Materials Characterization by Dynamic and Modulated Thermal Analytical Techniques

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Foreword

This publication, *Materials Characterization by Dynamic and Modulated Thermal Analytical Techniques*, contains papers presented at the symposium of the same name held in Toronto, Ontario, on May 25-26, 2000. The symposium was sponsored by ASTM Committee E-37 on Thermal Measurements. The symposium co-chairmen were Alan T. Riga, Cleveland State University, Cleveland, Ohio, and Lawrence Judovits, ATOFINA Chemicals, King of Prussia, Pennsylvania.

Overview

The dynamic and modulated thermal analysis technique symposium, May 2000, has now culminated in a timely presentation as an ASTM special technical publication (STP). The basis of many of the latest Differential Scanning Calorimetry (DSC) thermal methods is the modulation of temperature along with varying other parameters. The mode of modulation, a sinusoidal wave or a saw tooth curve, affords the thermal analyst an opportunity to study a physical or chemical change in greater detail.

The technical science presented is a timely event in the development of new thermal analytical techniques, interpretations, and applications. Major contributions to this science are the family of modulated temperature DSC (MTDSC) techniques, which are also known as temperature-modulated DSC (TMDSC) techniques. These innovative approaches to scanning calorimetry can distinguish a polymer glass transition temperature, T_g, from other overlapping thermal-physical properties and events. The window of measurement has been expanded for better sensitivity and higher resolution. A number of presenters/authors studied the factors effecting the T_g, such as the heating rate, modulation frequency or period, amplitude of the imposed wave, as well as the type of dynamic or modulated curve.

Professor Wunderlich found that MTDSC generated with a centrosymmetric saw-tooth oscillation could be considered a sinusoidal modulation with multiple frequency. Further, he observed that application of these methodologies can be used to calibrate heat capacity at very high precision. Reading et al. compared and developed programs for micro and macro thermal analysis based on MTDSC. He discovered that the modulated approach can be applied to analysis on the probe tip of an atomic force microscope (AMF), where a microanalysis can now be accomplished. Innovative applications of these methods include characterizing reacting polymer systems, relaxation behavior during chemical reactions, evaluating polymer melting and crystallization, kinetic parameters, and the factors effecting the T_g of elastomers in the temperature range of 160 to 270 K.

Price reported on the application of modulated temperature programs for TMA, with and without an underlying linear temperature change, affording methods for separating the reversible nature of thermal expansion from irreversible deformation. The latter arises from creep under the applied load or changes in dimensions due to relaxation orientation.

Riga, Cahoon, et al. used dielectric thermal analysis (DETA) to evaluate surfactants, dispersants, and electrorheological processes. Isothermal permittivity, conductivity, and tan delta curves (Debye plots) clearly differentiated various surface-active agents. The "real world" response time in an applied electric field is needed to rank Electrorheological (ER) fluids for semipassive shock absorbers. The ER response time is directly related to the readily determined DETA relaxation/polarization time.

As presented in this STP, frequency-varied dynamic and modulated methods included modulated thermogravimetric analysis (MTGA), modulated thermomechanical analysis (MTMA), DMA, and DETA, as well as MTDSC. The Thermal Measurements Committee E37 is actively working on developing and implementing Standard Test Methods for the frequency based methods, for example, specific heat capacity, diffusivity, and thermal conductivity by MTDSC. There are methods in place for calibrating and interpreting DMA and DETA. The committee will continue to serve the thermal science community by establishing these standard methods, as well as their accompanying precision and bias characteristics.

We would like to acknowledge and extend our appreciation for those that helped with the organization of the symposium and publication of this STP. A very special thanks to our symposium committee, which consisted of R. Blaine, R. Seyler, B. Cassel, K. L. Lavanga, and J. A. Foreman and to the ASTM staff which includes D. Fitzpatrick, A. Adams, and T. O'Toole. Finally, many thanks to the lecturers, presenters, and reviewers who contributed to make this a high quality technical achievement.

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