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ARTIFICIAL AGEING OF DOUBLE BASE ROCKET PROPELLANT
Effect on dynamic mechanical properties

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The ageing of double base rocket propellants (DB rocket propellants), which is a consequence of chemical reactions and physical processes that take place over time, has significant effect on their relevant properties (e.g. chemical composition, mechanical properties, ballistic properties, etc.). The changes of relevant properties limit the safe and reliable service life of DB rocket propellants. This is the reason why numerous research efforts are devoted to finding out reliable methods to measure the changes caused by ageing, to assess the quality at a given moment of time, and to predict remaining life-time of DB rocket propellants.

In this work we studied dynamic mechanical properties of DB rocket propellant artificially aged at elevated temperatures, in order to detect and quantify changes in dynamic mechanical properties caused by the ageing. Dynamic mechanical properties were studied using dynamic mechanical analyser (DMA).

The results obtained have shown that the ageing causes significant changes of DMA curve's shape and positions. These changes are quantified by following some characteristic points on DMA curves (e.g. glass transition temperatures; storage modulus, loss modulus and tanδ at characteristic temperatures, etc.). It has been found out that the most sensitive parameters to the ageing process are: storage modulus at viscoelastic and softening region, peak width and height on loss modulus curve, glass transition and softening temperature, and tanδ at viscoelastic region.

Keywords: *ageing, double base rocket propellants, dynamic mechanical analysis, glass transition temperature, loss modulus, softening temperature, storage modulus, tanδ*

Introduction

Ageing processes are associated with many fields of our lives; e.g. with living organisms, pharmaceutical and food products, construction materials, etc. For the safety reasons, the research and understanding of ageing processes is particularly important in the field of energetic materials, such as DB rocket propellants.

It is well known that nitrocellulose (NC), which is the main ingredient of DB rocket propellants, because of relatively low activation energy (120–190 kJ mol^{-1}) is subject to a slow chemical decomposition even at the room temperatures [1–5]. The thermal decomposition of nitrocellulose (NC) and nitroglycerine (NG) starts with the homolytic breakdown of the O–NO_2 bond of the aliphatic nitrate esters, thus forming nitrogen dioxide and corresponding alkoxyl radical [1, 2, 6–8]. The released NO_2 radical immediately undergoes consecutive reactions with other decomposition products, or with other propellant ingredients. During this process NO_2 is reduced to NO, N_2O, N and HNO_2 [1, 2, 6, 7].

Another main decomposition pathway is the neutral to acid hydrolysis of the nitrate esters. The reaction is catalysed by moisture and residual acids, or by water and acids formed during the decomposition process [8]. The summary reaction of the thermal decomposition is autocatalytic, and accompanied by heat generation [6]. Due to low heat conductivity of propellants, the heat released can accumulate in the propellant grain, and under certain conditions, such as height storage temperature, large diameter of propellant grain, etc., can lead to the propellant thermal explosion [6, 9].

Apart from ageing due to chemical reactions, DB rocket propellants are subjected to ageing due to physical processes such as diffusion and migration of low molecular constituents (e.g. nitroglycerine, phlegmatisers, plasticizers), crack formation and propagation that can be initiated by residual stress at rocket grain, etc. [10, 11].

The overall ageing of DB rocket propellants affects their mechanical and viscoelastic properties, such as tensile strength, modulus of elasticity, morphology, temperature of glass transition, etc. These changes can result in dangerous failures, e.g. explosion of rocket motor during the launching process. Therefore, the knowledge of viscoelastic and mechanical properties at a given moment of time, as well as prediction of behaviour of DB rocket propellants during the remaining time of storage under certain storage conditions is of great importance.

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Many researchers have studied the ageing of propellants caused by chemical reactions [1–3, 5–8, 12–15], but there is not so much information in opened literature on ageing due to physical processes [16–18]. It is obvious that chemical, physical, mechanical and structural stabilities are connected. For example, plasticiser migration and evaporation, splitting of nitrocellulose macromolecule will cause decrease of propellant structural integrity, and propellant mechanical stability [9, 16–18]. Unfortunately, there is no simple correlation between different kinds of stabilities: e.g., a propellant can be perfectly stable physically but unstable chemically, and vice versa [19].

A large number of tests have been used to assess relative propellant stability by comparing some relevant properties of a studied propellant to those of a reference (stable) propellant. However, to predict propellant stability during some period of time (i.e. its life-time), it is necessary to find out the processes which have the greatest influence on ageing, to determine rates of these processes and to quantify them as accurately as possible. Some of such quantitative methods are based on determination of stabiliser content, decrease of mean molar mass of NC, specimen mass loss, heat generation, mechanical properties, etc. [1, 7, 8, 20].

In this work we studied changes of dynamic mechanical properties of artificially aged DB rocket propellant in order to test the applicability of dynamic mechanical analysis (DMA) in rocket propellants stability studies. Some of the results obtained during our previous investigations of this topic are reported in papers [21–25].

Experimental

Material

The study was performed on the DB rocket propellant of the following chemical composition: ~54% of NC, ~35.0% of NG, ~3.0% of diethyl phthalate, and ~8% of other additives. The testing samples for dynamic mechanical measurements (DMA) were cut up from propellant grain into rectangular bare shape of the following dimensions: 50×10×2.5 mm.

Each of the constituents of the DB propellants has different thermal behaviour, and consequently different influence on an overall propellants' thermal ageing. For example, diethyl phthalate acts as a stabiliser – it catches the free radicals formed during decomposition of NC and NG. In the reaction between the stabiliser and free radicals, nitro-derivates of the stabiliser are formed. As the decomposition reactions are going on, the quantity of original stabiliser decreases, and finally drop to the zero. After that point, the rate of autocatalytic decomposition reactions drastically increases [6].

Nitroglycerine, as an energetic plasticiser, undergoes migration from propellant grain to surface, evaporation and decomposition. The consequence is decrease of elastic properties of the propellant grain.

Nitrocellulose, the main component of the DB rocket propellant, undergoes thermal decomposition reactions. Under rigorous conditions (higher ageing temperature, very long ageing time, etc.) these reactions can lead to scission of NC chain, which will effect mechanical properties of DB rocket propellant [6, 22].

Methods

Accelerated-ageing experiments

Prepared samples, having 50×10×2.5 mm size, were artificially aged in closed glass tubes at 90, 95 and 100°C temperatures. The volume of a glass tube was 100 cm^3, while the mass of the sample in the tubes was approximately 10 g. The aged propellant samples were periodically taken and their viscoelastic properties were tested using dynamic mechanical analyser.

Dynamic mechanical measurements

Dynamic mechanical measurements were carried out using TA Instruments, DMA 983 analyser. A liquid nitrogen cooling accessory was used for sub-ambient operations. The experiments were done under the following experimental conditions: temperature range from –120 to 100°C; heating rate 2°C min^{-1}; fix frequency of 1 Hz, and amplitude of deformation ±0.2 mm.

Such slow heating rate was chosen in order to reduce thermal lag between the heater and the sample, as well as to reduce thermal gradient within sample, while other parameters are chosen following the general guidelines for DMA measurements, as well as our own experience [21–23, 26].

Isothermal thermogravimetry measurements

Isothermal thermogravimetry (TG) measurements were carried out using TA Instruments SDT, Model 2960. TG measurements were carried out using samples weighing 1.0±0.2 mg. The samples were tested in open aluminium sample pans at 100°C, and under nitrogen atmosphere with a flow rate of 50 mL min^{-1}.

Results and discussion

DMA parameters of a material (storage modulus, loss modulus and tanδ) give us information about its mechanical and viscoelastic properties. On the other hand, they are very sensitive to molecular motion, transitions, relaxation phenomena, structural hetero-

geneity and morphology [10, 11]. Thus, the changes of DMA properties of the studied DB rocket propellant will give us information about structural changes that occurs during the propellant ageing [11].

DMA curve of non-aged (virgin) tested DB rocket propellant is shown in Fig. 1.

The storage modulus (E') of the tested DB rocket propellant in glassy state (below –90°C) is almost constant and has a maximum value of 8.6 GPa at –115°C. As temperature increases, the storage modulus decreases, showing a maximum decreasing rate at the glass transition region (in the temperature range from –60 to –10°C). In the glass transition region storage modulus decreases for about 7 times (from 8.6 GPa at –115°C to 1.3 GPa at 25°C). By further heating, another distinct change in the storage modulus occurs above 35°C. This change is connected with the softening of the propellant sample.

It is known that transition from the glassy to viscoelestic region does not occur at a strictly defined point – it occurs within a region, broadness of which depends on the material properties. It is taken by agreement [26] that the temperature of glass transition (T_g) is at the maximum of the loss modulus curve in the glass transition region. Thus, it was found out that the glass transition temperature of non-aged propellant was –41.98°C. A sharp drop of the loss modulus value at ~47°C corresponds to the softening temperature of the propellant sample.

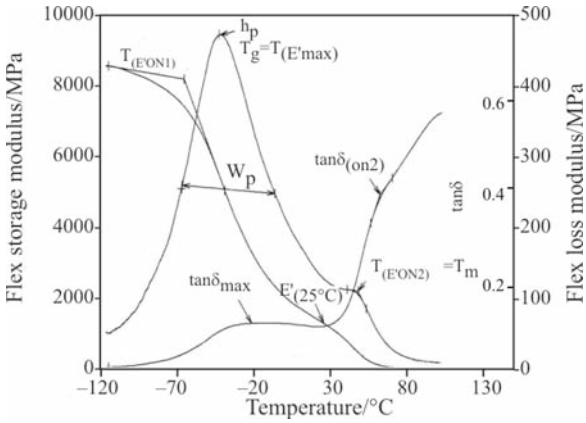

Fig. 1 DMA curve of non-aged DB rocket propellant (storage modulus, loss modulus and tanδ *vs.* temperature)

At the glassy state tanδ has a very low value (e.g. tanδ=0.0074 at –115°C), which is a consequence of the low flexibility of the nitrocellulose chain kinetic units in the glassy state. The tanδ has local maximum at the glass transition region ($\tan\delta_{max}$=0.1054), while it drastically increases in the softening region due to highly increased flexibility of nitrocellulose macromolecules.

In order to detect and quantify changes of the DMA properties of DB rocket propellant caused by ageing, several characteristic points on the E'–T, E''–T, and tanδ–T curves were followed. These points are illustrated in Fig. 1 and explained in Table 1.

Changes of DMA properties with ageing

As an example, the changes of individual DMA properties during the ageing at 90°C are illustrated in Figs 2–4. The same behaviour was also found for 95 and 100°C ageing temperatures.

Storage modulus

It can be seen from Fig. 2 that ageing causes a shift of the E'–T curve to higher temperatures, as well as to higher values of modulus in the viscoelastic region. In the glassy region (below –90°C) a small decrease of the modulus was observed.

It is known that an increase of the storage modulus is connected with the reduction of macromolecules flexibility [10]. The reduction of the flexibility of nitrocellulose macromolecules, in the

Table 1 Characteristic points/parameters on DMA curves followed during the ageing

Characteristic points on E'–T curves	Denotation	Unit
Storage modulus at 25°C	$E'_{(25°C)}$	MPa
Extrapolated onset temperature at the beginning of transition from glassy to viscoelastic state	$T_{(E'ON1)}$	°C
Characteristic points on E''–T curves	**Denotation**	**Unit**
Peak width at half height	W_p	°C
Peak height	h_p	MPa
Glass transition temperature (peak maximum temperature)	T_g	°C
Extrapolated onset temperature at the beginning of transition from viscoelastic to viscous state (softening point)	$T_{(E''ON1)}$	°C
Characteristic points on tanδ-T curves	**Denotation**	**Unit**
Tanδ maximum in viscoelastic region	$\tan\delta_{max}$	/
Extrapolated onset temperature at the end of transition from viscoelastic to viscous stage	$T_{(tan\delta ON2)}$	°C

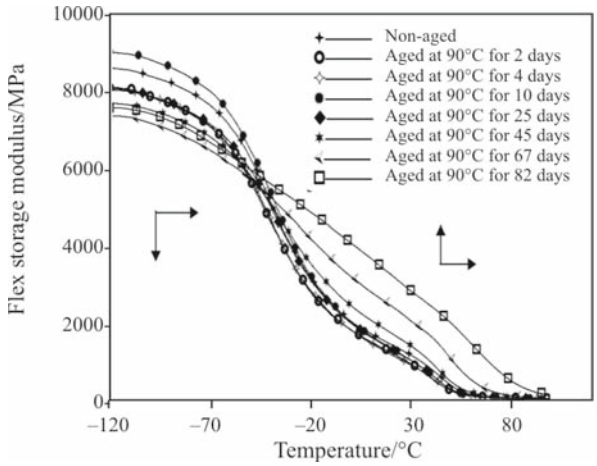

Fig. 2 Flex storage modulus of DB rocket propellant samples aged for different periods of time at 90°C *vs.* temperature

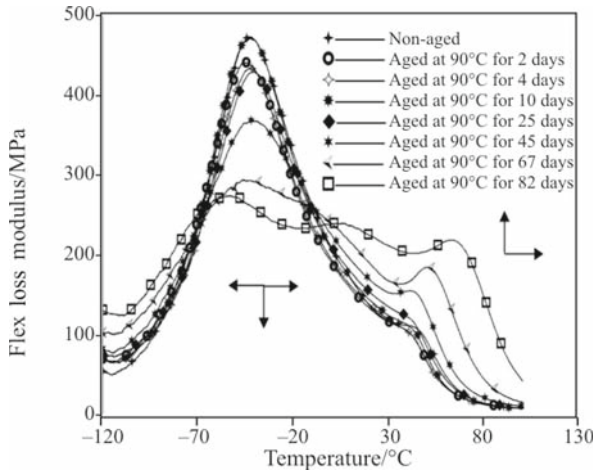

Fig. 3 Flex loss modulus of DB rocket propellant samples aged for different periods of time at 90°C *vs.* temperature

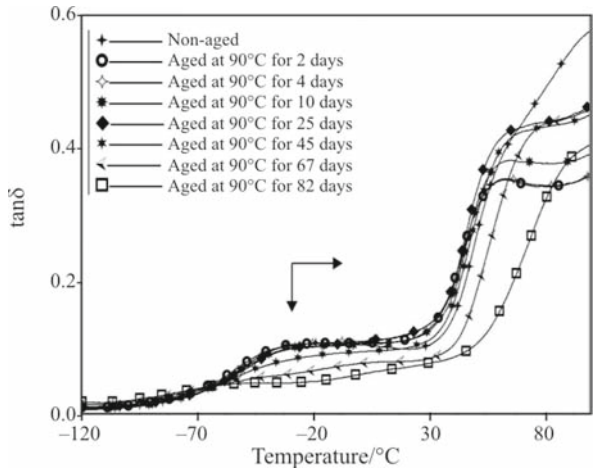

Fig. 4 Tanδ of DB rocket propellant samples aged for different periods of time at 90°C *vs.* temperature

case of the tested DB rocket propellant, is a consequence of the decrease of NG (which acts as a plasticiser) amount due to its migration from the propellant grain centre to the surface, and its vaporization and decomposition. A combined result of these physical processes and chemical reactions is shortening of the distance between nitrocellulose macromolecules, and an increase of intermolecular interactions. Consequently, the flexibility of the nitrocellulose chain's kinetic units decreases with ageing.

It is obvious from Fig. 2 that the selected characteristic points on the E'–T curve change distinctively with ageing. For example, the storage modulus at 25°C, $E'_{(25℃)}$, after 82 days of ageing at 90°C changes for about 130% in respect to the starting value (Fig. 5). As expected, the time to achieve the same degree of change decreases with the increase of ageing temperature.

A sharp drop of extrapolated onset temperature at the beginning of transition from the glassy to viscoelastic region, $T_{(E'ON1)}$, in the case of a non-aged DB rocket propellant occurs at about –67°C. $T_{(E'ON1)}$ and remains almost unchanged in the early ageing stage (e.g. about 40 days of ageing at 90°C; 30 days of ageing at 95°C; 10 days of ageing at 100°C), Fig. 6. After that period, a sharp drop of $T_{(E'ON1)}$ occurs, indicating initiation of intensive thermal degradation reactions accompanied by scission of nitrocellulose macromolecule chain and decrease of nitrocellulose molecular mass.

The reduction of nitrocellulose chain flexibility causes decrease of $T_{(E'ON1)}$, and increases of the softening temperature, which results in the broadening of the viscoelastic region. It is known that the broadening of the viscoelastic region is connected with the increase of structural heterogeneity of the system [10, 11]. The increase of heterogeneity in the case of the tested DB rocket propellant is connected with migration, evaporation, and decomposition of NG, as well as with the scission of nitrocellulose chain.

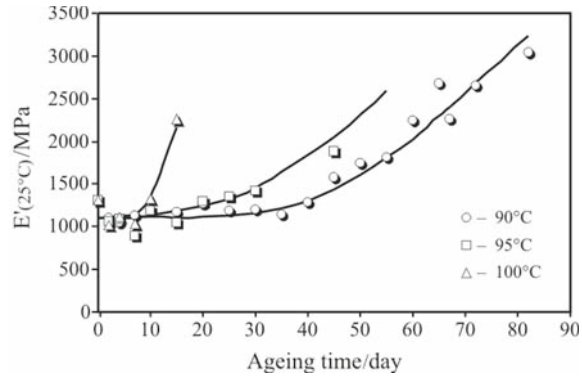

Fig. 5 Change of storage modulus at 25°C with ageing time at 90, 95 and 100°C

The increase of storage modulus at 25°C with ageing time (Fig. 5) is also a consequence of the reduced flexibility of nitrocellulose chain.

Loss modulus

Figure 3 shows that significant qualitative and quantitative changes of the E''–T curves occur with ageing. For example, peak height at the glass transition region decreases, peak width increases, and the complete E''–T curve shifts to higher temperatures.

The most distinctive qualitative change visible from E''–T curve is an increase of the peak width (Fig. 7) and appearance of two separate peaks after sufficiently long ageing time (e.g. after 67 days of ageing at 90°C). Such behaviour is a strong indication of considerable increase of structural heterogeneity of the system. As mentioned earlier, this is a consequence of combined action of physical processes (migration and evaporation of NG) and chemical reactions of decomposition of NG and NC.

According to the viscoelastic theory [10], the peak height in the glass transition region is dependent on molecular mass and degree of crystallinity – bigger macromolecules will give a higher peak. The decrease of loss modulus peak height in the glass transition region with the ageing (Fig. 8) may be explained by the decrees of nitrocellulose molecular mass due to scission of nitrocellulose chain.

The temperature of glass transition (T_g) shows interesting behaviour with ageing – it shifts slightly to higher temperatures at the beginning of ageing, and after certain time it shifts rapidly to lower temperatures. Such behaviour may be explained by facts that at the initial stage of ageing dominant process is nitroglycerine evaporation from the propellant grain (consequence of this process is decrease of flexibility of NC chains, and increase of T_g [10]), while at the later ageing stage the scission of NC chain becomes dominant process that causes an increase of structural heterogeneity and decrease of T_g. The time at which rapid decrease of T_g occurs corresponds to the time of appearance of two peaks on the E''–T curve (Fig. 9), i.e. to the time at which an intensive scission of nitrocellulose chain starts.

tanδ

tanδ, which is very sensitive to motion of kinetic units of macromolecular chain, decreases with ageing time and shifts to higher temperatures (Fig. 4). This becomes clear if one follows the change of the maxi-

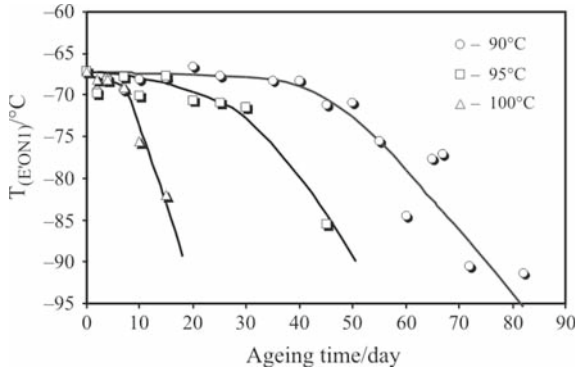

Fig. 6 Change of extrapolated onset temperature on E'–T curve at the beginning of transition from glassy to viscoelastic stage with ageing time at 90, 95 and 100°C

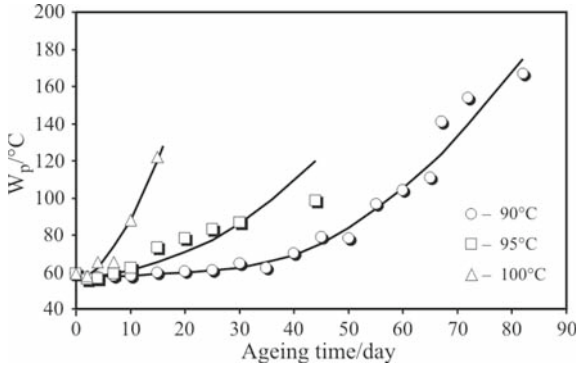

Fig. 7 Change of peak width in glass transition region with ageing time at 90, 95 and 100°C

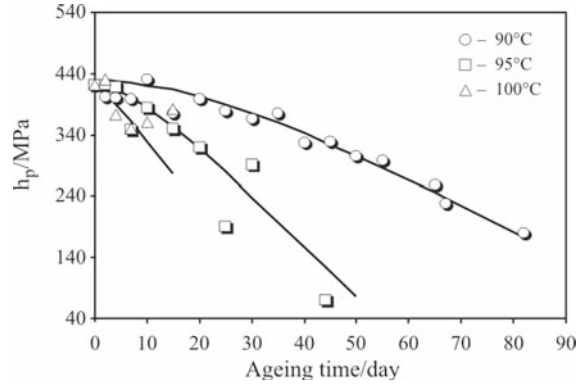

Fig. 8 Change of peak height with ageing time at 90, 95 and 100°C

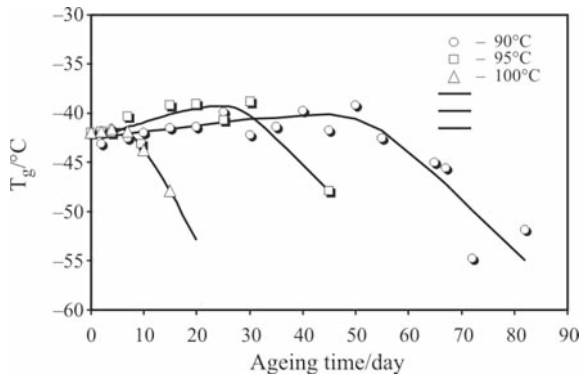

Fig. 9 Change of glass transition temperature with ageing time at 90, 95 and 100°C

mum value tanδ in the glass transition region ($tan\delta_{max}$) and onset temperature on the tanδ–*T* curve in the softening region $T_{(tan\delta ON1)}$, (Figs 10 and 11).

It is obvious from Figs 10 and 11 that at the beginning of ageing the changes are not too pronounced, while after certain ageing time they become very fast (e.g. this period is about 40 days at 90°C; 30 days at 95°C, and 10 days at 100°C). Such changes of tanδ confirm the earlier statement that ageing causes a decrease of NC chain flexibility due to the plasticizer amount decrease.

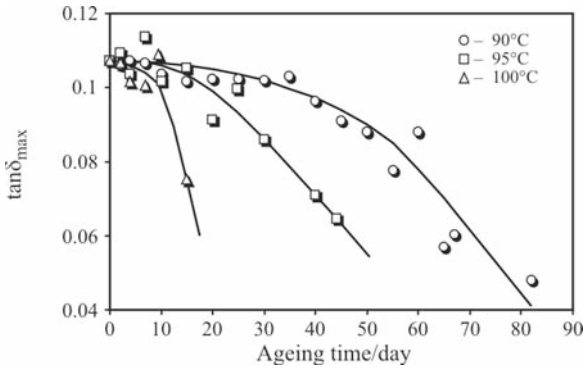

Fig. 10 Change of maximum value of tanδ in glass transition region with ageing at 90, 95 and 100°C

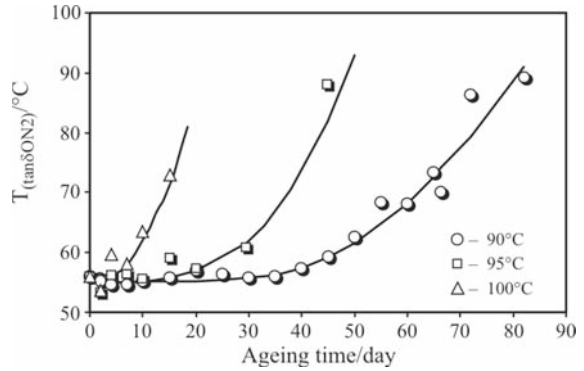

Fig. 11 Change of extrapolated onset temperature in softening region on tanδ–*T* with ageing at 90, 95 and 100°C

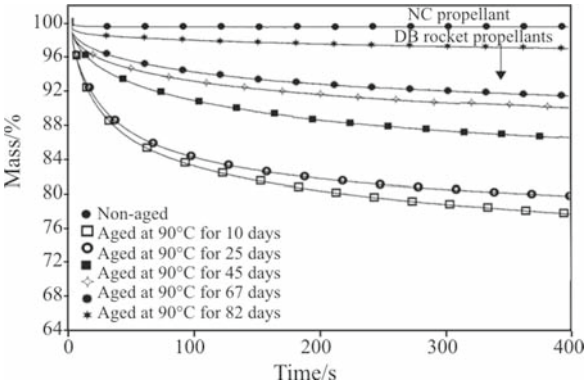

Fig. 12 Isothermal TG curves of DB rocket propellants aged for different period of time at 90°C and NC non-aged propellant

Isothermal TG curves

It was shown in our previous work [21] that isothermal thermogravimtry (TG) measurements may be used to determine (roughly) amount of NG in DB propellant samples. In order to prove the statement that the observed changes of DMA parameters of DB rocket propellant during ageing are strongly connected with NG amount (which acts as a plasticiser) in the propellant sample, a series of isothermal TG experiments were carried out, Fig. 12. Isothermal TG experiments were carried out using opened aluminium pans at 100°C.

The experiments have shown that the mass loss of NC propellant containing about 98% of NC (which is connected with evaporation of residual solvent and decomposition of NC) at 90°C is less than 2% after 400 min [21]. Under the same conditions, mass loss in the case of non-aged DB propellant is about 25% after 400 min. This means that the mass loss in the case of DB propellant, at 90°C, is mostly due to NG evaporation. Therefore, isothermal TG measurements presented in Fig. 12, clearly show that the dominant process during the artificial ageing of DB rocket propellant at 90–100°C is evaporation of NG in early stage, and then degradation of NG and NC at later stages.

Since the amount of NG decreases with ageing time, isothermal curves of non-aged propellant samples have a higher mass loss after the same ageing time than the samples aged for a longer period of time. As the amount of nitroglycerine in DB rocket propellant sample decreases with ageing, the mass loss at the same time period decreases, too. For example, the TG curve of the sample aged for 82 days at 90°C becomes very close to the TG curve of NC propellant – this means that the amount of nitroglycerine in this sample is close to zero. In other words, after 82 days of ageing at 90°C, the DB rocket propellant samples will loose the plasticiser almost completely. As shown earlier, this has strong effect on DMA properties.

Conclusions

The results presented in this paper, which are a part of more extensive study on the dynamic mechanical behaviour of DB rocket propellant during artificial ageing at elevated temperatures, have shown that the dynamic mechanical properties of the studied DB rocket propellant significantly change with the ageing time and temperature.

The ageing process was studied by following the changes of several DMA parameters and characteristic points on DMA curves. The changes indicate that in the early stage of ageing dominant process is evaporation of NG (which results in relatively slow de-

crease in nitrocellulose chain flexibility with the ageing time, i.e. in slow changes of followed characteristic points on DMA curves). In the later stage of ageing, an intensive scission of nitrocellulose macromolecule chain occurs, causing rapid changes of characteristic points on DMA curves. The most pronounced evidence of intensive scission of nitrocellulose macromolecule chain is the appearance of another peak on the $E''–T$ curve. It occurs after approximately 40 days of ageing at 90°C, 30 days of ageing at 95°C, and 10 days of ageing at 100°C, and it coincides with the beginning of fast changes of the majority of the followed parameters on DMA curves.

It was found out that the most sensitive parameters/characteristic points to the ageing process are: storage modulus at 25°C, peak width and height on the loss modulus curve, glass transition temperature, tanδ maximum in the viscoelastic region and extrapolated onset temperature at the end of the glass transition.

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