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GLASS TRANSITION TEMPERATURES OF POLYMER MATERIALS, MEASURED BY THERMOMECHANICAL ANALYSIS

INFLUENCE OF RATES OF HEATING AND COOLING

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The linear expansions of two materials have been measured, a double-base propellant and a carboxyl-terminated polybutadiene. The glass transition temperature, T_g and expansion coefficients below and above T_g have been calculated. The influence of the heating and cooling rates and sample thickness has been investigated. The results show that the value of T_g is dependent on the rates of heating and cooling but not on the sample thickness. Extrapolating to zero rate gives the same T_g for both heating and cooling. The expansion coefficients are not influenced by the rates of heating and cooling or by the sample thickness.

In measurements of the glass transition temperatures T_g of polymers it has been found that the value of T_g is dependent on the rate of heating. Strella [1] has made an investigation of T_g for two polymers by DTA. He found an increase of T_g with increasing heating rate. Further, Boyer [2] mentions in his review the influence of the heating rate on the value of the glass transition temperature. The dependence of T_g on the heating rate has also been investigated by Wolpert et al. [3] with DTA measurement, and by Prud'homme et al. [4] when measuring heat capacity with DSC. Nielsen [5] states that the glass transition is generally measured in experiments which correspond to a time scale of seconds or minutes. If the time scale in the experiments is shortened, the apparent T_g is raised, and if the time scale is lengthened to hours or days, T_g is lowered. Shen and Eisenberg [6] have come to the same conclusion in their review.

The reason for this investigation was that in measurements of the expansion coefficients and T_g of polymer materials the value of T_g varied with the rate. In order to have a reliable value of T_g it was necessary to establish the influence of different rates of heating and cooling with this particular apparatus. At the same time it was of great interest to know the influence of the sample thickness on the results.

Experimental

Materials

The investigation was made on two materials. One is a double-base propellant, that is the propellant is mainly made of nitrocellulose and nitroglycerine. The nitroglycerine functions as a plasticizer for the polymer nitrocellulose.

Table 1

Polymer 434331

Component	Parts
HC-434	100.00
EPON 812	8.08
CrDIPS	1.00

The other material is a polymer with the composition according to Table 1. HC-434 is a liquid carboxyl-terminated polybutadiene (CTPB). EPON 812 is a liquid epoxide, a triglycidyl ether of glycerol. CrDIPS is a metal chelate, bis-(3,5-diisopropylsalicylato)hydroxoaquochromium(III), which is used as a catalyst for the reaction between CTPB and epoxide [7]. Polymer 434331 was cast in sheets with thicknesses of about 1 mm or 2.5 mm and cured at 70° for 24 hours.

Methods

The apparatus used for the investigation was a Perkin-Elmer TMS (thermomechanical analyzer), with which it is possible to measure the thermal expansions of rather thin specimens and also to make penetration tests on polymer materials.

With the double-base propellant, expansion tests were made on small tablets with a thickness of about 1 mm. The width of the tablets was about the same as the diameter, 3.6 mm, of the probe tip resting on the tablet. The load on the probe was 3.5 g. The furnace-heat sink around the sample was cooled with liquid nitrogen down to 123 K. The cooling time was about 30 minutes until the temperature reached 123 K. After that this temperature was held for about 10 minutes. Then the temperature was raised up to about 300 K with different heating rates and registration of the expansion. The heating rates were 1.04, 2.08, 4.16 and 8.32°/min.

Polymer 434331 was more thoroughly investigated. Tablets with two levels of thicknesses were used, about 1 mm and about 2.5 mm. The expansion tests were made by cooling the samples with the rates 1.04, 2.08, 4.16 and 8.32°/min from 300 K down to 123 K, where the temperature was held for about 30 minutes before the samples were again heated up to 300 K with the same rate as on cooling.

Polymer 434331 was also investigated with penetration tests. The sample was cooled with liquid nitrogen down to about 170 K. The penetration probe was placed on the sample with a load of 7 g. The diameter of the tip resting on the sample surface was about 0.5 mm. After about 15 minutes the samples were heated with the rates 1.04, 2.08 and 4.16°/min.

Results

Double-base propellant

The result of a measurement of the linear expansion of the double-base propellant is seen in Fig. 1, which shows the linear expansion as a function of temperature when heating with a rate of 4.16°/min. The curve consists of two straight lines with different slopes. The intersection of the extrapolated lines gives the glass transition temperature, T_g, at this rate of heating. From the slope of the line below T_g it is possible to calculate the thermal expansion coefficient, α_g, in the glassy region. The slope of the line above T_g gives the expansion coefficient, α_r, in the rubbery region.

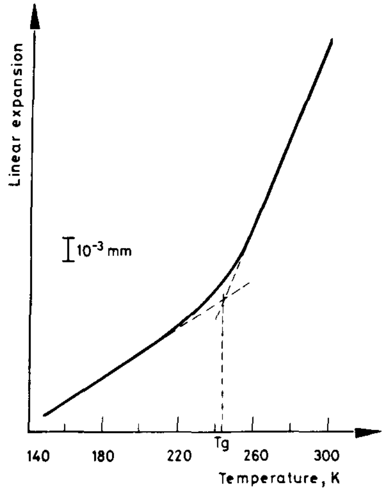

Fig 1. Linear expansion of a double-base propellant. Specimen thickness = 0.99 mm. Heating rate: 4.16°/min

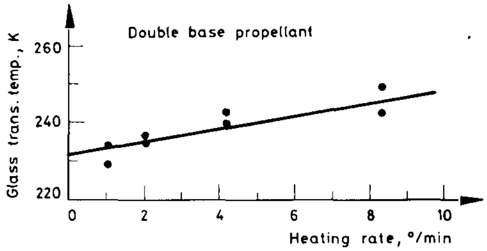

Fig. 2. Glass transition temperature of a double-base propellant as a function of the heating rate

The glass transition temperature, T_g, was examined at different heating rates. The result of T_g as a function of heating rate is shown in Fig. 2. The slope of the regression line has a statistically significant deviation from zero, which means that T_g really is a function of the heating rate. If T_g is expressed in K and the heating rate v in °/min, the line has the equation

$$T_g = 232 + 1.73\ v. \qquad (1)$$

With increasing heating rate the value of T_g increases. When the heating rate goes towards zero, the glass transition temperature of this propellant is 232 K.

The linear expansion coefficient below T_g, α_g, as a function of the heating rate is shown in Fig. 3. The slope of the regression line does not have a significant deviation from zero. Thus, α_g is not dependent on the heating rate and the line is drawn parallel to the rate axis. The average of α_g for all the measurements is 59×10^{-6} K^{-1} with a standard deviation of 3×10^{-6} K^{-1}.

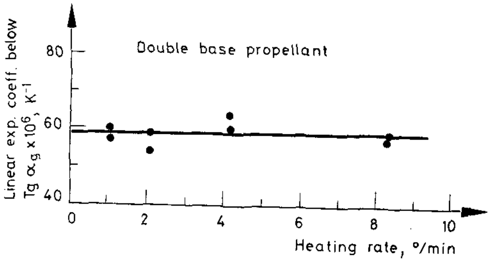

Fig. 3. Linear expansion coefficient, α_g, in the glassy region as a function of the heating rate

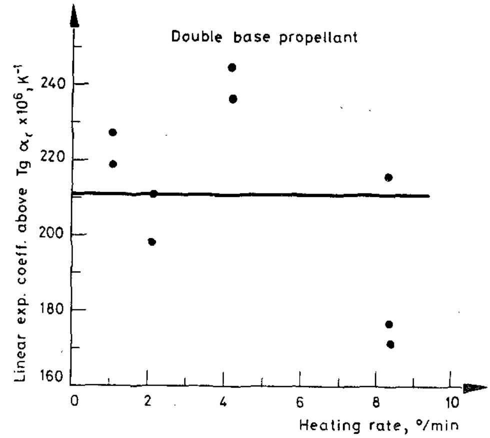

Fig. 4. Linear expansion coefficient, α_r, in the rubbery region as a function of the heating rate

Figure 4 shows the linear expansion coefficient in the rubbery region, α_r, as a function of the heating rate. α_r is not dependent on the heating rate either. Again the line is drawn parallel to the rate axis. The average of α_r for all the measurements is 211×10^{-6} K^{-1}, with a standard deviation of 25×10^{-6} K^{-1}.

Polymer 434331

A more thorough investigation was made with the polymer. Both expansion and penetration tests were made.

Expansion

The result of a linear expansion measurement is shown in Fig. 5. The intersection between the lines gives the glass transition temperature, T_g, and the slopes below T_g and above T_g give the linear expansion coefficients, α_g and α_r, respectively.

The results of the experiments with different specimen thicknesses and different heating and cooling rates are shown in Table 2.

Table 2

Results from linear expansion measurements on polymer 434331. Rate of heating or cooling = $= v$. Glass transition temperature = T_g. Expansion coefficient below $T_g = \alpha_g$ and above $T_g = \alpha_r$.

v, °/min	Specimen thickness, mm	Cooling			Heating		
		T_g, K	$\alpha_g \times 10^6$ K^{-1}	$\alpha_r \times 10^6$ K^{-1}	T_g, K	$\alpha_g \times 10^6$ K^{-1}	$\alpha_r \times 10^6$ K^{-1}
1.04	0.87	195	85	289	198	91	243
1.04	0.85	195	—	284	198	—	269
2.08	0.99	189	84	282	199	85	260
2.08	0.85	187	93	243	203	97	262
4.16	0.85	187	95	291	204	97	259
4.16	0.89	184	109	283	208	94	234
8.32	1.00	174	93	296	212	78	240
8.32	0.88	—	—	276	—	—	250
1.04	2.50	191	95	289	198	104	260
1.04	2.45	193	105	291	197	108	281
2.08	2.52	190	96	291	200	100	263
2.08	2.47	190	96	284	201	106	258
4.16	2.47	186	100	295	201	85	250
4.16	2.47	182	117	298	202	90	259
8.32	2.47	174	119	276	211	101	261
8.32	2.50	175	112	296	210	86	259

Regression analysis shows that the thickness of the specimens has no influence on the results. Therefore, both groups of thicknesses were taken together when calculating the results.

The regression lines for the glass transition temperature as a function of the heating or cooling rate are shown in Fig. 6.

The slopes of both lines have a significant deviation from zero. This means that the heating and cooling rates influence the value of T_g. When a sample is heated, T_g increases with increasing heating rate. For cooling, T_g decreases with increasing cooling rate. When cooling and heating rates are extrapolated to zero, T_g will be about the same in both cases.

The linear expansion coefficient in the glassy region, α_g, is not depending on the heating or cooling rate, as is seen in Fig. 7. The slope of the regression line did not have a significant deviation from zero. Hence, the line was drawn parallel to the rate axis. The expansion coefficient in the rubbery region, α_r, is also indenpendent of the rate of cooling or heating, but the difference between the results for α_r for heating or cooling is statistically significant. It has a higher value for cooling. This is seen in Fig. 8.

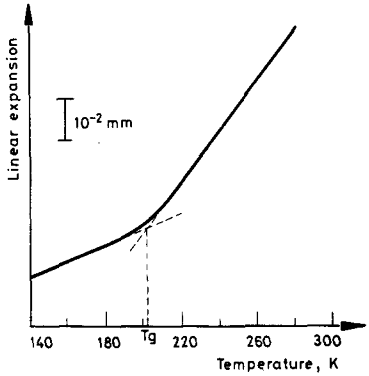

Fig. 5. Linear expansion of polymer 434331. Specimen thickness = 2.47 mm. Heating rate: 4.16°/min

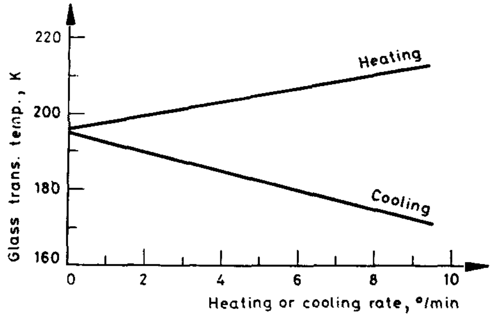

Fig. 6. Glass transition temperature of polymer 434331 as a function of the heating and cooling rates in expansion measurements

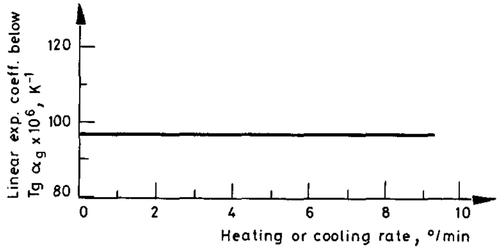

Fig. 7. Linear expansion coefficient, α_g, in the glassy region as a function of the heating or cooling rate

Table 3

Polymer 434331. Linear expansion measurements. Influence of the heating and cooling rate v (°/min) on the glass transition temperature, T_g, K and the linear expansion coefficient below T_g, α_g, K^{-1}, and above T_g, α_r, K^{-1}. Standard deviation = s.

Quantity	Cooling	Heating
T_g	$195 - 2.54v$ (2)	$196 + 1.76v$ (3)
α_g	97×10^{-6}	
s	10×10^{-6}	
α_r	285×10^{-6}	257×10^{-6}
s	13×10^{-6}	11×10^{-6}

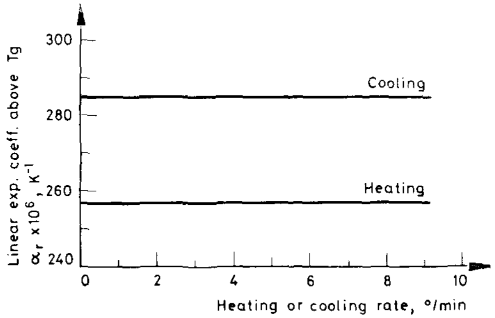

Fig. 8. Linear expansion coefficient, α_r, in the rubbery region as a function of the heating or cooling rate

The results of this investigation are summarized in Table 3, where formula (2) gives the influence of the cooling rate on the value of T_g, and formula (3) the influence of the heating rate on T_g. The values of α_g and α_r are also given.

Penetration

Penetration tests were also made on polymer 434331. An example of such a test is given in Fig. 9. The probe for penetration tests rested on the surface of the cooled sample. With heating at different rates, the pin of the probe penetrated the sample at a certain temperature. The straight lines before and after the penetration are extrapolated. The intersection between the lines was considered the glass transition temperature, T_g.

In Fig. 10 T_g in K is plotted as a function of the heating rate v in °/min. The slope of the line has a statistically significant deviation from zero. The equation of the line is

$$T_g = 196 + 2.99\,v\,. \tag{4}$$

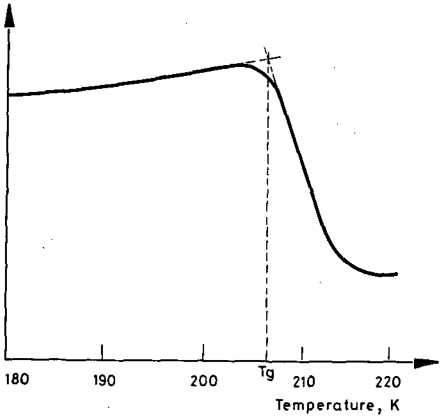

Fig. 9. Penetration test on a polymer sample. Load = 7 g. Heating rate = 4.16°/min. Specimen thickness = 2.52 mm

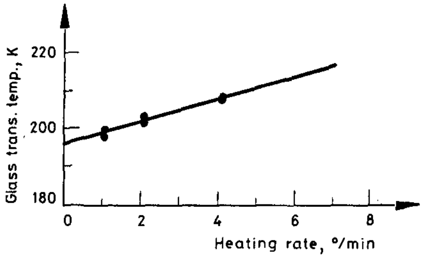

Fig. 10. Glass transition temperature of polymer 434331 as a function of the heating rate in penetration test

On extrapolation to zero rate, T_g is 196 K, which corresponds very well to the expansion measurement result.

Discussion

From the results it is evident that it is very important to state the heating or cooling rate with which the measurements were made when giving values of the glass transition temperature, T_g. The glass transition temperature is the temperature at which, during heating, the frozen polymer chains begin partly to move. This movement is time-dependent. With heating at a high rate the beginning of the movement is delayed until a higher temperature is reached than at lower rates. With cooling at a high rate the chain movements are still possible at a lower temperature than is the case at a lower rate of cooling. In order to get a good picture of the glass transition temperature for a material, it seems to be advisable to make measurements at different rates of heating or cooling and extrapolate the results to zero rate. T_g at zero rate seems to be a value which one possibly could take as a material constant. At the same time it can be of great value to know how the heating or cooling rate influences the glass transition temperature.

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RÉSUMÉ — On a mesuré la dilatation linéaire de deux matériaux, un agent de propulsion à base double et un polybutadiène avec un carboxyle comme groupe terminal. On a calculé la température T_g de la transition vitreuse ainsi que les coefficients de dilatation au-dessous et au-dessus de T_g. L'influence des vitesses de chauffage et de refroidissement ainsi que l'épaisseur de l'échantillon ont été étudiées. Les résultats montrent que la valeur de T_g dépend des vitesses de chauffage et de refroidissement, mais pas de l'épaisseur de l'échantillon. L'extrapolation à la vitesse zéro donne la même valeur de la température T_g lors du chauffage et du refoidissement. Les coefficients de dilatation ne sont influencés ni par les vitesses de chauffage ou de refroidissement ni par l'épaisseur de l'échantillon.

ZUSAMMENFASSUNG — Die lineare Ausdehnung wurde an zwei Stoffen, einem doppelbasischen Triebstoff und einem Polybutadien mit Carboxyl-Endung gemessen. Die Glas-Übergangstemperatur T_g und die Ausdehnungskoeffizienten unterhalb und oberhalb von T_g wurden berechnet. Der Einfluss der Aufheiz- und Abkühlgeschwindigkeiten und die Stärke der Probe wurden geprüft. Die Ergebnisse zeigen, daß der Wert von T_g der von Aufheiz- und Abkühlgeschwindigkeit, nicht aber von der Probenstärke abhängt .Die Extrapolierung auf die Geschwindigkeit 0 ergibt denselben T_g-Wert bei Aufheizung und Kühlung. Die Ausdehnungskoeffizienten werden durch die Aufheiz- und Abkühlgeschwindigkeit oder durch die Probenstärke nicht beeinflusst.

Резюме — Было измерено линейное расширение двухкомпонентного ракетного топлива и полибутадиена с концевыми карбоксилами. Были вычислены температура стеклования T_g и коэффициенты расширения ниже и выше T_g. Исследовано влияние скорости нагрева и охлаждения, а также толщины образца. Результаты показали, что T_g зависит от скорости нагрева и охлаждения, но не от толщины образца. Экстраполяция к нулевой скорости давала тоже самое T_g как при охлаждении, так и при нагревании. Коэффициенты расширения не затрагиваются как скоростью нагрева и охлаждения, так и толщиной образца.

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