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ON THE REPRESENTATION OF RELATIONSHIPS OBTAINED BY THERMAL CHARACTERIZATION TECHNIQUES

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ABSTRACT

A method for obtaining an average relationship for data obtained by thermal characterization techniques is described. The principle of the method is the introduction of the concept of reduced temperature, θ, using the relation

$$\theta_{ij} = k_j (T_{tr})_i$$

where T_{tr} is the transition temperature, i corresponds to a given sample of fixed material, j corresponds to a point j of curve i, and $k_j = 0.1, \ldots, 1.0, \ldots$

This gives a transition temperature which is equal to the average value for all experiments performed on different samples for a given material under study. The utility of the method is demonstrated by the investigation of the thermal behaviour of keratin fibres.

INTRODUCTION

Differential thermal analysis, DTA, and dynamic thermogravimetry, DTG, were developed as analytical tools over a century ago; many methods using dynamic conditions of heating have since been adapted for characterization of compounds and materials [1]. A few attempts have been made to demonstrate the representation of data obtained by the thermal characterization techniques, TCT, and especially to plot average relationships vs. temperature, T. However, the inconstant composition of the material investigated, which occasionally occurs in practice, and the small weight of the samples tested using TCT, lead to diversity of the relationships obtained from the various samples of a given material. This is valid to a great extent for polymer compounds and materials produced therefrom [2].

In earlier work [3] a method was developed for an average relationship obtained in the investigation of polyester fibres by thermomechanical analysis.

The aim of the present work is to describe this method in detail and to show its application to the demonstration of relationships by TCT, and

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likewise by DTA and TGA. The utility of the method is shown by means of an example investigating the thermal behaviour of keratin fibres, especially using TMA and dynamic calorimetry, DC.

METHODS

It is well known [1] that the thermal methods of analysis are classified as integral and differential methods. Principal relationships vs. temperature for both methods are given in Figs. 1 and 2, where Z is some kind of physical parameter and Z' is dZ/dt. Usually the peak temperature corresponds to

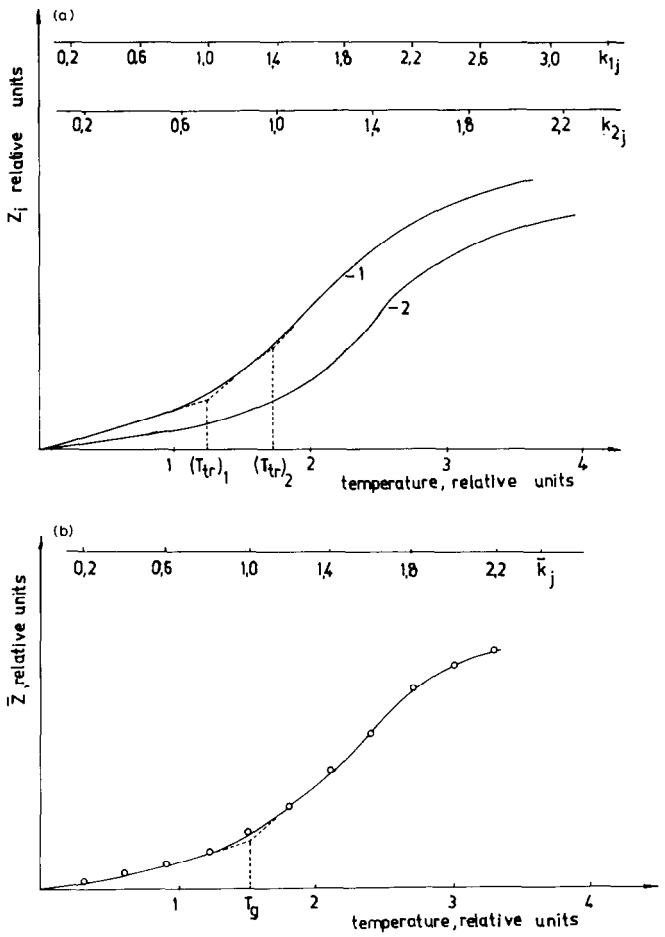

Fig. 1. Theoretical curves obtained by an integral method of thermal analysis. (b) Average curve for the data presented in (a).

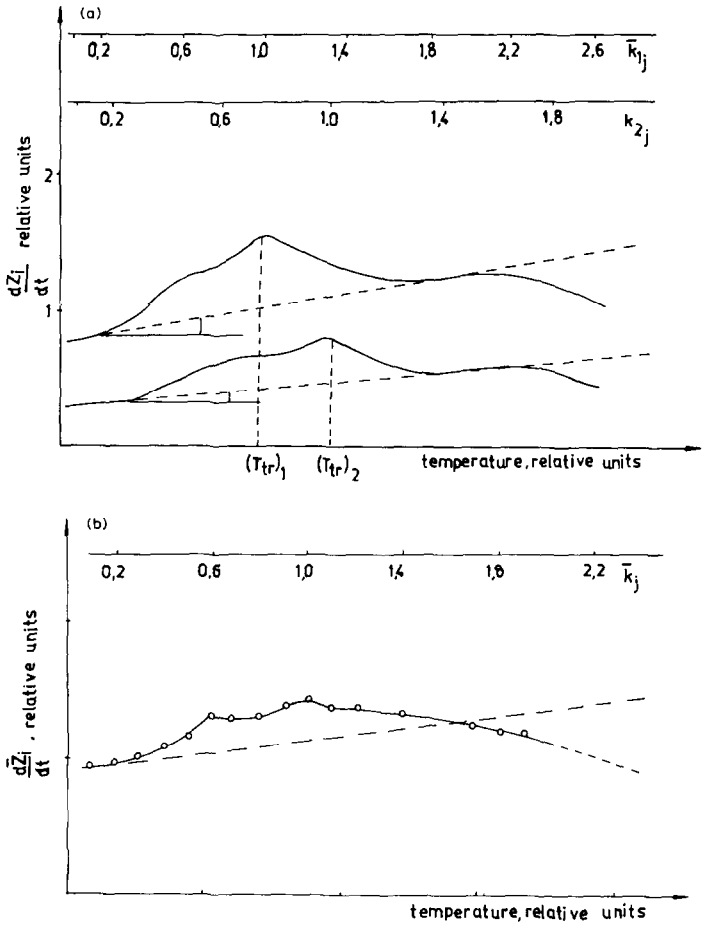

Fig. 2. (a) Theoretical curves obtained by a differential method of thermal analysis. (b) Average curve for the data presented in (a).

the transition temperature, T_{tr}, in the case of differential thermal methods of analysis. In the case of the integral methods T_{tr} is determined by the cross-point of the extrapolated straight lines before and after the transition process. If there is a difference between the traces resulting from various samples of a given material it is necessary to decide the representation of an average relationship. The T_{tr} is determined as an average value of T_{tr} for all samples of a given material studied. Therefore, the condition of the average relationships is as follows

$$\bar{T}_{tr} = \frac{1}{n} \sum_{i=1}^{n} (T_{tr})_i \tag{1}$$

where $\bar{T}_{tr}$ is the average transition temperature and i corresponds to a given

sample of fixed material. The average relationship then can be obtained using the relations

$$\bar{Z}_j = \frac{1}{n}\sum_{i=1}^{n}(Z_{ij}) \quad \text{and}$$
$$\bar{Z}'_j = \frac{1}{n}\sum_{i=1}^{n} Z'_{ij} \tag{2}$$

where $\bar{Z}_j$ and $\bar{Z}'_j$ are the average values of the physical parameter determined and the first derivative, respectively, and j corresponds to any point j of the average curve and the curve i respectively. It is impossible, however, to obtain the average relationship with a similar shape using relations (2) only; moreover, condition (1) will not also be fulfilled. Therefore it is necessary to introduce the concept of a reduced temperature, θ [3], using the relation

$$\theta_{ij} = k_j(T_{tr})_i \tag{3}$$

where $k_j = 0.1, 0.2, 0.3, \ldots, 1.0, \ldots$

It can be established that the average relationships $\bar{Z} = Z(\theta)$ and $\bar{Z}' = Z'(\theta)$ are such that condition (1) is executed. For $\bar{T}_{tr}$ the value of k_j is equal to 1.0. Therefore

$$\bar{\theta}_j = \frac{1}{n}\sum_{i=1}^{n}\theta_{ij} = \frac{1}{n}k_j\sum_{i=1}^{n}(T_{tr})_i = \bar{T}_{tr} \tag{4}$$

The application of the method described is shown in Figs. 1 and 2. As can be seen from these figures, the average relationships obtained have similar shapes. In the case of differential thermal methods, it is necessary to obtain an average angle for the basic line (Fig. 2).

EXPERIMENTAL

Fibres from Bulgarian merino sheeps' wool were investigated. The characteristics of fibres used were as follows: average thickness 22.57 μm (64 quality), average staple length 62.07 mm and residual grease content 0.04%.

The DC investigations were carried out using a differential calorimeter of our own design [4], based on a variation of the original design of Calvet [5], working in dynamic conditions. The following experimental conditions were used: heating rate 5 °C min^{-1}, initial weight of the samples 200 mg, temperature accuracy ± 0.5 °C, heat power accuracy $\pm 10^{-3}$ J s^{-1}. The samples were made by cutting the fibres into 0.5–1.0 mm lengths.

TMA experiments were carried out by means of an apparatus of our own design consisting of a microscope and a furnace, heated at a constant rate of 1.5 °C min^{-1}. An elementary woollen fibre was placed inside the furnace with one of the ends fixed and the other one loaded with a preset weight

equal to 200 mg. The displacement of a mark on the sample was measured and this permitted evaluation of the fibre deformation at any point. The error of the deformation measurement was within 0.1% and temperature accuracy $\pm 0.5\,^{\circ}C$.

RESULTS AND DISCUSSION

The utility of DTA for characterization of keratin fibres was first demonstrated by Schwenker et al. [6] twenty years ago, but few attempts to elucidate the conditions required for obtaining reproducible traces. According to Crighton et al. [7] both the sample preparation and experimental procedures are critical factors, and that is why a complicated procedure for sample preparation has been used. Dynamic calorimetry thermograms for five test samples of Bulgarian merino wool are given in Fig. 3. Two overlapping temperature transitions indicated within the temperature range 210–250 °C can be observed. This double melting peak of α-keratin has been explained [7] by the separate melting of helical material. A difference between the traces represented in Fig. 3 is observed. The curve resulting from the application of the method proposed for obtaining an average relationship is given in Fig. 4, and it can be seen that the resultant curve has a similar shape. The peak temperature has the average value of peak

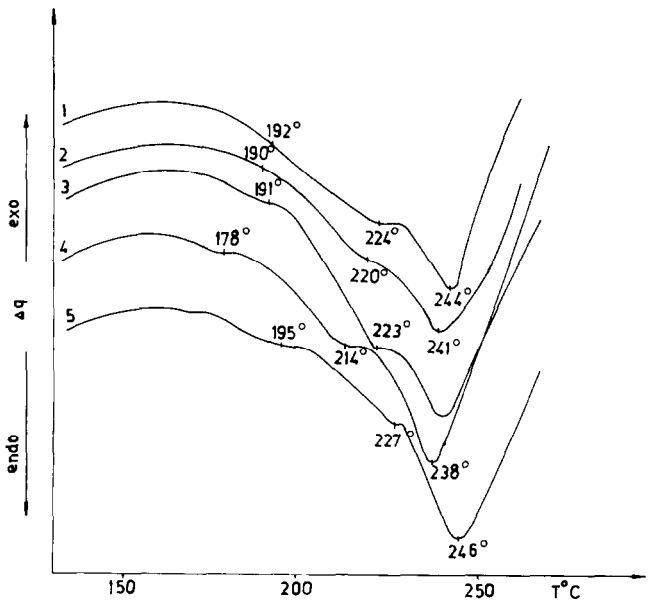

Fig. 3. Thermograms obtained by dynamic calorimetry for 64-quality Bulgarian merino sheeps' wool.

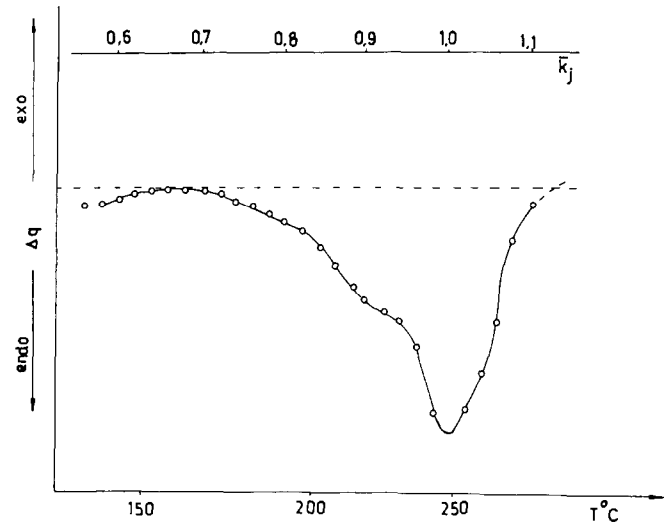

Fig. 4. Average curve for the data presented in Fig. 5.

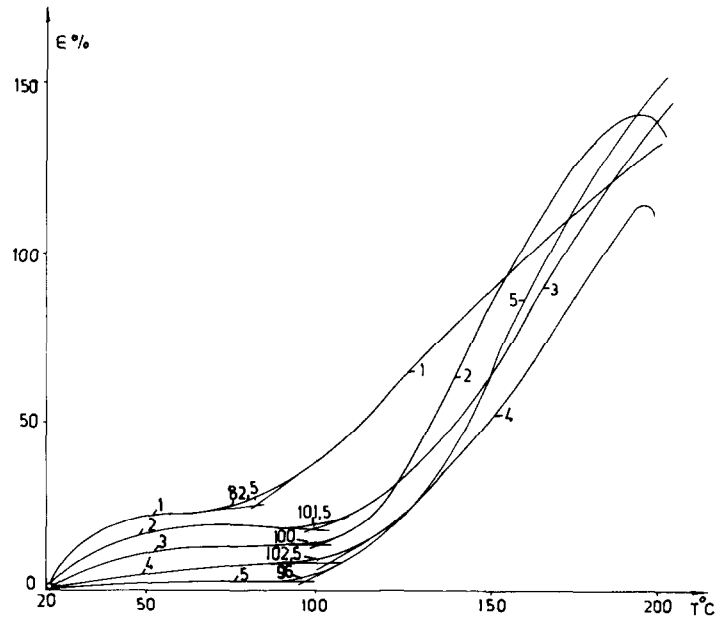

Fig. 5. Thermograms obtained by thermomechanical analysis for 64-quality Bulgarian merino sheeps' wool.

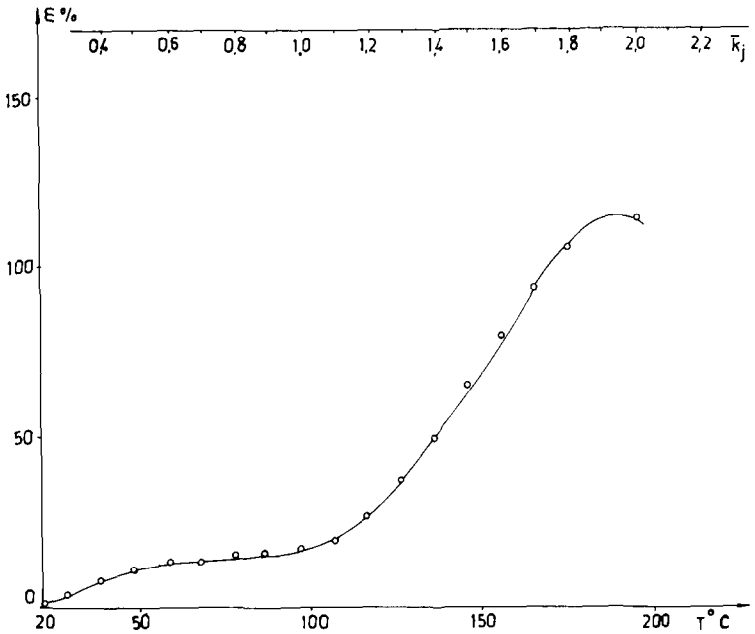

Fig. 6. Average curve for the data presented in Fig. 3.

temperatures of DC thermograms in Fig. 3, but the result for the enthalpy, ΔH, calculated using peak area does not correspond precisely with the average value for five traces represented in Fig. 3. Therefore, we come to the conclusion that values of ΔH_i for all the samples of a given material must be obtained separately, and then the average value of them taken. The deformation vs. temperature relationships (thermomechanical curves) for five samples of Bulgarian 64-quality merino wool are given in Fig. 5. The α–β transition of keratin was used as $\bar{T}_{tr}$ for obtaining the average TM relationship, given in Fig. 6. In our earlier work [8,9] the thermal behaviour of 64-quality Bulgarian merino wool was investigated and the determination of the α–β transition using TM curves has been demonstrated. The α–β transition of keratin is indicated within the temperature range 80–100 °C, which has been reported by other authors [10,11]. As can be seen in Fig. 6 the average relationship obtained has a similar shape, and condition (1) applies. This result demonstrates that the proposed method better describes the mechanical behaviour of the textile materials during heating.

CONCLUSIONS

The representation of data obtained by TMA of keratin fibres discussed in this paper is the same as that of the special case dealt with in the previous paper [3], related to thermomechanical studies of polyester fibres. However,

as TMA is one of the thermal methods of analysis, a more generally applicable method is derived in the present paper than in the previous one. This permits the development of a method for representation of the relationships obtained by thermal characterization techniques using the concept of reduced temperature. It is shown that this concept can be introduced in more complicated relationships obtained for given samples of the material studied. It is also clearly shown hat the concept of reduced temperature is very useful and effective in the representation of data obtained by thermal characterization techniques for 64-quality Bulgarian merino sheeps' wool.

REFERENCES

1 W.W. Wendlandt, Thermal Methods of Analysis, Wiley, New York, 1964.
2 Techniques and Methods of Polymer Evaluation. Vol. 2. Thermal Characterization Techniques. P.E. Slad and L.T. Jenkins (Eds.), Marcel Dekker, New York, 1970.
3 Ch. Bechev and J. Mishinev, Zav. Lab., 45 (1979) 765.
4 Ch. Bechev. J. Mishinev and K. Dimov, Chim. Ind. (Bulg.), February (1982) 58 pp.
5 E. Calvet and H. Prat, Microcalorimetrie, Chimija, Moscow, 1976.
6 R.K. Schwenker, K. Lanis and J. Beek, Text. Res. J., 30 (1960) 624.
7 J.S. Crighton, W.M. Findon and F. Happey, J. Appl. Polym. Sci., Appl. Polym. Symp., 18 (1977) 847.
8 E. Kanchev, R. Jlcheva and Ch. Bechev, Melliand Textilber. February (1978) 58.
9 Ch. Bechev, G. Nikolov and E. Kanchev, J. Therm. Anal., 28 (1983) 341.
10 H.D. Weigmann and C.J. Dansizer, J. Appl. Polym. Sci., Appl. Polym. Symp., 18 (1977) 795.
11 P. Alexander and F. Hudson, Wool, its Chemistry and Physics, Chapman and Hall, London, 1954.