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Compression stress relaxation in carbon black reinforced HNBR at low temperatures

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Abstract

Findings of a study of stress relaxation behaviour of hydrogenated nitrile butadiene rubber (HNBR) at nominal compressive strains up to 0.4 and temperatures above and below the glass transition temperature T_g are reported. Two formulations of a model HNBR with 36 % acrylonitrile content and carbon black (CB) loading of 0 and 50 phr were investigated. The relaxation function of HNBR is found to be independent of strain at temperatures right above the T_g or at times longer than 10^{-3} sec for the deformations employed. CB imparts higher long-term stiffness and also larger relaxation strength at times longer than 10^{-4} sec to the HNBR, but it does not affect the relaxation behaviour of the rubber in the time span from 10^{-3} to 10^4 sec. In addition, the relationship between the strain energy function of HNBR and temperature is demonstrated to have a complex concave-downward shape which is affected by two competing contributions of entropy elasticity and the stress relaxation.

Keyword: stress relaxation, rubber, low-temperature, viscoelastic properties, glass transition, HNBR

1. Introduction

The mechanical behaviour of elastomers is known [1] to be affected by temperatures due to their entropic nature. In fact, from the Gaussian theory of rubberlike elasticity it follows that the strain energy function (W) of a deformed elastomer proportionally increases with temperature. For instance, the theory entails the following expressions for the strain energy function and the nominal stress S in uniaxial loading [1]:

$$W = \frac{1}{2}nkT(\lambda^2 + 2\lambda^{-1} - 3) = \frac{1}{2}G(\lambda^2 + 2\lambda^{-1} - 3) \quad (0)$$

$$S = nkT\left(\lambda - \frac{1}{\lambda^2}\right) = G\left(\lambda - \frac{1}{\lambda^2}\right) \quad (0)$$

where $\lambda = l + \varepsilon$ is the stretch ratio, n is the number of network chains per unit volume, k is the Boltzmann constant, T is temperature, and G is the shear modulus.

On the other hand, elastomers also exhibit a viscoelastic behaviour [2]. At temperatures far above the glass transition temperature, the viscoelastic contribution to the strain energy is small and often negligible, and the stress-strain response of elastomers is well described by hyperelastic models. As the temperature approaches the glass transition region, the viscoelasticity begins to play a greater role. One of the practically important consequences, especially for sealing applications, is stress relaxation (SR). When an elastomer is subjected to a specified constant deformation the stress in the material will decay. For a sealing material, SR results in a decrease of contact pressure potentially leading to reduced sealing capability. SR also correlates well with the compression set in elastomer seals [3].

Stress relaxation is rather extensively studied in industrially important elastomers at temperatures above T_g in connection with their aging and chemical degradation, e.g. in [4-10]. However, there are few studies dedicated to SR at low temperatures, specifically near the glassy region, even though some industrial equipment with elastomer components can be permanently or periodically exposed to such temperatures [11, 12]. Neglecting the effect of SR at these low temperatures may lead to catastrophic consequences [13].

Early attempts to understand and characterize SR at low temperatures were undertaken in the 1940s [14-16]. Some of the most comprehensive investigations of the phenomenon in the glassy and transition regions were made in [17-20] on polyisobutylene and other amorphous polymers. The authors also demonstrated the equivalence of time and temperature effects on the relaxation behaviour of these materials which is now known as the time-temperature superposition (TTS) principle. The superposition in its simplest form is performed by means of horizontal translation of a viscoelastic quantity along the logarithmic time axis (the time scale becomes reduced by a shifting factor a which is a function of temperature). It was later shown that the temperature variation of the horizontal shifting factor is independent of strain [21, 22].

Various aspects of low-temperature SR were subsequently reported in literature [21-32]. Particularly, Bartenev and colleagues [26, 27] assert that elastomers exhibit unique relaxation mechanisms with relatively low activation energy when subjected to low strains in the glass transition region. The relaxation process occurs in elastomers held in the temperature region near T_g and is believed to be caused by breakage of ordered supramolecular micro-domains formed at low temperatures. These domains create apparent cross-links between the polymer chains at low temperatures and, thus, are responsible for the observed increase in the material stiffness [26, 27]. This assertion is in line with the recent work on polymer blends of polybutadiene and styrene butadiene rubber [33] that suggests that rubber-like and glassy-like domains coexist in elastomers exposed to temperatures near the glass transition. The authors [33] concluded that the glassy domains progressively form with cooling in the glass transition region, and, as a result of their formation, the segmental movements of the polymer chains become more and more constrained.

Another important question is whether the strain and the state of strain have any effect on the relaxation function of elastomers at low temperatures. Assuming the total deviatoric stress response of a deformed elastomer consists of the contributions of the long-term hyperelastic stress component $S_{eq}(\lambda)$ and the viscoelastic (time-dependent) stress component $S_{VE}(\lambda, t)$, the time and

strain effects on the stress response are separable if

$$S_{VE}(\lambda, t) = S(\lambda)\psi(t) \quad (0)$$

Where $\psi(t)$ is the relaxation function. The separability of time and strain is typically evident from a parallel nature of relaxation curves taken at various strains. Glucklich and Landel [22] demonstrated in their short-term relaxation experiments in uniaxial and biaxial extension of styrene-butadiene rubber (SBR) at temperatures down to $-45\text{ }^{\circ}\text{C}$ (about $15\text{ }^{\circ}\text{C}$ above the T_g) that the time and strain effects on the material strain energy function are separable. However they predicted that the invariance would not hold at temperatures far below the minimum used in their experiments. The topic of strain invariance of the relaxation behaviour was later investigated by Tada et al [34] who employed 3 modes of deformation and confirmed the separability of time and strain effects using both carbon black filled and unfilled SBR in the rubbery region. It is also worth noting that many studies [22, 32, 34, 35] conclude that the SR behaviour in filled and unfilled elastomers is independent of the state of strain (with an exception of volumetric compression).

The research activities in the aforementioned literature have only concentrated on relatively short-term SR with a major focus on the rubbery region, while the region near T_g is often unexamined. It remains inconclusive whether the strain-time separability holds in elastomers cooled down to their glass transition temperature and below. Hence, the primary objective of this work is to study the finite-strain relaxation behaviour of a model hydrogenated nitrile butadiene rubber (HNBR) compound under ambient and sub-ambient conditions near the T_g . The data at some temperatures below the glass transition were also collected and reported here. However, these results are given less attention because of their limited practical importance. The relaxation properties at elevated temperatures are also of interest, especially for carbon black reinforced elastomers, and therefore high-temperature physical stress relaxation is also covered in this work.

The secondary objective of this work is to elucidate the effect of carbon black on the relaxation dynamics and the relaxation strength of the HNBR. The third objective is to verify that TTS can be applied to form SR master curves and identify viscoelastic material parameters required for modelling in FEA software. The lack of available the physical relaxation data for HNBR was also a motivation for this work, although some short-term compression stress relaxation results for an HNBR compound have recently become available [36].

2. Materials and experimental procedure

2.1 Materials and processing

A typical elastomer formulation widely used in demanding sealing applications is studied. The composition is based on hydrogenated nitrile butadiene rubber with 96 % saturated polybutadiene with 36 % acrylonitrile content and varied carbon black (CB) content of either 0 or 50 phr. The compound formula is detailed in Table 1.

Table 1 Composition of the elastomers used in this work

Component	Content, parts per hundred rubber (phr)
HNBR	100

Antioxidant	3
Stearic acid	0.5
Zinc oxide	5
Magnesium oxide	10
Plasticizer	20
Peroxide	10
N-330 HAF carbon black	0 or 50

These two compounds are further designated as filled and unfilled HNBR for simplicity. The compounds (except the peroxide) were first combined in an internal mixer and then mixed with the peroxide in a two roll mill. Compression moulding and vulcanization in a press at 170 °C for 20 min was then followed. Finally, a post-curing operation at 150 °C for 4 h in an oven was carried out. More information about the processing and the basic material test data is available in a previous publication [37].

As with all polymers, HNBR shows changes in structure and mechanical performance over time in service, depending on factors such as the local chemical environment and temperature, and previous works have described some of these changes [38, 39]. However, all the tests reported in this paper were performed on materials in an unaged state, i.e. soon after manufacture.

The materials have a T_g of about -16 °C as determined by the position their DMTA tan delta peaks [3, 38] measured at 1 Hz frequency or -23 °C as determined from DSC results (the heating rate was 20 °C/min) [37].

2.2 Test methods

A test series was developed to measure stress relaxation behaviour at temperatures from -40 °C up to +110 °C. The relaxation testing was done in compression, while uniaxial tensile testing was employed in order to observe the basic changes in the mechanical behaviour with cooling and define the temperature limits of rubberlike elasticity of the compounds.

2.2.1 Uniaxial tensile test

The stress-strain behaviour in quasi-static uniaxial extension was investigated using a Zwick universal testing machine equipped with a thermal chamber, a contact extensometer and a 1 kN load cell. The specimen geometry was in accordance with ISO 37 type 2. Each specimen was fixed in the machine by mechanical grips and pre-loaded to 0.5 N before stretching. The specimens were exposed to the testing temperature for 30 min prior to the commencing the test. All tensile tests were carried out at a strain rate of 0.025 s⁻¹.

2.2.2 Compression stress relaxation (CSR)

Sub-zero compression stress relaxation (CSR) experiments were carried out on a special test rig illustrated in Figure 1 (hereafter called the "manual method"). The main principle is that a specimen is manually compressed between lubricated steel plates by a screw to a predefined deformation. The applied deformation was controlled by means of the screw rotation. The specimens were maintained at the constant strain and temperature while the force was recorded. Test times were chosen to

observe stress decay preferably until attaining the equilibrium where possible. The times were, thus, between 3 hours and 15 days.

Prior to loading the rigs, the specimens were positioned in a freezing cabinet and kept there at the desired temperature for at least 12 hours. The temperature fluctuations inside the freezing cabinet were ± 0.4 °C; the values reported in the paper are mean values. The experiments at most conditions except for temperatures lower than -20 °C were repeated to ensure reproducibility.

The accuracy of the experimental data obtained by compressing specimens using the "manual method" was checked for a few cases by a more conventional test method using the universal testing machine. The discrepancy between these two set-ups was \leq ca. 3 %. This small discrepancy is believed to be caused by the imperfect control of the loading rate in the "manual method".

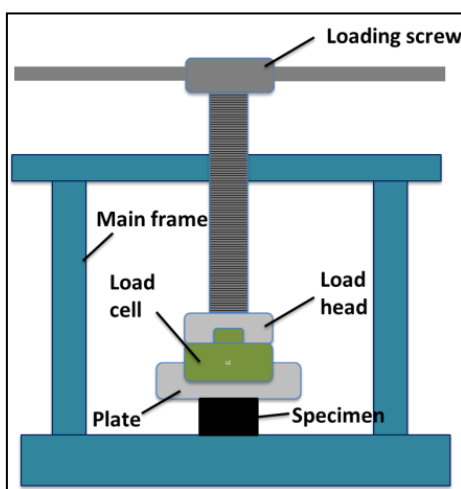


Figure 1 Schematic of the compression rig used in the "manual method".

CSR at temperatures above 0 °C was performed using a Netzsch-Gabo Eplexor 150 DMTA machine with a 1.5 kN load cell and parallel plate specimen holders, operating in compression mode.

The compression specimens had a cylindrical shape with 20 mm nominal diameter and 10 mm height. For measurements below -20 °C, smaller specimens of 10 mm diameter and 6 mm height were used due to the increased level of stiffness of the material and the limited capacity of the force sensors.

The investigated range of nominal compressive strains ϵ was 10-40 % which is relevant for elastomer seals. The loading and subsequent relaxation was performed stepwise with a nominal strain step length of 5 %. The maximum degree of compression at temperatures near and lower than the T_g was, however, reduced to 15-30% due to the high stiffness of the materials in the glassy state. Prior to the relaxation experiments, the specimens were pretreated with 4 full deformation cycles in order to minimise the Mullins effect [40]. Pre-studies (not presented here) showed that the data were inconsistent without this pre-treatment, specifically for the carbon black containing material. The specimens were left unloaded to recover their original shape for at least 48 hours after the pre-treatment and prior to each test.

3. Results and discussion

3.1 The effect of low temperatures

The quasi-static uniaxial tensile test data, illustrated in Figure 2, demonstrate the influence of sub-zero temperatures on the stress-strain behaviour of the HNBR compounds.

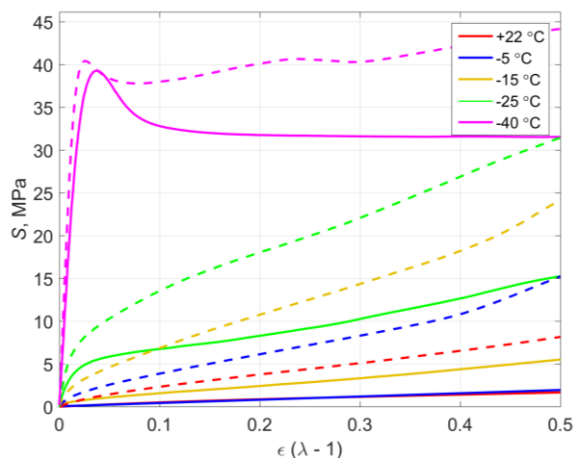


Figure 2 Representative nominal tensile stress-strain curves of the unfilled (solid lines) and filled (dashed lines) HNBR at the indicated temperatures.

Exposure to low temperatures generally leads to an increase of the stiffness of HNBR. The low-temperature effect on the elastic modulus is more pronounced at small strains. The large initial modulus is not sustained during further extension. It gradually declines with strain and takes values that are an order of magnitude lower (which are much closer to the modulus data observed in the rubbery state) than that at the initial loading. The increase of stiffness at small strains in the transition region (ca. -16 to -23 °C) is more pronounced in the filled HNBR, while the small-strain tensile behaviour at -40 °C is rather similar in both elastomers.

The most drastic difference is observed between the curves at and below the T_g , especially at small strains (<0.05). A yielding phenomenon is quite apparent at -40 °C in both compounds while it does not seem to occur at the higher temperatures used in the experiment. This complicated behaviour is alike that observed in other glassy polymers, such as PMMA. Therefore, the SR at temperatures below -25 °C will not be evaluated in detail. The ultimate failure strain was not attained in HNBR stretched to 50% at -40 °C at the strain rate of 0.025 s^{-1} . It is likely that the brittleness limit of HNBR at this strain rate lies at an even lower temperature. The material becomes softer with larger extensions and is capable to deform more due a phenomenon of stress-induced or “forced” elasticity [41] and also likely due to adiabatic heating, see e.g. [33]. Bukhina and Kurlyand [41] discuss in more detail the various factors affecting the loading response of elastomers in the glassy region.

It is interesting to note that the difference between the curves at +22 and -5 °C of the unfilled HNBR is small enough that they almost overlap. This rather small difference in the material tension behaviour can mislead to a conclusion of an insignificant temperature dependency of the material stiffness in this temperature region. This, however, is not the case, and the apparent similarity is a result of 2 competing effects: a change of stiffness due to its explicit temperature relation owing to its entropic origin and the stress relaxation processes occurring simultaneously with the deformation. The relaxing part of stress appears to grow with cooling which will be demonstrated in details

further here, while the temperature effect on the entropic elasticity will be taken into account in section 3.2.

The effect of temperature on the relaxation behaviour of the unfilled HNBR compound is shown in Figure 3.

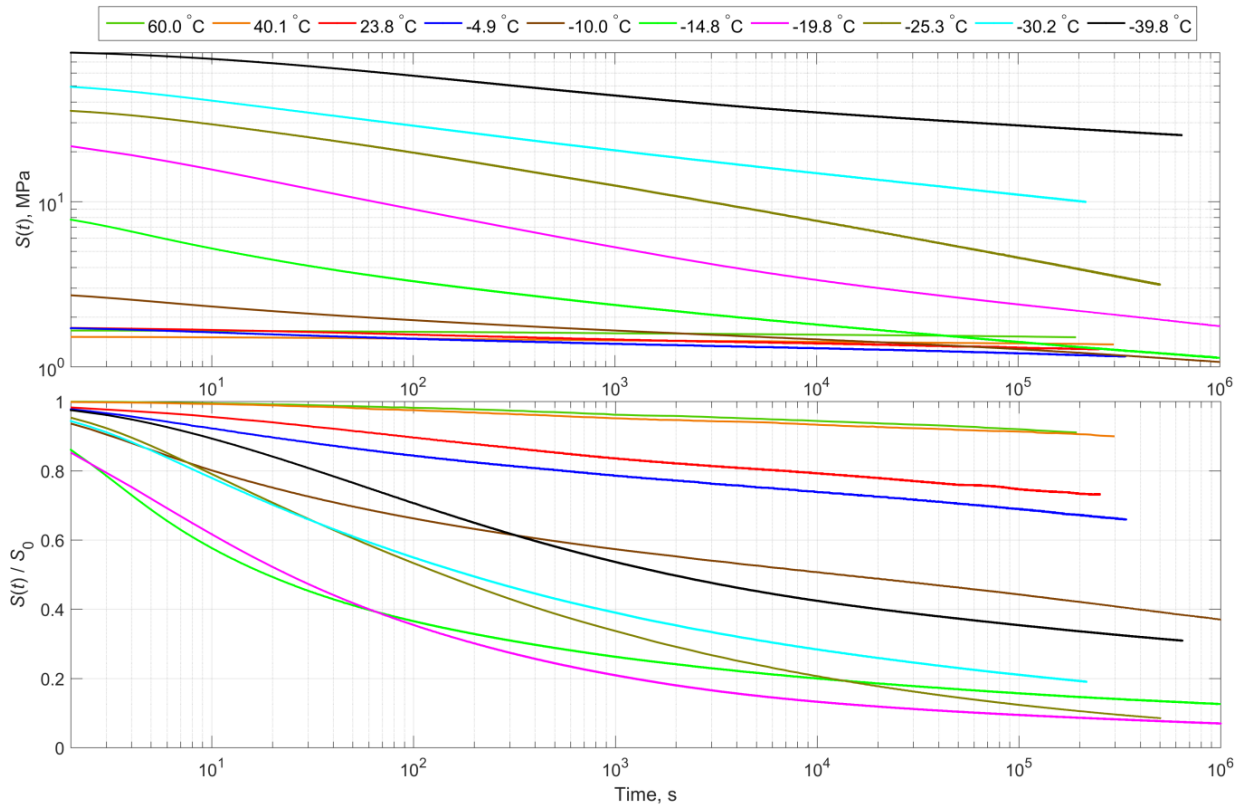


Figure 3 CSR curves of unfilled HNBR at 20 % nominal compression at the indicated temperatures. Top – logarithmic plot of the nominal stress as a function of time; bottom – semi-logarithmic plot of the nominal stress normalized by the maximum (instantaneous) stress value as a function of time.

As expected, the cold environment leads to stiffening of HNBR which is manifested in an increase in the instantaneous compressive stress. This is followed by a rapid drop of the stress. The relaxation curves behave qualitatively in agreement with those reported for polyisobutylene [20]. It is possible to identify 3 characteristic regions: the rubbery, the transition and the glassy region. The rubbery region exhibits the lowest rates of relaxation and the material reaches the equilibrium state much faster than in the other regions. At this temperature polymer molecules are believed to have a greater ability to move, and most relaxation processes occur almost instantaneously with deformation. Hence, the relaxation is not as pronounced as when under sub-ambient conditions.

The time window of the compression experiment becomes comparable with the relaxation times in the HNBR exposed to lower temperatures, which is manifested in the observed increase of the relaxation rates. The transition region is, thus, characterized by the most marked SR with the greatest relaxation rates near T_g (the curves at -14.8 °C, -19.8 °C and -25.3 °C). Despite the sharp stress decay at short times, the cooled elastomer in this region requires much more time to achieve the equilibrium state than at ambient temperature. Nevertheless the stress values at longer times are comparable with those in the rubbery state. Furthermore, the HNBR might even have a lower stress

magnitude at long times (lower long-term stiffness) in the sub-zero conditions than at ambient or elevated temperatures due to the entropic nature of the material.

Although the curves in the glassy region have somewhat lower rates of relaxation, noticeable stress decay is also observed. The SR results at the lowest temperature of about $-40\text{ }^{\circ}\text{C}$ are rather surprising as the material exhibits a reduction of the initial stress by a factor of 2 after 10^3 seconds and by a factor of 3 after 10^6 seconds (ca. 12 days). The result may suggest that the molecular motion in the glassy state is not completely frozen and some rearrangement of the deformed polymer chains still occur in spite of the imposed freezing conditions. This observation cannot be explained by the adiabatic heating during the load ramp phase since the relaxation rate keeps on being rather high over the whole time span of the experiment. A potential explanation can be as the following. The HNBR investigated here is a copolymer of saturated and unsaturated butadiene units with acrylonitrile units with the ratio between butadiene and acrylonitrile (64:36). It seems likely that there must be some butadiene rich regions which may be mobile down to below $-100\text{ }^{\circ}\text{C}$ [33, 42], therefore they can still allow some stress relaxation activity below the apparent T_g of the material. It should be noted that the unloaded specimens fully recovered their original height after their warming up (within the accuracy of a calliper measurement).

The effect of temperatures on the stress relaxation in the carbon black reinforced compound is illustrated in Figure 4. As expected and reported elsewhere [43] carbon black imparts greater long-term stiffness on the elastomer. The impact of low temperatures on the relaxation behaviour is qualitatively similar to the unfilled rubber. The instantaneous stress response of the reinforced HNBR increases with cooling, however the relaxation processes in the reinforced material take much more time. The relaxation rates seen in the transition and glassy regions of the filled HNBR are smaller than those observed in the unfilled compound near T_g . For instance, the average relaxation rate in the unfilled HNBR at $-20\text{ }^{\circ}\text{C}$ is approximately 16 % per decade, whereas it decreases to approximately 12.6 % per decade in the filled HNBR at the same temperature. This is believed to be due to the impeded segmental mobility of the macromolecular chains in the vicinity of the carbon black particles. As a consequence, the filled compound requires much more time to approach the equilibrium state. Nevertheless, the stress decay in the reinforced HNBR is prominent even below the glass transition temperature. The latter, for instance, exhibits a double decrease in the compressive stress approximately after 10^4 seconds of the experiment at $-39.3\text{ }^{\circ}\text{C}$.

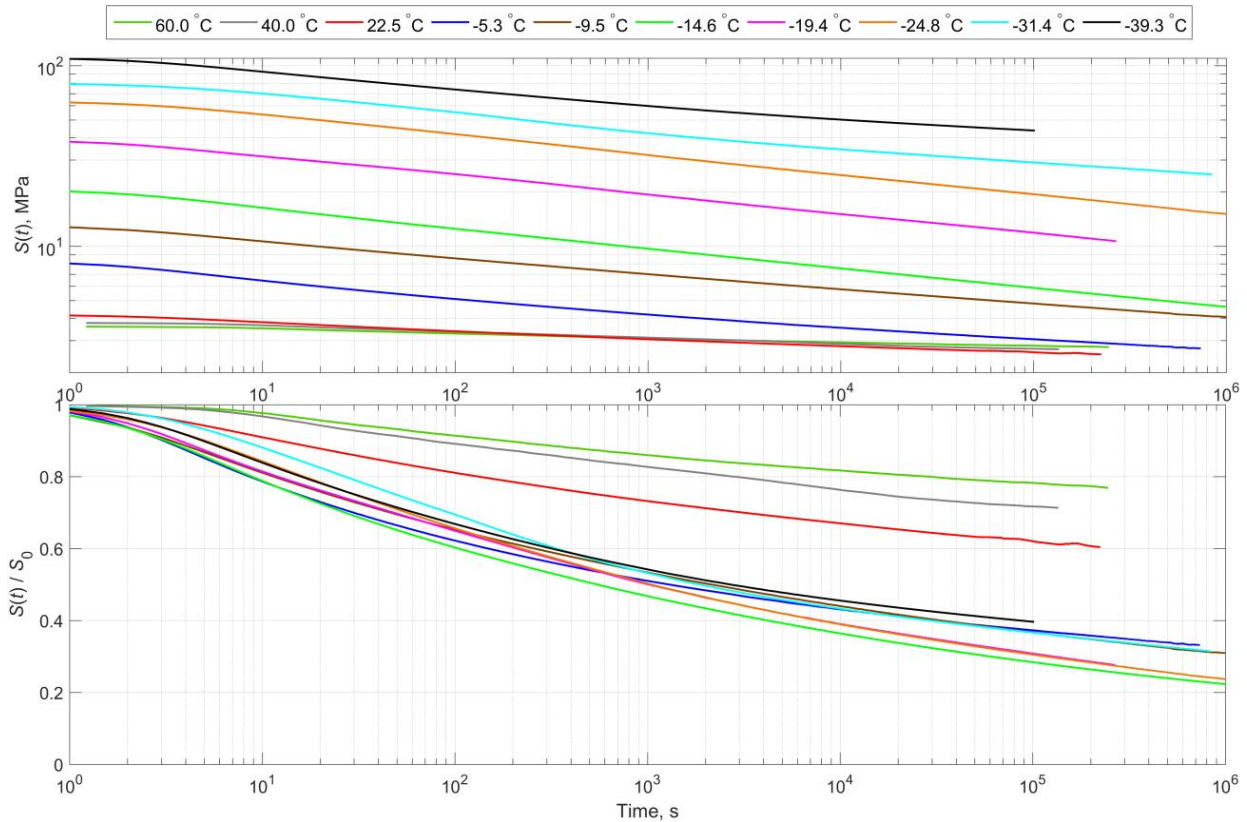


Figure 4. CSR curves of filled HNBR at 20 % nominal compression at the indicated temperatures (the CSR data at -39.3 °C was measured at 15 % compression and scaled to 20%). Top – logarithmic plot of the nominal stress as a function of time; bottom – semi-logarithmic plot of the nominal stress normalized by the maximum (instantaneous) stress value as a function of time.

3.2 The effect of temperature on the strain energy function and long-term stiffness

Before further analysis of the relaxation behaviour of HNBR, the aforementioned temperature dependence of the material stiffness will be addressed. The strain energy function of deformed elastomers is often modelled with viscoelastic (transient) and hyperelastic contributions. The latter, as explained in the introduction, is affected by temperature due to its entropic origin [1]. As such, a temperature raise would result in a proportional increase of the strain energy function and the stiffness of the elastomer. On the other hand, the material stiffness at short and intermediate times increases with cooling as, for example, demonstrated in Figure 3 and Figure 4. Therefore, these competing temperature effects should be clearly distinguished from each other.

Figure 5 a-b) depict the step strain stress relaxation response at various temperatures and Figure 5 c-d) show a surface plot of the normalized strain energy density computed by integrating the isochronal stress-strain data. It is quite evident that the long-term stiffness of the base HNBR is temperature dependent in accordance with the established basics of rubber elasticity. The minimal strain energy density is observed at -10 °C after about 3 hours of stress relaxation. The temperature behaviour of the material at shorter times is more complicated due to a noticeable transient component of stress which increases with further cooling. There exists a local minimum of the short-time strain energy density at about 10 °C, below which it steeply increases owing to a

growing contribution of the relaxing part. Above 10 °C, it becomes steadily larger with temperature.

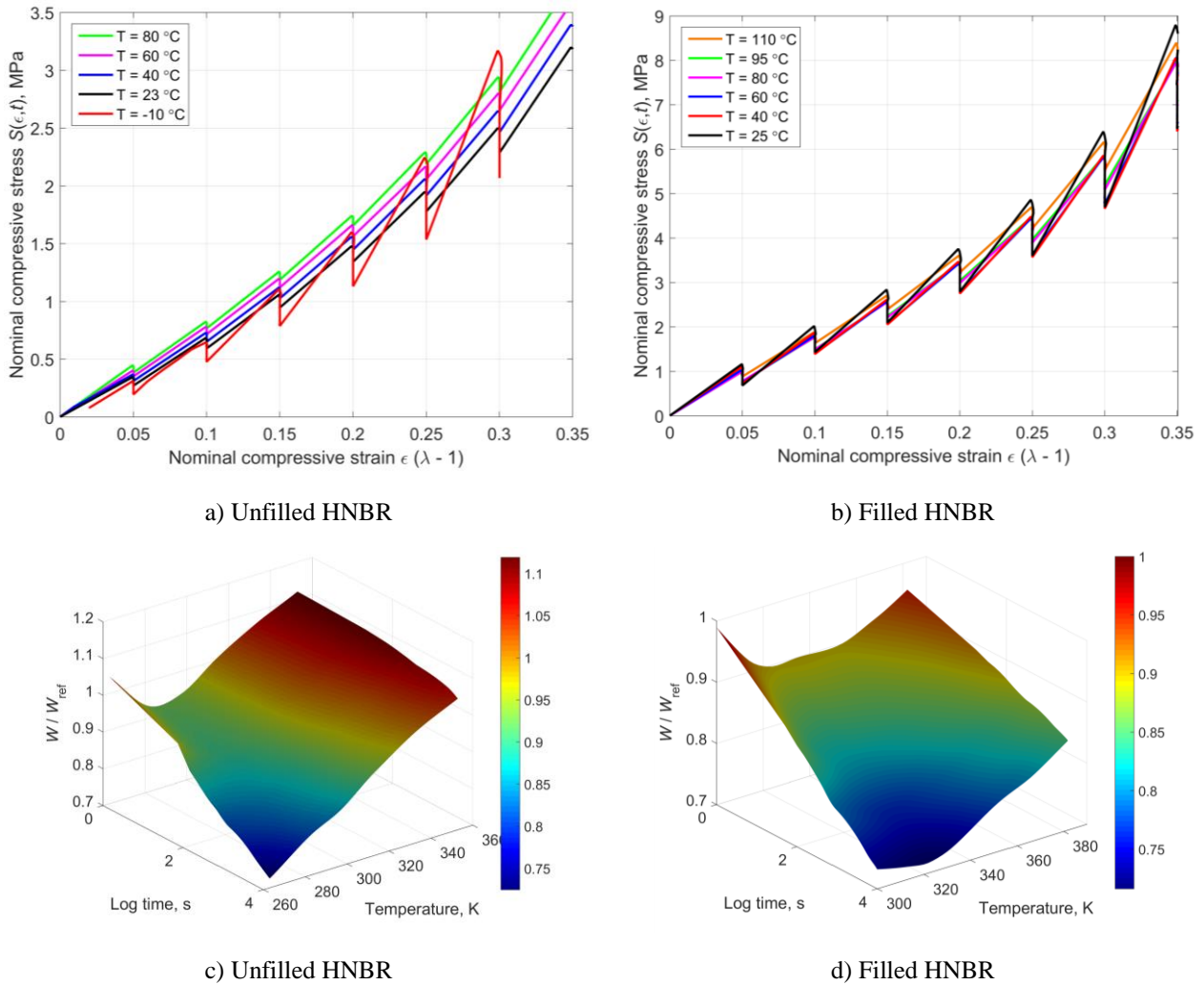


Figure 5 a-b) Effect of temperature on the step strain CSR response (Eplexor data plotted using linear interpolation between points, the strain rate here is approximately 0.005 s^{-1}) and c-d) the time-temperature contour plot of the corresponding strain energy density function for the indicated compounds. The strain energy density data are interpolated by cubic splines and normalized by the values of the instantaneous strain energy density obtained at ambient temperature

The difference between stress-strain curves of the reinforced HNBR at various temperatures is not as clear as in the unfilled rubber. Certainly, the viscous contribution to the instantaneous stress response is much stronger in the filled elastomer than in the unfilled elastomer. The filled elastomer exhibits the highest strain energy density at the ambient temperature in the temperature range depicted in Figure 5. It is believed that this large transient component masks the entropic contribution the material stiffness. The entropic part, on the other hand, is seen to dominate at elevated temperatures and at long times (Figure 6). A local minimum of the strain energy function at short times is also observed in the reinforced HNBR, however it is shifted to about 80°C . Similar temperature relations of the material stress response which had concave-downward shapes with inflection points lying within $70\text{-}120^\circ\text{C}$ were observed in carbon black filled SBR compounds [44].

The inflection point is also evident here at longer times, although it is shifted to lower temperatures (approximately 50°C).

The effect of temperature on the long-term strain energy functions of both compounds is compared in Figure 6.

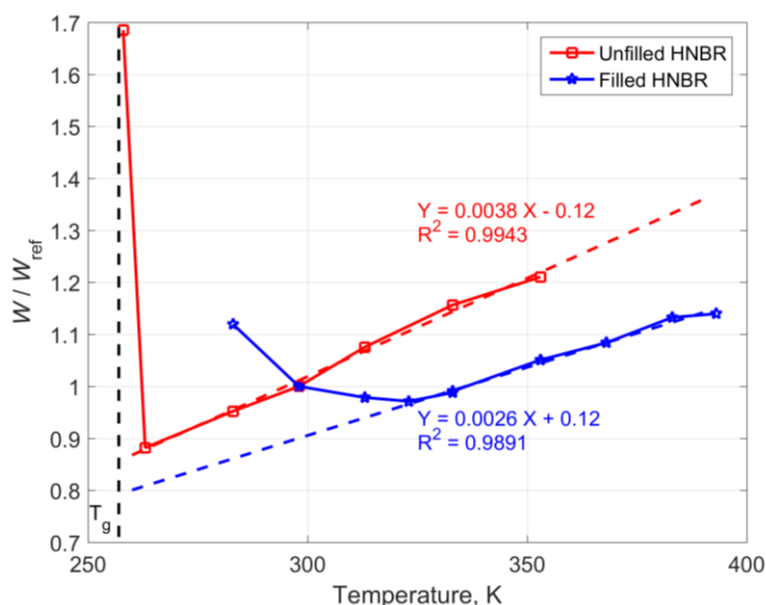


Figure 6 10000-sec isochrones of the normalized strain energy density having the same significance as in Figure 5 plotted as functions of absolute temperature. The data are corrected accounting for the thermal dilatation [37]. The coloured dashed lines represent linear fit in the range of 263-353 K and 333-393K for the unfilled and filled HNBR respectively.

The change from entropic elasticity to the internal energy elasticity at longer times occurs quite abruptly in the unfilled HNBR in the vicinity of T_g , whereas the transition region in the filled compound is more smooth and, as pointed out above, shifted to higher temperatures if compared to the unfilled HNBR. The variation of the material strain energy function with temperature in the entropy-dominated elasticity region is quite well described by a linear relation in both compounds. However, the slope of this relation is higher in the unfilled HNBR than in filled HNBR. The difference can be explained by the presence of carbon black (50 phr which is equivalent to 20.4 vol. %) which has a non-entropic origin and softens with temperature. In addition, the tightly bound regions of HNBR [43] local to the surface of the CB particles might contribute to the difference.

Figure 7 summarises the findings in this section.

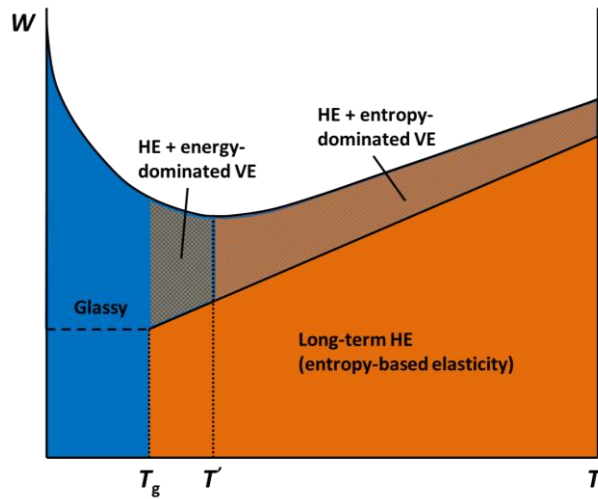


Figure 7 Schematic of the temperature variation of the strain energy function of HNBR which is composed of hyperelastic (HE) and viscoelastic (VE) parts

The strain energy function of HNBR has a complex concave-downward shape when plotted against the temperature. The position of the minimum strain energy on the temperature scale T' is defined by the the experiment relaxation time (or the strain rate), but it cannot be lower than the T_g . Below this point the temperature-dependent stress response of HNBR is presumed to be governed by the internal energy based mechanisms, while the long-term response might still be hyperelastic and follow the entropic temperature relation if temperatures above T_g are considered. It is likely that the volume fraction of glassy-like domains becomes high enough to make the internal energy contribution stronger here. The entropy elasticity, on the other hand, begins to dominate at temperatures above the inflection point T' . The position of T' can also be shifted to higher temperatures by addition of filler as observed in the carbon black reinforced HNBR. Therefore, the temperature effect on the instantaneous response of filled rubber might be masked by a considerable transient stress component at shorter times, since this has a tendency to increase with cooling.

3.3 Time-temperature superposition

The obtained CSR data and shape of the overlapping parts of the segments at and above T_g suggests that a master curve of $S(t)$ or $E(t)$ can be constructed using the TTS principle and assuming that the materials are thermo-rheologically simple, i.e. their viscoelastic response can be translated along the log time scale with temperature. In addition, it is assumed that the relaxation at moderate temperatures is governed only by the physical mechanisms, but not by any chemical changes. The results collected at temperatures below $-25\text{ }^\circ\text{C}$ were not used in TTS.

An approach allowing for unrestricted horizontal and vertical shifting of the time segments [45] was utilized and implemented in MATLAB as a minimization problem. The following function was minimized with respect to the horizontal and vertical shifting parameters $a(T)$ and $b_{\text{num}}(T)$ for each isothermal time segment being shifted:

$$err = \frac{1}{n} \sum_{i=1}^n \frac{(y_i(t_i) - y_i(a(T), b_{num}(T), t_i))^2}{(y_i(t_i))^2}$$

Here y_i are the experimental values of stress S at times t_i , y_i are the values of the stress relaxation function interpolated by a polynomial and n is the number measurement points in each segment. The effects of entropy-elasticity as well as the density change associated with cooling or heating are taken into account using values of the vertical shifting factor $b(T)$ obtained from the slopes of the relationships in Figure 6, i.e. 0.0038 and 0.0026 per degree Kelvin for unfilled and filled compounds respectively. The numerical vertical shifting factor $b_{num}(T)$ bears no physical significance and is used in the optimisation routine merely to obtain smoother master curves. Therefore, the values of $b_{num}(T)$ which were between 0.98 to 1.02 are not reported here. Short-time CSR data corresponding to 15x the loading ramp time in each segment were ignored in order to minimise the errors associated with the ramp effect [46]. In spite of the simplifications mentioned, this approach, as demonstrated in Figure 8 and Figure 9, yields a decent representation of the relaxation functions of the filled and unfilled elastomers over a large time span.

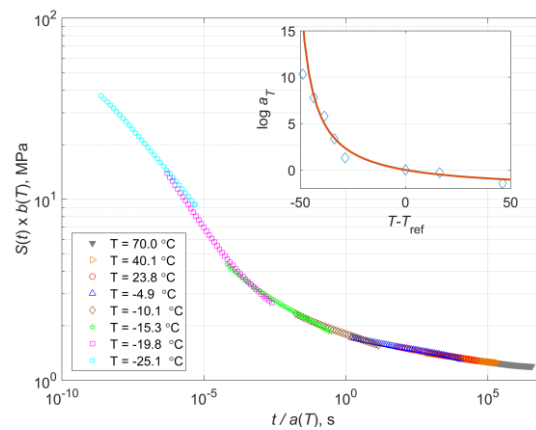


Figure 8 Representative CSR master curve for the unfilled HNBR. 20 % nominal compression and $T_{ref} = 23.8$ °C. The inset depicts the variation of the horizontal shifting factor with temperature and its fitting by the WLF equation (solid line).

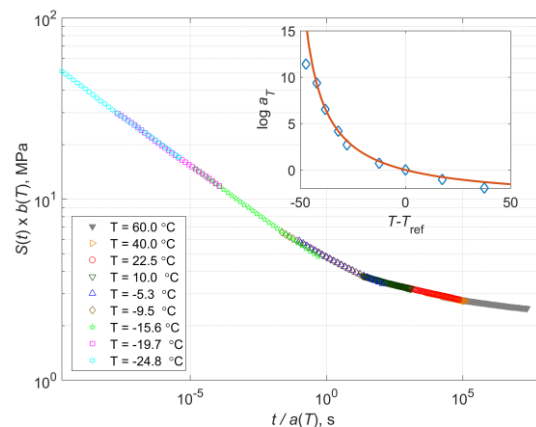


Figure 9 Representative CSR master curve for the carbon black filled HNBR. 20 % nominal compression and $T_{ref} = 22.5$ °C. The inset depicts the variation of the horizontal shifting factor with temperature and its fitting by the WLF equation (solid line).

3.4 The effect of strain

The master curves are further used to evaluate the effects of strain and filler on the relaxation behaviour of HNBR. The effect of strain is analysed here while the effect of the filler is considered in the next section.

Tada et al [34] suggest that the relaxation functions of rubber compounds should be analysed and compared after subtracting the equilibrium stress values. Taking this into consideration, a relaxation function $\psi(t)$ is introduced and computed as follows:

$$\psi(t) = \frac{S(t) - S_{eq}}{S(t_1 = t_{min}) - S_{eq}} \quad (0)$$

where S_{eq} is the equilibrium (long-term) stress, $S(t)$ is the stress at time t .

The effect of strain on the relaxation function of HNBR is illustrated in Figure 10. It is evident that at times $\geq 10^{-3}$ s the relaxation dynamics of HNBR are not influenced by the compressive strain imposed in the experiment. This time threshold corresponds to approximately between T_g+1 and T_g+8 °C depending on method used to define the T_g [37, 38]. Hence, it is fair to state the relaxation behaviour of HNBR held at above the glass transition temperature is to a good approximation independent of strain in the range of deformations experienced in sealing applications. That results in an important conclusion that the strain and time effects can be separated if the elastomer is maintained at temperatures above T_g . This, in turn, entails a simpler analysis and model implementation into FEA software.

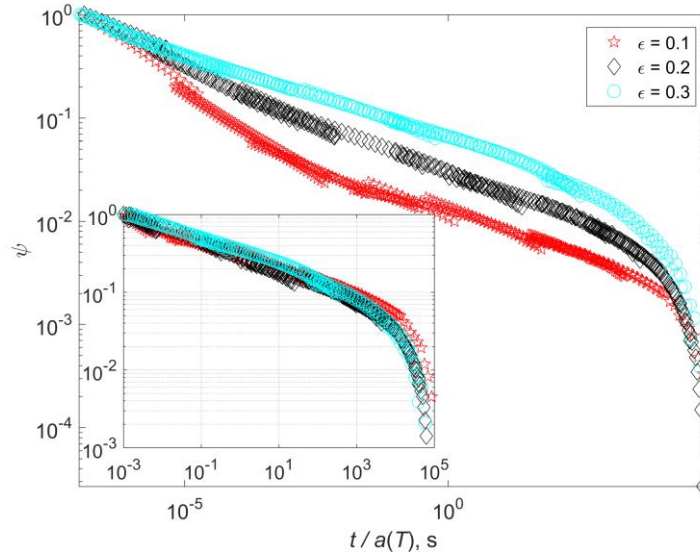


Figure 10 The relaxation functions of the unfilled HNBR at the indicated nominal compressive strains (short-time cut-off at 10^{-7} s). The inset shows the same at times $\geq 10^{-3}$ s.

However, the separability of time and strain does not hold when the material is cooled down to or below the glass transition temperature. Indeed, the relaxation functions at shorter ($< 10^{-3}$ s) experimental times exhibit different shapes, as shown in Figure 10. The deviation between the relaxation curves progressively grows with reduction of the time scale of the experiment. This mismatch between the curves is not surprising taking into account that the mechanical behaviour of

elastomers in the glassy and near-glassy state becomes much more complex and includes yielding phenomena, as mentioned before or studied in more detail elsewhere [33]. Furthermore, it seems from the shape evolution of the relaxation curves that each strain step incurs a shift from the glassy (or the transition) to rubbery region. This might indicate that strain can probably be utilized as a reduced variable for the glassy and transition regions of rubber, however a larger data set would be required to confirm this.

3.5 The effect of carbon black

The effect of carbon black on the relaxation behaviour of the HNBR is illustrated in Figure 11.

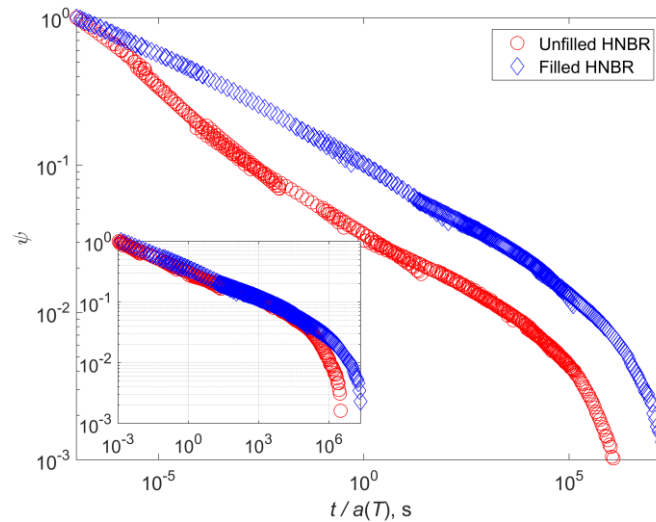


Figure 11 The relaxation functions $\psi(t)$ of filled and unfilled HNBR at 20 % nominal compression (short-time cut-off at 10^{-7} s). The inset shows the same at times $\geq 10^{-3}$ s.

Carbon black imparts higher stiffness to the HNBR, but it is seen that it does not yield much impact on the relaxation behaviour of the polymer in its rubbery region. The relaxation functions for the reinforced and non-reinforced compounds are in very good agreement with each other in a time interval from 10^{-3} to about 10^4 s which supports the results presented elsewhere for SBR [34]. Therefore, it can be concluded that the carbon black does not affect the relaxation dynamics of the studied HNBR in the mentioned time span or at temperatures above the T_g .

The relaxation functions at short ($< 10^{-3}$ s) and long ($> 10^4$ s) times, on the contrary, deviate substantially. At long times (or at high temperatures) the unfilled HNBR attains the equilibrium state faster than the carbon black reinforced counterpart, which results in lower rates of the stress decay until they diminish to nearly zero. At short times (or as mentioned before at low temperatures in the vicinity of T_g) carbon black seems to hinder the relaxation processes in the polymer, and they occur at a lower rate in the unfilled HNBR.

Finally, the relaxation spectra of the materials are compared. The relaxation spectrum is a very useful characteristic of an elastomer that enables the prediction of other viscoelastic characteristics, e.g. the compression set [3]. The generalized Maxwell model is deployed to fit the CSR master curves using the sign control method (SCM) [47] and obtain the viscoelastic parameters for both compounds. The model used has the following discrete form:

$$S = \varepsilon \left(E_{eq} + \sum_{i=1}^n E_i e^{-t/\tau_i} \right)$$

where τ_i are the relaxation times, E_i are the spectral strengths, E_{eq} is the equilibrium modulus. The relaxation spectra are depicted in Figure 12.

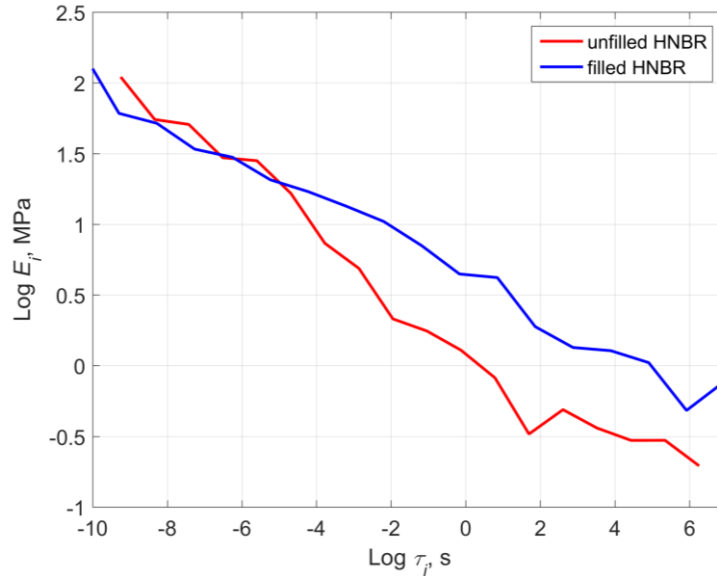


Figure 12 The effect of carbon black on the relaxation spectrum of HNBR at 20 % nominal compression.

It is apparent that the carbon black filled HNBR exhibits higher relaxation strengths in its relaxation spectrum at intermediate and long times (approximately higher than 10^{-4} s) if compared to the relaxation spectrum of the unfilled rubber at the same temperature. At the glass transition and below it, the effect of carbon black on the relaxation strength of HNBR becomes negligible.

4. Conclusions

The experimental measurements successfully showed changes of the stiffness of carbon black filled (50 phr) and unfilled hydrogenated nitrile butadiene rubber (HNBR) due to stress relaxation at temperatures below and above the T_g . It is experimentally demonstrated that the elastomers can attain the equilibrium state even near the glass transition temperature provided there is enough time for the relaxation to take place.

The stress relaxation significantly affects the mechanical behaviour of HNBR at low temperatures. It is demonstrated that the stiffness of the material at temperatures above the glass transition and at moderate strains is determined by two phenomena which have opposing impacts on it. The first effect is related to the entropic nature of rubber elasticity, and, thus, manifested in a decrease of the modulus with temperature reduction down to the T_g . The second effect consists of a steady increase of the transient component of stress (or the time-dependent part of the modulus) with cooling. As a result of these two competing processes, the temperature variation of the strain energy function of the HNBR has a complex concave-downward shape with an inflection point above the T_g . Generally, HNBR exhibits relaxation-dominated stiffness below the inflection point of the strain energy curve and the entropy-dominated stiffness above. The inflection point is shifted to higher temperatures in

the carbon black reinforced HNBR.

The stiffness changes with time and temperature cannot be fully predicted by simple time temperature superposition. Due to the entropic elasticity effect, a temperature correction factor (vertical shifting) needs to be introduced for a more accurate application of the time-temperature superposition principle. These vertical correction factors are found to relate with temperature as 0.0038 and 0.0026 per degree Kelvin for the unfilled and carbon black filled HNBR compounds respectively when the reference temperature is taken as 298 K (+25 °C).

Carbon black is shown to impart greater long-term stiffness and also larger relaxation strength to the HNBR at times longer than 10^{-4} s. On the other hand, the relaxation dynamics of HNBR at times from 10^{-3} to 10^4 s are found to be unaffected by the addition of carbon black. At the T_g or deeper into the glassy region, the relaxation rates are found to be lower in the carbon black filled HNBR than in the unfilled HNBR. On the contrary, the relaxation rates in the filled HNBR appeared greater at elevated temperatures (or at times $> 10^4$ s).

From the analysis of the normalized relaxation functions of HNBR at different compression ratios, it is evident that the strain and time effects in HNBR are uncoupled at times longer than 10^{-3} s (which corresponds to a temperature of $T_g + 1\div 8$ °C in the relaxation experiment). The results, thus, confirm that the time-strain separability in elastomer mechanical behaviour might extend to down to T_g which was not apparent from the earlier publications on the subject [22, 34]. This can greatly simplify the analysis of the elastomers and has a large impact on the modelling of elastomer articles (e.g. seals) in practice. Generally, the obtained results can help designers and material engineers to implement temperature-dependent material models in their analysis problems and build better rubberlike material constitutive relationships which include temperature and time as variables.

6. Declaration of interest

The authors declare that they have no conflict of interest.

7. Acknowledgments

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References

- [1] L.R.G. Treloar, The physics of rubber elasticity 3rd ed., Oxford University Press, Oxford, New York, 2005.
- [2] C.M. Roland, Viscoelastic behavior of rubbery materials, Oxford University Press, Oxford ; New York, 2011.
- [3] A.G. Akulichev, B. Alcock, A.T. Echtermeyer, Elastic recovery after compression in HNBR at low and

- moderate temperatures: Experiment and modelling, *Polymer Testing* 61 (2017) 46-56.
- [4] F. Bjork, O. Dickman, B. Stenberg, Long-Term Studies of Rubber Materials by Dynamic Mechanical-Stress Relaxation, *Rubber Chem Technol* 62(3) (1989) 387-425.
- [5] F. Björk, B. Stenberg, Stress relaxation of a nitrile rubber surrounded by an oil that increases the network density, *Polymer* 31(9) (1990) 1649-1657.
- [6] S. Ronan, T. Alshuth, S. Jerrams, N. Murphy, Long-term stress relaxation prediction for elastomers using the time-temperature superposition method, *Mater Design* 28(5) (2007) 1513-1523.
- [7] B. Slay, W. Webber, Stress relaxation of elastomer compounds, *Sealing Technology* 2011(2) (2011) 9-12.
- [8] J.H. Zhao, R. Yang, R. Iervolino, B. van der Vorst, S. Barbera, The effect of thermo-oxidation on the continuous stress relaxation behavior of nitrile rubber, *Polymer Degradation and Stability* 115 (2015) 32-37.
- [9] W. Zheng, X.Y. Zhao, Q.G. Li, T.W. Chan, L.Q. Zhang, S.Z. Wu, Compressive stress relaxation modeling of butadiene rubber under thermo-oxidative aging, *Journal of Applied Polymer Science* 134(12) (2017).
- [10] A. Kommling, M. Jaunich, D. Wolff, Revealing effects of chain scission during ageing of EPDM rubber using relaxation and recovery experiment, *Polymer Testing* 56 (2016) 261-268.
- [11] K.W. Taylor, Performance Characteristics of Oilfield Proven Elastomers in Low-Temperature Seal Applications, 23rd Annual Offshore Technology Conference, Offshore Technology Conference, Houston, Texas, 1991, pp. 193-206.
- [12] J. Goodson, T. Tilton, Effects of low temperatures on elastomeric sealing elements in downhole completion tools, Proceedings of the International Offshore Mechanics and Arctic Engineering Symposium, 1992, pp. 231-240.
- [13] D. Baker, Why Challenger failed, *New Sci.* 1525(Sep. 11) (1986) 52, 54-56.
- [14] J.R. Beatty, J.M. Davies, Time and Stress Effects in the Behavior of Rubber at Low Temperature, *Rubber Chem Technol* 23(1) (1950) 54-66.
- [15] J.R. Beatty, A.E. Juve, Stress Relaxation of Some Rubber and Synthetic Rubber Vulcanizates in Compression, *Rubber Chem Technol* 23(4) (1950) 786-802.
- [16] G. Allen, G. Gee, B.E. Read, Stress Relaxation in Elastomers by Visco-Elastic Mechanisms .1. Natural Rubber at High Rates of Strain and Low Temperatures, *Transactions of the Faraday Society* 55(9) (1959) 1651-1659.
- [17] G.M. Brown, A.V. Tobolsky, Elastoviscous properties of polyisobutylene. II. Relaxation of stress in whole polymers of different molecular weights at low temperatures, *J Polym Sci* 6(2) (1951) 165-176.
- [18] A.V. Tobolsky, J.R. McLoughlin, Elastoviscous properties of polyisobutylene. V. The transition region, *J Polym Sci* 8(5) (1952) 543-553.
- [19] E. Catsiff, A.V. Tobolsky, Stress-relaxation of polyisobutylene in the transition region (1, 2), *Journal of Colloid Science* 10(4) (1955) 375-392.
- [20] A.V. Tobolsky, E. Catsiff, Elastoviscous properties of polyisobutylene (and other amorphous polymers) from stress-relaxation studies. IX. A summary of results, *J Polym Sci* 19(91) (1956) 111-121.
- [21] T.L. Smith, R.A. Dickie, Effect of finite extensibility on the viscoelastic properties of a styrene-

butadiene rubber vulcanizate in simple tensile deformations up to rupture, *Journal of Polymer Science Part A-2: Polymer Physics* 7(4) (1969) 635-658.

[22] J. Glücklich, R.F. Landel, Strain energy function of styrene butadiene rubber and the effect of temperature, *Journal of Polymer Science: Polymer Physics Edition* 15(12) (1977) 2185-2199.

[23] Y. Takano, Y. Suzuki, T. Kurihara, The stress relaxation of some rubber vulcanizates at low temperatures (in Japanese), *NIPPON GOMU KYOKAISHI* 39(9) (1966) 674-682.

[24] R.A. Dickie, T.L. Smith, Viscoelastic Properties of a Rubber Vulcanizate Under Large Deformations in Equal Biaxial Tension, Pure Shear, and Simple Tension, *T Soc Rheol* 15(1) (1971) 91-110.

[25] G.M. Bartenev, Y.V. Zelenev, Low-Temperature Relaxation Processes in Rubberlike Polymers, *Dokl Akad Nauk Sssr* 154(3) (1964) 661-664.

[26] G.M. Bartenev, A.M. Kucherskii, Low Temperature Relaxation Phenomena in Rubber-Like Polymers at Low Deformations, *Vysokomol Soedin A* 12(4) (1970) 794-801.

[27] G.M. Bartenev, A.M. Kucherskii, G.I. Radaeva, Influence of Deformation Rate on Low-Temperature Relaxation Processes in Elastomers, *Vysokomol Soedin B* 19(8) (1977) 564-567.

[28] L.A. Akopyan, G.M. Bartenev, M.V. Zobina, B.K. Avrushchenko, Temperature-Dependence of Contributions of Discrete Relaxational Processes in Elastomers, *Vysokomol Soedin B* 28(4) (1986) 301-303.

[29] G.M. Bartenev, A.M. Kucherskii, G.I. Radayeva, Relaxational processes in elastomers at small strains according to data of relaxational spectrometry, stress-strain and thermomechanical curves, *Vysokomol Soedin a* 23(2) (1981) 283-290.

[30] M.V. Karasev, G.M. Bartenev, Relaxation Transitions in Linear and Cross-Linked Cis-Polyisoprene above the Glass-Transition Temperature, *Plaste Kautsch* 33(2) (1986) 55-57.

[31] G.M. Bartenev, S.V. Baglyuk, V.V. Tulinova, Relaxational Transitions in Poly(Butadiene-Acrylonitriles) above Glass-Transition Temperature, *Vysokomol Soedin a* 30(4) (1988) 821-828.

[32] G.M. Bartenev, A.G. Barteneva, Relaxation properties of polymers, "Khimiya" Publishers, Moscow, 1992.

[33] P. Shi, H. Montes, F. Lequeux, R. Schach, E. Munch, Linear and non linear mechanical properties of miscible polymer blends near glass transition, *Université Pierre et Marie Curie - Paris VI*, 2013.

[34] T. Tada, K. Urayama, T. Mabuchi, K. Muraoka, T. Takigawa, Nonlinear stress relaxation of carbon black-filled rubber vulcanizates under various types of deformation, *Journal of Polymer Science Part B: Polymer Physics* 48(12) (2010) 1380-1387.

[35] L.A. Akopyan, G.M. Bartenev, M.V. Zobina, Relaxation Processes at Various Types of the Stressed State, *Vysokomol Soedin B* 26(9) (1984) 694-697.

[36] F. Rouillard, P. Heuillet, B. Omnes, Viscoelastic characterization at low temperature on an HNBR compound for sealing applications, *Constitutive Models for Rubber VIII*, CRC Press 2013, pp. 591-594.

[37] A.G. Akulichev, B. Alcock, A. Tiwari, A.T. Echtermeyer, Thermomechanical properties of zirconium tungstate/hydrogenated nitrile butadiene rubber (HNBR) composites for low-temperature applications, *J Mater Sci* 51(24) (2016) 10714-10726.

[38] B. Alcock, J.K. Jørgensen, The mechanical properties of a model hydrogenated nitrile butadiene

rubber (HNBR) following simulated sweet oil exposure at elevated temperature and pressure, *Polymer Testing* 46(0) (2015) 50-58.

[39] B. Alcock, T.A. Peters, R.H. Gaarder, J.K. Jørgensen, The effect of hydrocarbon ageing on the mechanical properties, apparent crosslink density and CO₂ diffusion of a hydrogenated nitrile butadiene rubber (HNBR), *Polymer Testing* 47 (2015) 22-29.

[40] L. Mullins, Effect of Stretching on the Properties of Rubber, *Rubber Chem Technol* 21(2) (1948) 281-300.

[41] M.F. Bukhina, S.K. Kurlyand, Low-temperature behaviour of elastomers, VSP, Leiden ; Boston, 2007.

[42] C.M. Roland, K.L. Ngai, Segmental Relaxation and Molecular-Structure in Polybutadienes and Polyisoprene, *Macromolecules* 24(19) (1991) 5315-5319.

[43] J.L. Leblanc, Filled polymers : science and industrial applications, CRC Press, Boca Raton, 2010.

[44] X. Li, Y. Dong, Z.R. Li, Y.M. Xia, Experimental Study on the Temperature Dependence of Hyperelastic Behavior of Tire Rubbers under Moderate Finite Deformation, *Rubber Chem Technol* 84(2) (2011) 215-228.

[45] J. Honerkamp, J. Weese, A note on estimating mastercurves, *Rheol Acta* 32(1) (1993) 57-64.

[46] A. Flory, G.B. McKenna, Finite Step Rate Corrections in Stress Relaxation Experiments: A Comparison of Two Methods, *Mech Time-Depend Mat* 8(1) (2004) 17-37.

[47] R.D. Bradshaw, L.C. Brinson, A Sign Control Method for Fitting and Interconverting Material Functions for Linearly Viscoelastic Solids, *Mech Time-Depend Mat* 1(1) (1997) 85-108.