulus $G''(\omega)$ it is also the most sensitive to pressure. Meaning, that even at relatively small applied hydrostatic pressures the increase of loss modulus $G''(\omega)$ is higher compared to other two materials.

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