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THERMOMECHANOMETRY, A PROPOSED NOMENCLATURE FOR THERMOANALYTICAL TECHNIQUES BASED ON CHANGES IN MECHANICAL CHARACTERISTICS*

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ABSTRACT

A new term, thermomechanometry, has been proposed to the ICTA Nomenclature Committee as a group name for thermoanalytical techniques based on changes in mechanical characteristics. ICTA has adopted two terms: thermomechanical analysis and dynamic thermomechanometry as defined techniques in this group. A more general group name has not been defined in ICTA nomenclature. Dimensional changes caused by thermal and mechanical means are classified and the difference between thermodilatometry and thermomechanometry is shown. Viscoelastic deformations are classified according to the variation of the properties of a material with time. The effect of temperature on the static or quasi-static mechanical deformation and dynamic deformation are classified as the basis of thermomechanical analysis and dynamic thermomechanometry. Some references are given from recent publications by the author's laboratory on these techniques.

INTRODUCTION

The new nomenclature in thermal analysis has been proposed by the Nomenclature Committee of The International Confederation for Thermal Analysis (ICTA) as the fourth report and approved[1] at the business meeting of ICTA in Kyoto, August, 1977.

The Committee gave the following new definition to thermal analysis: A group of techniques in which a physical property of a substance** is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme.

With this definition, the committee classified most thermoanalytical techniques

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[**] Substance is to be understood in the sense of substance and/or its reaction product(s).

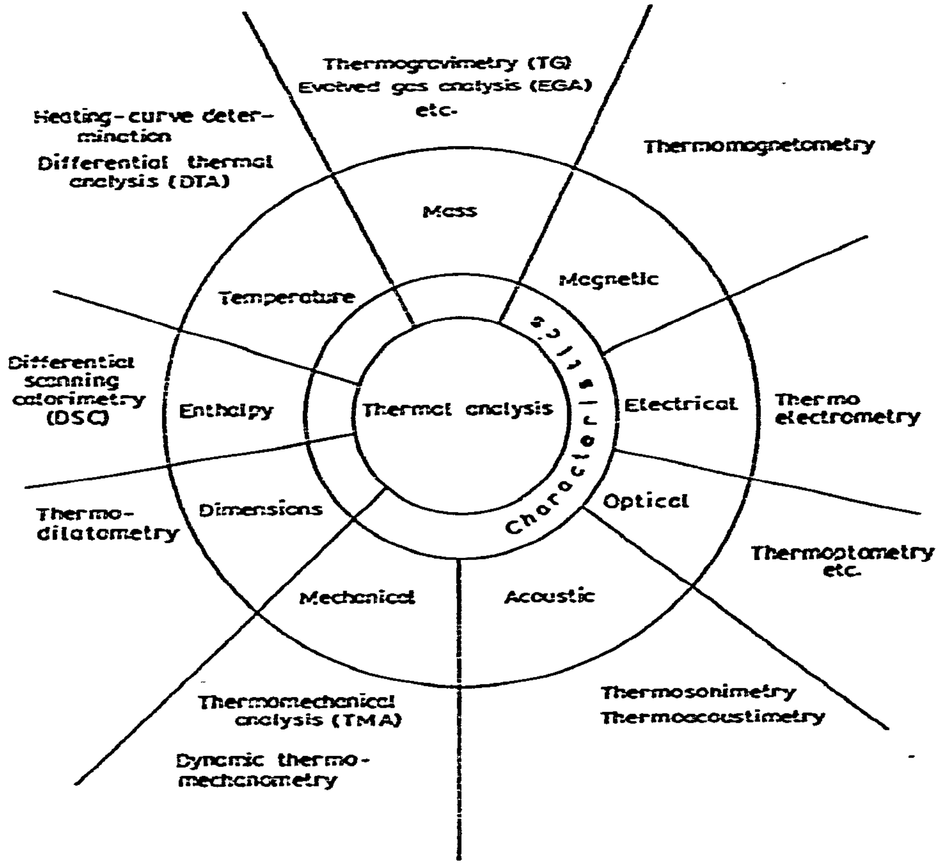

Fig. 1. ICTA classification of defined thermoanalytical techniques into groups based on changes in a physical property or characteristics to be measured.

by the physical property to be measured as in Fig. 1, in which mechanical characteristics were adopted to classify some defined techniques into one of nine main groups.

During the discussion, the committee first intended to define a group name for each group of techniques, and I proposed the term *thermomechanometry* as the name for the group based on changes in mechanical characteristics. Unfortunately, the group names have finally been dropped from the classification by the committee. The committee agreed, however, to assume *thermomechanical analysis* and *dynamic thermomechanometry* as defined techniques in this group. The former term, usually abbreviated as TMA, is very familiar to thermal analysts, particularly in the field of polymer research. The latter may sound very strange, however, as it is a new word based on my proposal.

Before the first nomenclature in thermal analysis was published[2] by the ICTA Committee in 1968, nomenclature was left to the arbitrary naming proposed by the developer of a new technique. In 1967, I wrote a long review (in Japanese) on thermal analysis based on changes in viscoelastic properties and called it *thermorheological* *analysis*[3]. In this review, I classified many existing techniques by the mode of deformation, i.e. tensile, flexural, torsional, and more general deformation, and also by the loading condition, i.e. static or unidirectional and dynamic or vibrational deformations.

In 1972, the ICTA Committee on Standardization agreed to make recommendations for reporting the thermal analysis data by thermomechanical techniques. I drafted the report and the final recommendations were published in the name of the chairman of the committee[4].

In 1974, when the nomenclature committee came to describe a family tree of thermal analysis, I proposed a tentative nomenclature in thermomechanical technique. I was very hesitant, as a Japanese, to recommend a new English term, although, of course, it was easy to coin a Japanese equivalent. However, I proposed thermomechanometry for the whole technique and static thermomechanometry and dynamic thermomechanometry for subdivisions. The existing techniques are easily classified into these subdivisions. So-called thermomechanical analysis (TMA) is classified into the static thermomechanometry and torsional braid analysis (TBA) into dynamic thermomechanometry. By this wording, I deliberately avoided the use of the expression thermomechanical analysis in parallel with the ICTA proposal[2] to use thermogravimetry in place of thermogravimetric analysis. At that time, the nomenclature committee did not directly respond to my proposal.

In April 1976, a member of the committee, Dr. T. Daniels, drafted the first nomenclature of thermomechanical techniques for the nomenclature committee, partially adopting my proposals. His recommendations were thermomechanometry for the group name and thermoanalytical strain measurement and thermoanalytical damping measurement for the techniques. These terms were apparently conscious of TMA and TBA. Personally, I could not agree with these narrow definitions.

This proposal was revised and finally confirmed by the committee at its meeting in Salford in 1976. This is a part of the report by the committee as written before.

The term thermomechanical was first used by Russian scientists. Professor V. A. Kargin and his collaborators in Moscow reported[5] on an indentation thermomechanical analysis of polymers at the end of 1940's and they reported many other types of thermomechanical curves following this pioneering work. The commercial instrument for thermomechanical analysis was originated by Du Pont as an attachment for their DTA apparatus in the middle 1960's. A similar attachment for the DSC instrument was soon constructed by Perkin-Elmer. These instruments were widely applied to polymer research in the United States. Many experimental systems in thermomechanometry have been developed in addition to these commercial instruments. However, the term TMA is commonly applied only to the application of the Du Pont or Perkin-Elmer instruments.

In contradiction of the reason for the rejection of TGA, ICTA adopted the term TMA. This may be fortunate for instrument manufacturers and the users of these instruments.

In this report, I would like to analyze the various techniques included in thermomechanometry by the more general definition in the ICTA nomenclature. The term thermomechanometry was proposed to, but has not yet been adopted by, ICTA.

DEFINITIONS

In the ICTA definitions, we can find a close relationship between thermomechanometry and thermodilatometry. The following definitions have been given in ICTA nomenclature[1] with a slight modification to the word order. The terms in parentheses correspond to the respective lines in the second parentheses.

Thermodilatometry	is a technique in which	a dimension of a substance under negligible load
Thermomechanical analysis		the deformation of a substance under non-oscillatory load*
Dynamic thermomechanometry		dynamic modulus and/or damping of a substance under oscillatory load**

is measured as a function of temperature whilst the substance is subjected to a controlled temperature programme.

In these definitions, thermodilatometry is based on the change of a dimension of the substance under no load and thermomechanometry is based on the deformation of the substance under non-oscillatory or oscillatory load. Deformation is also derived with the change of dimensions. To differentiate these two techniques, we must first consider the difference between the dimensional changes caused by thermal energy and by the mechanical work applied on the substance.

DIMENSIONAL CHANGE AND DEFORMATION

The dimensions of the substance in three rectangular coordinates define its size and shape. The volume is also derived from these dimensions. The dimensional changes are caused by thermal and mechanical means.

If we subject the substance to thermal energy, the substance undergoes thermal expansion. This is the basis of *thermodilatometry*. Conversely, if we remove thermal energy from the substance, a thermal shrinkage, that is negative expansion, is observed. Hereafter, we include thermal shrinkage in thermal expansion with this meaning.

If thermal energy is applied to the substance isotropically, the substance expands uniformly in three dimensions, which causes an isotropic change of volume. It is called *volume thermodilatometry*. On the other hand, if we have a sample of

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* The mode, as determined by the type of stress applied (compression, tension, flexure or torsion), should always be stated.

** Torsional braid analysis is a particular case of dynamic thermomechanometry in which the material is supported on a braid.

nonisotropic shape, such as a bar, fiber, plate, film etc., we may observe a particular change in one dimension, i.e. length or thickness. In this case, we have *linear thermodilatometry*.

If the sample has an anisotropic character in itself, the sample may expand nonisotropically under uniform heating. In this case, the sample changes its shape by thermal stress. For these samples, we can also apply volume thermodilatometry if we have a means of measuring the total volume change. A mercury dilatometer is an example of such a means.

The mechanical change of dimensions of the sample is called *deformation*. The deformation is expressed by the change of volume or mechanical distortion of the shape. The former is measured by volumetric strain or bulk strain, i.e. the ratio of volume change and initial volume. If we observe an isotropic increase of the volume, it is called expansion. In this case, we also include compression into expansion as a negative expansion, as in thermal expansion. Volumetric deformation is caused by normal stress. The positive normal stress is called pressure and the negative one is tension. These normal stresses act on the surface of the substance perpendicularly.

The mechanical distortion of the sample is caused by shear stress and measured by shear strain. When shear stress is applied tangentially to material surface, it causes no deformation perpendicular to the surface. In this case, the dimensional change of the substance appears anisotropically.

Generally speaking, the deformation of the substance is caused by a more complex state of stress. The simple deformations by tensile or flexural stress give extension or bending deformations of the substance, which are general strains including both volumetric and shear strains.

In time, the deformation of the substance causes fracture. Common mechanical tests are operated up to this point and the ultimate stress is called the strength. The strength depends upon the rate of deformation. With rapid deformation, we measure impulse strength. In fatigue experiments, we measure the fracture of the substance by repeated deformations. In these mechanical tests, we measure deformations, but the sample is destroyed and is not recoverable.

Usually, observations of mechanical deformation are carried out at uniform temperature. However, in some cases, the evolution of heat by mechanical deformation is observed and a special device is needed to keep the sample temperature constant. During isothermal mechanical deformation measurements at high temperatures, the substance may degrade thermally and this will be reflected in its mechanical behavior. Thus, the thermal and mechanical deformations often affect each other.

TIME EFFECT

Mechanical properties of matter are characterized by the effect of time on deformation. When we put a uniform stress (or strain) on the substance, we have two cases. If we observe no time effect on the deformation, we have an equilibrium deformation called elastic deformation. In this case, we can measure the elastic modulus by the ratio of stress and elastic strain. The inverse modulus is called elastic compliance. If we find a time effect at a uniform stress (or strain), it is called non-equilibrium viscoelastic deformation. The typical time effects are observed as stress relaxation at a constant strain and creep at a constant stress.

If the substance flows under stress indefinitely, we also have two cases. First is the steady viscous flow which shows no time dependency of the flow rate under a constant stress (or strain rate). In this case, we can measure the coefficient of viscosity as the ratio of stress and strain rate. We can differentiate volumetric flow and shear flow in this case. Time-dependent non-steady-state flow gives us thixotropic or anti-thixotropic behavior.

When we put the substance under a dynamically oscillating stress (or strain), we also have steady-state and non-steady-state behaviors. At the steady-state vibrations, the stress and strain oscillate in phase for elastic materials and out of phase for viscous materials. The common viscoelastic materials give us a phase difference between stress and strain oscillations intermediately. From these forced oscillation techniques, we can obtain the elastic and viscous constants of the substance. Resonance methods are also useful for the determination of similar constants.

We can also obtain elastic and viscous components from the non-steady-state dynamic measurements, such as damped free oscillation techniques. Some impulse deformations, such as a rebound test of viscoelastic balls, can be used to measure viscous dissipation of the deformation energy.

TEMPERATURE EFFECT

The effect of temperature on mechanical properties is the basis of *thermomechanometry*. Static or quasi-static application of the mechanical load to the sample at a controlled temperature programme constitutes *thermomechanical analysis*.

Thermomechanical analysis

If the mechanical deformation forms a uniform strain at a constant stress, it gives mechanical constants for each material; for an elastic substance, the elastic modulus is temperature-dependent; for viscous materials, we obtain a curve for the temperature dependence of the viscosity coefficient. For viscoelastic materials, we have the relaxation modulus or creep compliance at a given time plotted against temperature. These measurements require a substance of known size and shape in order to determine the change of dimensions with temperature under loading. Thermomechanical curves have been widely used for determining the softening temperature, at which the modulus of the sample decreases very quickly.

If it is difficult to get a definitely shaped sample for measurement, we may use the more general mode of deformation at a constant load (but not at constant stress). The most commercial thermomechanical analyzers take this form by using a mode chosen from penetration, extension, compression or flexural deformations. The ICTA definition of thermomechanical analysis describes this sort of measurement. In this case, we measure only a deflection or movement of the loading body relative to the sample surface. These measurements do not give us an absolute value of the viscoelastic characteristics*, but are still very useful for measuring the relative changes of mechanical properties with temperature. They give thermomechanical curves from which the softening points of substances are commonly determined.

A combination of mechanical and thermal dimensional changes gave us an interesting measurement of thermal shrinkage[8]. After stretching a film of polypyromellitimide at room temperature, the tensile stress was removed from the sample. Initially, the cold-drawn film sample shrank quickly and then gradually, but it still retained an amount of tensile strain. When we measured thermodilatometric curves of these extended films at uniform heating, we obtained thermal shrinkage curves. From the curves, we could find three different molecular relaxations above room temperature for this particular polymer, which were completely coincident with those obtained by dynamic mechanical and dielectric measurements[9]. By analyzing shrinkage curves obtained at various heating rates, we could kinetically analyze the thermal shrinkage process of this polymer.

Dynamic thermomechanometry

The effect of temperature on dynamic mechanical properties is the basis of *dynamic thermomechanometry*. For this purpose, we can use several oscillation modes and corresponding commercial instruments; tensile, Toyo-Baldwin Rheovibron, flexural, Du Pont Dynamic Mechanical Analyzer, and torsional, torsional pendulum. From tensile and flexural measurements, we can determine the complex tensile modulus $E^* = E' - iE''$, where E' is the tensile storage modulus, E'' the loss modulus, and $E''/E' = \tan\delta$, the loss tangent. From torsional measurements, we obtain corresponding shear moduli: G^*, G', G'', and $\tan\delta = G''/G'$. We have measured the temperature dependences of torsional properties[9] and tensile properties[10] of polypyromellitimide films. For these measurements we need specimens of a definite initial shape and size to calculate the absolute values of the viscoelastic properties.

If it is difficult to get a definitely shaped specimen, we can use a substrate to hold the sample during dynamic measurements. Typical of dynamic thermomechanometry with substrate, Lewis and Gillham[11] have proposed torsional braid analysis (TBA). TBA is widely used to determine the relative dependence of mechanical characteristics on temperature. Lewis and Gillham suggested the use of glass fiber braid to support polymer sample at torsional vibrations. Kambe and Oikawa[12] used a straight bundle of carbon fibers as a substrate for aromatic polymers. Similar composite materials could be applied to measure the tensile vibrations of these materials[10].

Many other dynamic thermomechanometry measurements have been reported

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* Hwo and Johnson[6] suggested that the modulus could be calculated from the penetration data obtained by thermomechanical analysis. Gillen[7] has shown the means of obtaining compliance by a similar technique.

by using other vibration modes with a substrate. Naganuma et al.[13] used a helical copper spring coated with a polymer film. They measured the tensile oscillations of the spring to determine the relative dynamic properties of the polymer coating.

CONCLUSION

Thermomechanometry is a new term proposed to define a new branch of thermal analysis which has a wide range of applications with a variety of techniques in mechanical measurements. Now thermomechanical analysis and dynamic thermomechanometry have been defined by ICTA as techniques in this branch of thermal analysis.

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