Overview

This Special Technical Publication (STP) represents a compilation of presentations from an international symposium addressing the Assignment of the Glass Transition which was held 4-5 March 1993 in Atlanta, GA. The symposium and this subsequent publication reexamine an age-old phenomenon in amorphous and semicrystalline materials, the glass transition. Perspectives from the physics, materials science, engineering, and manufacturing communities for both organic and inorganic materials were shared in the two-day symposium. Five invited lectures and eighteen papers by authors from four countries were presented in four sessions including Theory and Overview, Instrumental Techniques, Materials, and Applications.

The symposium was the fourth in a continuing series on the use of thermal analysis in materials science sponsored by ASTM Committee E–37 on Thermal Measurements and marked the 20th anniversary of this committee. The symposium also enjoyed cooperative sponsorship from the Plastics Analysis Division of the Society of Plastics Engineers (SPE-PAD) and the North American Thermal Analysis Society (NATAS). I, R. J. Seyler (Eastman Kodak), served as the symposium organizer with the support of committee members Charles M. Earnest (Berry College), R. Bruce Cassel (Perkin-Elmer), and Alan T. Riga (Lubrizol).

This book follows the same organizational structure as the symposium and includes 20 of the 23 technical presentations. At the behest of numerous participants I have agreed to include my technical introduction and conference summary remarks in this publication. These summary remarks represent my personal observations of the salient points expressed throughout the symposium and some of the challenges that remain with regard to glass transition assignments. An enthusiastic and interactive audience participation throughout the symposium contributed measurably to the overall success of this symposium. Two audience discussion points by Ronald P. Tye (Ulvac Sinku Riko) were directed at a number of authors. Since these points were recurring throughout the presentations and discussions, it was decided that closure would be handled *en masse* at the beginning of the text. I encourage the reader to regard these points with due consideration prior to reading the text.

Assignment of the Glass Transition was a particularly appropriate subject matter for an ASTM E–37 technical symposium. The committee has a standard test method using differential scanning calorimetry (DSC) for obtaining T_g (E 1356) and has just approved a second standard test method using thermomechanical analysis (TMA) (E 1545). It is also in the process of developing additional standard test methods for the glass transition using dynamic mechanical analysis (DMA) and tensile mode TMA, as well as considering a dielectric analysis approach.

The **Theory and Overview** section includes the invited lectures which provide an excellent review of the glass transition and its measurement using thermal analysis techniques. Wunderlich in the opening paper discusses the thermodynamic aspects of the glass transition with a primarily organic polymer viewpoint. The structural relaxation process concept offered by Moynihan has been more openly embraced by the inorganic glass and physics communities. When taken together, these two papers offer a unique, perhaps "modern," perspective of the glass transition. One notable feature of the structural relaxation process concept is the use of a "fictive temperature" to define the glass transition temperature. Chang and Saffell both further the cause for use of a fictive temperature from calorimetry or

scanning calorimetry data. The paper by Chang is a particularly well prepared treatise on calorimetry observations of the glass transition. Ultimately, one must measure a glass transition temperature, which is no trivial matter. The lectures by Bair, Earnest, Bidstrup and Day, and Chartoff, et al. review the glass transition measurement and associated difficulties for each of the thermal analytical techniques DSC, TMA, dielectric analysis, and DMA, respectively. The reader is strongly encouraged to become familiar with the numerous extrinsic factors cited by these authors and how they impact the respective measurements to assign a glass transition temperature for a material.

A variety of properties undergo significant changes in the glass transition interval. The **Instrumental Techniques** section examines several additional measurement procedures or compares the utility of several alternatives. Assessment of thin film (organic, inorganic, and metallic) properties has been identified as a serious analytical need both within ASTM E–37 and the scientific community at large. Grate establishes a viable option for thin films using acoustic wave sensors. Wiedemann compares the utility of optical measurements both as a complement to and as an alternative to the more traditional DSC and TMA procedures. The concept of an extrinsic parameter impacting measured values is reinforced in the paper by O'Neill and Handa where gas pressure as a component of the specimen "atmosphere" causes different temperature assignments.

The **Materials** section offers a sampling of the classes of materials that can exhibit a glass transition. Despite layman references to melting of glass, inorganic glasses are generally recognized as amorphous materials and therefore undergo a glass transition. Martin shows how the chemical composition of an inorganic glass can both shift the temperature interval of the glass transition and modify its appearance and ability to be measured. The paper by Cassel and Riga (liquid crystal) and the one by Weiss (ionomers) examine two classes of polymers in which the existence of a glass transition remains somewhat controversial. The elastomers discussed by Sircar remind us that the glass transition can occur at subambient temperatures and that material properties are significantly different above and below the glass transition. Moscato and Seyler use poly(ethylene terephthalate) as a model semicrystalline material to show how both crystallinity and process history can greatly affect the glass transition. They further suggest that these effects can be so unique as to result in directionally different glass transition temperatures within the same specimen.

The final section, **Applications,** offers the reader some practical experiences in assigning glass transition temperatures. Rodriguez provides an excellent complement to the Chartoff lecture by sharing practical experiences using DMA for three commercial glassy polymers. Assessment of differences and utility of EPDM roofing materials were addressed by Paroli and Penn. Jankowsky et al. demonstrate the value of glass transition measurements to define application limits with toughened epoxy composites examples. In the final paper, Gupta brings a "whole laboratory" perspective to glass transition measurements by examining automotive coatings with DSC, DMA, and TMA methods.

It was the intent of Committee ASTM E–37 in sponsoring this symposium and the subsequent STP to review the current understanding of the glass transition and the measurement practices being applied to its identification. This would serve as a technical resource for the various task groups in subcommittee E–37.01 which are engaged in preparing or revising standard test methods to ensure their utility, relevance, and quality. I believe all of this and more has been accomplished here. One point in particular has become pervasive in E–37 thinking: We are assigning a reproducible temperature from explicit experimental protocols to represent the glass transition interval, not measuring an unequivocal glass transition temperature. This conversion in thinking is critical for successful communication between laboratories measuring the glass transition phenomenon in materials and is being

integrated into all of our standard test methods. It is hoped that this text will be as useful a resource to others as well.

The undertaking of any such technical activity as the symposium and this STP cannot succeed without a tremendous amount of support and participation. A very special thanks to my symposium committee Drs. Earnest, Riga, and Cassel and the ASTM staff including Margie Lawlor, Dorothy Savini, Rita Hippensteel, and Therese Pravitz. Many thanks also to the lecturers, presenters, and volunteer reviewers who have made this a quality technical accomplishment.

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