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POTENTIAL TEMPERATURE STANDARDS FOR TORSIONAL BRAID ANALYSIS

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In torsional braid analysis (TBA) the thermocouple junction is not in contact with the specimen, and therefore temperature standards are necessary. However TBA is devised only for application to high polymers, which are not appropriate for standards. The transition and fusion temperatures of several substances of low molecular weight, such as water, *o*-terphenyl, potassium nitrate and *n*-azoxyanisole, have been studied by TBA, and their applicability as standards to TBA is discussed. It is found that water, *o*-terphenyl and potassium nitrate can be used as standards.

In thermal analyses, the properties of a sample or the phenomena taking place in it are observed as a function of temperature, so that the accuracy of temperature measurement is very important. Nevertheless, the accuracy is decreased as a result of the measurement being made during heating or cooling of the sample, and a temperature gradient inevitably exists within and around the sample. The Committee on Standardization of the International Confederation for Thermal Analysis has already certified three sets of differential thermal analysis (DTA) standards [1] for comparison of instrumentation; other attempts are now being made to establish other sets of standards for DTA, and appropriate substances for thermogravimetry (TG) are also being searched for.

However, the need for TG standards is greater than for DTA standards, because it is difficult for the thermocouple junction to be in contact with the sample in TG. The situation is similar in torsional braid analysis (TBA), because contact between the thermocouple and the sample can not be made in TBA [2]. Furthermore, TBA has mainly been applied to high polymers, and in only a few cases to substances of low molecular weight [3]. High polymers are not suitable as standards, because the transition points and the melting points of high polymers depend on a number of factors, such as thermal history, molecular weight, heating rate, and so on.

With the above points in mind, the authors have studied the transitions and meltings of several substances of low molecular weight by TBA. In this paper, the results are reported and the applicability of these substances as standards is discussed.

Experimental

Apparatus

The TBA apparatus used is an automated one constructed in our laboratory, and a schematic drawing is given in Fig. 1. The glass braid for electrical use is made of glass yarns (Asahi Fiber Glass Co., Ltd. ECE 225 – 1/0) containing about 3000 single filaments. The impregnated glass braid, 100 mm long and about 0.5 mm

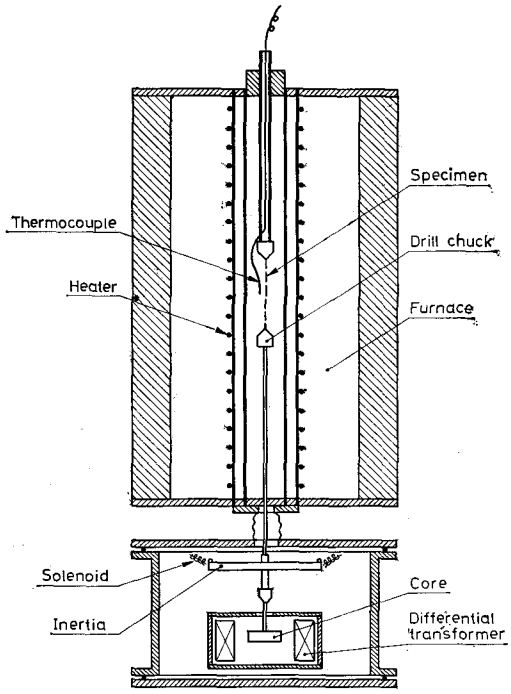

Fig. 1. The TBA apparatus

thick, is hung down in the center of a stainless steel tube located in an electrical furnace. In order to diminish the temperature gradient around the specimen, a 60 cm long furnace and two stainless steel tubes are used. At the top of the specimen, the specimen is fixed with a drill chuck and a stainless steel rod. At the lower end of the specimen, a wheel-like inertia plate made of brass is attached through another stainless steel rod. The specimen is excited magnetically with two steel pieces on the inertia plate and two solenoid coils, to oscillate every 1 or 2 minutes. The mechanical damping oscillation is converted to an electrical signal with a differential transformer, the core of which is freely suspended without friction. The neutral position of the differential transformer is adjusted automat-

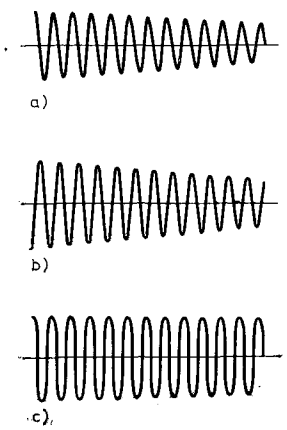

Fig. 2. Output signals of the damping oscillation; (a) output of the D. C. amplifier of the differential transformer, (b) that of the differentiation circuit, and (c) that of the logarithmic circuit. The sample is epoxy resin

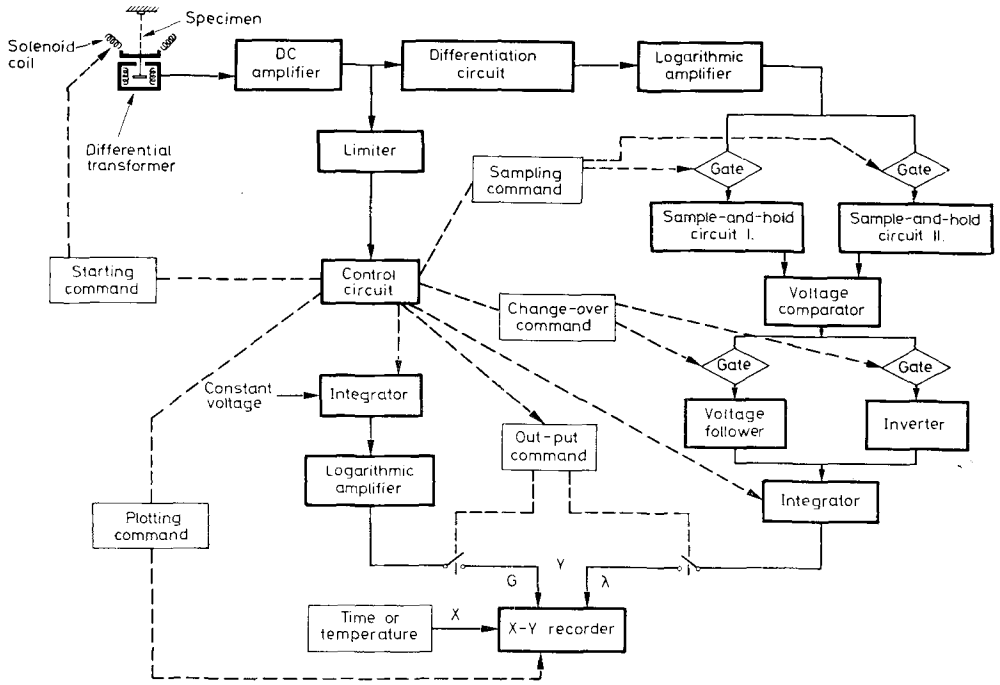

Fig. 3. Block diagram of the automatic data processor, composed of the operational amplifiers of integrated circuits

ically or manually. A typical signal obtained for epoxy resin is reproduced in Fig. 2 (a).

From the frequency, the shear modulus, G, of the composite is calculated, i.e.

$$G = (8\pi Il/r^4)f^2 \quad (1)$$

where I, l, r and f are the moment of inertia, the length of the specimen, the radius of the specimen and the frequency, respectively. Since it is difficult to measure the dimensions of the specimen and as it is not necessary to estimate the absolute value, the relative shear modulus or the square of the frequency is usually recorded in TBA curves. The logarithmic decrement, λ, is determined from the ratio of two adjacent amplitudes.

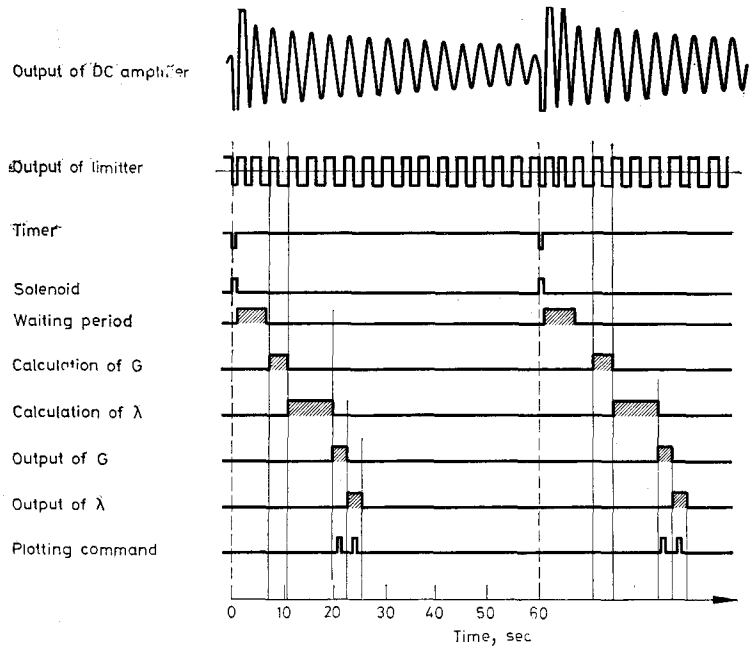

Fig. 4. Time chart of data processing

To eliminate the tedious labour of calculating the relative moduli and the logarithmic decrements from the output signals such as in Fig. 2 (a), obtained every 1 or 2 minutes, the calculation is performed with an automatic data processor composed of operational amplifiers of integrated circuits assembled in our laboratory. The automatic data processor has been described elsewhere [4]. The block diagram of the automatic data processor is shown in Fig. 3. The calculation of the shear modulus and the logarithmic decrement is made according to the time chart shown in Fig. 4. The shear modulus is calculated by integrating a constant voltage

during one cycle. The logarithmic decrement is obtained by comparing two adjacent amplitudes and the accuracy is improved by accumulating the compared values during a few cycles. A typical example of the plot is reproduced in Fig. 5.

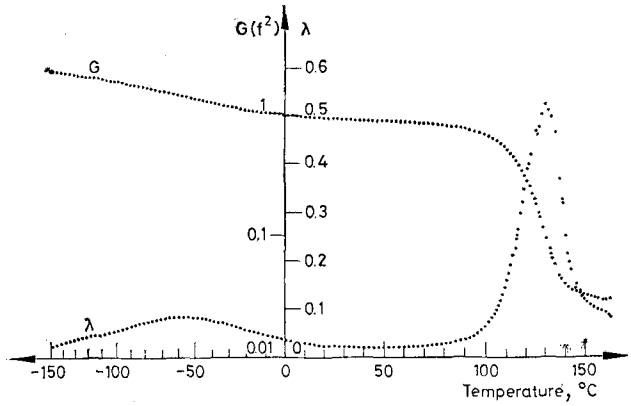

Fig. 5. Typical plot of the modulus and the logarithmic decrement versus the temperature obtained for epoxy resin

Materials – McAdie described general criteria for the standards [1]. In TBA, special criteria should be taken into account. Since the sample must be impregnated into the glass braid, the material should not react with the glass braid, and it should melt at a relatively low temperature, below the softening point of the glass ($<450°$), so that the material can be impregnated. Moreover, the material should not change during this procedure. Sharp changes should be observed in the TBA curves of both the shear modulus and the logarithmic decrement on the transition of the material. It is desirable that the material be used as standard for other types of thermal analysis. There are a few substances fulfilling these criteria. The substances chosen and tested in this report are *o*-terphenyl, water, potassium nitrate and *p*-azoxyanisole.

Potassium nitrate was supplied by Rigaku-Denki Co., Ltd. as a standard for DTA and differential scanning calorimetry, and o-terphenyl was the sample used in the international test program for the standards of DTA and supplied by the U. S. National Bureau of Standards. Both were used as received. Water was distilled three times, and *p*-azoxyanisole was purchased from Tokyo Kasei Co., Ltd. and recrystallized twice from ethanol solution. The specimen was made by dipping the glass braid into a melt of the sample.

Results and discussion

First, *p*-azoxyanisole was examined with regard to its transformations from solid to liquid crystal and from liquid crystal to isotropic liquid. The TBA curve obtained is shown in Fig. 6. It can be seen that the transition from solid to liquid

crystal is clear, but the transition from liquid crystal to isotropic liquid can hardly be detected, presumably because the change in mechanical properties on the latter transition is too small. It is deduced from the above results that the transition occurring in the solid can be detected by TBA.

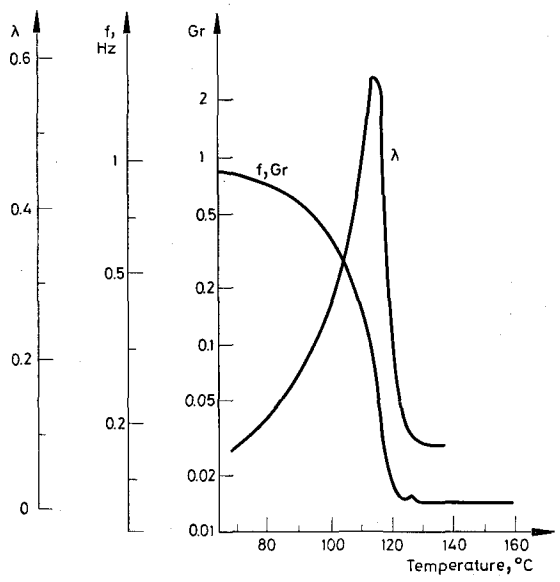

Fig. 6. TBA curve of *p*-azoxyanisole

Next, the fusions of water and *o*-terphenyl were studied by TBA. The recorded TBA curves are shown in Figs 7 and 8. In both cases the fusion is clearly observed, and there is another change at a lower temperature than the fusion. However, the nature of this change is not known for *o*-terphenyl. As regards the change for water, Naganuma [5] observed the same phenomenon in his "dynamic spring analysis", in which the mechanical properties of a copper spring coated with the sample are measured with the Vibron (an apparatus for measuring forced tensile oscillations) [6]. Mechanical relaxation phenomenon is also observed in isothermal runs [7] and this change therefore seems to be due to the mechanical relaxation phenomenon in ice.

With regard to the crystalline transition of an inorganic substance suitable as a temperature standard, that of potassium nitrate is the only one for which TBA measurement was successful. The TBA curves are reproduced in Fig. 9. Both the crystalline transition and the fusion are detected.

In the above-mentioned TBA curves, the temperatures at the peak in the curve of the logarithmic decrement are suitable for reproducible measurement and correspond to the reported values of the transition. As regards the curves of the

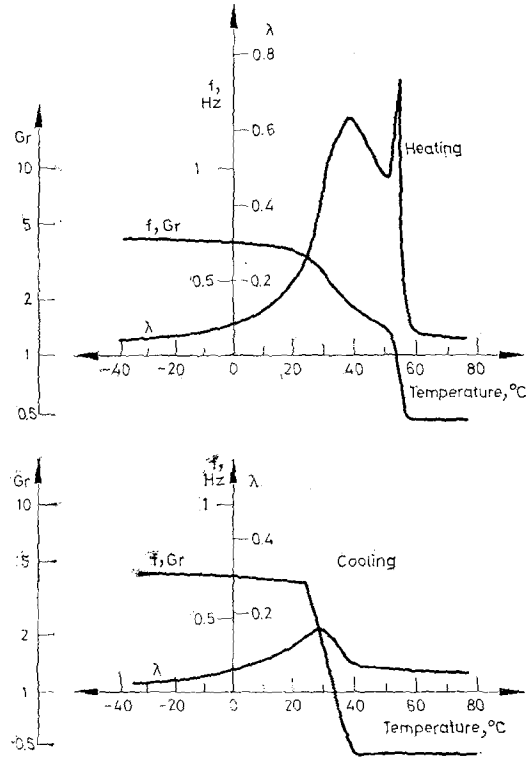

Fig. 7. TBA curves of *o*-terphenyl

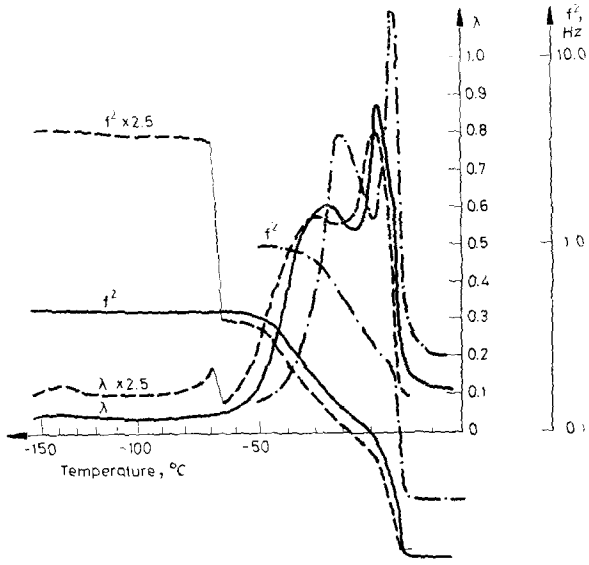

Fig. 8. TBA curves of distilled water
— — — 0.1°/min, ——— 0.5°/min, — · — · — 1°/min.

Table 1

The observed temperatures of transition

Substance	Rate of heating or cooling* (°C/min)	Peak in λ curve (°C)	Extrapolated completion in G curve (°C)	Reported value (°C)	Reference
Water	+0.13	−7.8	−0.08		
	+0.5	−6.0	0.0		
	+1.0	−1.2	0.05		
KNO_3 (crystalline transition)	+0.5	129.2	131.8	127.7	[8]
	−0.5	114.5	118.2	—	
KNO_3 (fusion)	+0.5	324.5	330.0	337	[8]
	−0.5	325.0	329.5	—	
o-terphenyl	+0.5	54.4	56.8	56.19	[9]
	−0.5	28.8	41.0	—	
p-azoxyanisole (crystalline transition)	+0.5	114.0	118.2	118	[10]
	−0.5	—	98.5	117	[11]
d-azoxyanisole (fusion)	+0.5	—	127.5	136	[10]
				135	[11]

* The plus sign and minus sign mean heating and cooling, respectively.

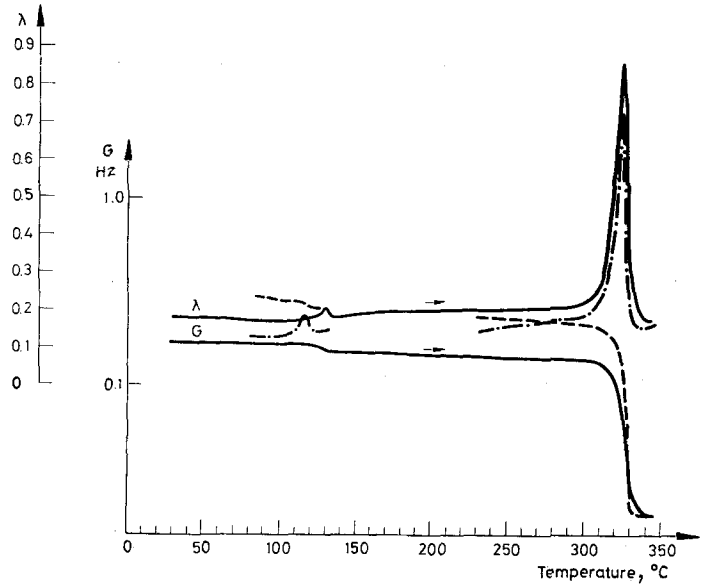

Fig. 9. TBA curves of potassium nitrate
Rate of heating ——— or cooling — — — —; 2°/min → | 0.5°/min | ← 2°/min → | ← 0.5/min

modulus, the extrapolated completion temperatures coincide with the reported values. These estimated values are listed in Table 1. It can be seen from the tabulated data that the crystalline transition of potassium nitrate and the fusion of water and *o*-terphenyl are in good agreement with the extrapolated completion temperatures, but the peak is generally lower than the reported value.

p-Azoxyanisole is not suitable as a standard, because of its chemical instability and the difficulty of purification.

It is concluded from the results that the phase transitions of substances of low molecular weight, including the crystalline transitions of inorganic substances, can be utilized as temperature standards in TBA, and that the extrapolated completion temperature is suitable to be so utilized. Relaxation phenomena of the substances of low molecular weight are also detectable in TBA, but the relaxation phenomenon is not suitable for use as the standard, because it depends on the heating rate and other experimental factors. As described above, the criteria on which potential transitions for the temperature standards are selected are more severe for TBA than for DTA. Besides those described by McAdie [1], additional criteria should be taken into account. Among the inorganic substances, the melting points of nitrates are relatively low and appropriate for preparation of the specimens, but the measurement is likely to suffer from the deliquescence of the sample, as the surface of the specimen is very large compared with its volume, and further the specimen is open to the atmosphere. For instance, we have not yet succeeded in detecting any transition of ammonium nitrate by TBA in ambient atmosphere, presumably because of its high deliquescence. It is therefore necessary to choose transitions from among other types of substances, even if they are organic ones, though the latter are not good as temperature standards.

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RÉSUMÉ — Du fait que la soudure du thermocouple de mesure de la température n'est pas en contact avec l'échantillon, il est nécessaire dans cette technique d'utiliser des étalons de température. La technique par analyse avec fil de torsion (torsional braid analysis, TBA) a été développée spécialement pour être appliquée aux hauts polymères mais ceux-ci ne peuvent pas servir pour l'étalonnage. Ayant observé que les températures de transition et de fusion de plusieurs substances de faibles poids moléculaires, comme l'eau, l'*o*-terphényle, le nitrate de potassium et le *p*-azoxyanisol étaient décelées par TBA, on discute la possibilité de les utiliser pour l'étalonnage. Les résultats montrent que l'eau, l'*o*-terphényle et le nitrate de potassium se prêtent à cette utilisation.

ZUSAMMENFASSUNG — Die Torsionsfaden-Analyse (torsional braid analysis, TBA) wurde zum Einsatz bei Hochpolymeren entwickelt, welche sich als Standard-Substanzen nicht bewähren. Da der Anschluß der Thermoelemente nicht in Berührung mit der Probe kommt, werden deshalb zur Analyse spezielle Temperature-Eichsubstanzen benötigt. Übergangs- und Schmelztemperaturen verschiedener Substanzen niedrigen Molekulargewichts, wie Wasser, *o*-Terphenyl, Kaliumnitrat und *p*-Azoxyanisol wurden mittels TBA erfaßt und ihre Eignung als Standardsubstanz für diese Methode erörtert. Aufgrund der Ergebnisse können Wasser, *o*-Terphenyl und Kaliumnitrat als Standardsubstanzen eingesetzt werden.

Резюме — Для анализа необходимы температурные стандарты, так как при соединении температурная термопара не соприкасается с образцом. Ранее торсионный шнуровой анализ (TBA) был применен только к высокомолекулярным соединениям, которые непригодны как стандарты. В данной работе с помощью TBA наблюдали температуры перехода и плавления таких низкомолекулярных веществ как вода, *o*-терфенил, нитрат калия и азоксианизол. Обсуждена применимость этих веществ в TBA в качестве стандартов. На основании полученных результатов утверждается, что вода, *o*-терфенил и нитрат калия могут быть использованы как стандарты.