

On Fictive and Real Kinetics of the Glass Transition

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The apparent activation energy, E_a , of the glass transition and the dynamic fragility index, m , are characteristic properties of the molecular (or atomic) interactions in supercooled melts of glass-forming materials. These properties are related to the glass-forming ability, the kinetics of relaxation in the glassy state and the stability of glasses.

These parameters can be determined using differential scanning calorimetry (DSC) by measuring the cooling rate dependence of the glass transition. Such measurements are associated with two major problems. The first is due to the influence of the thermal inertia on the measured curves, and the second is linked to the stability of the materials. There are organic compounds that cannot be cooled from the melt due to stability limitations. Such glasses are produced using techniques like lyophilization or spray drying. Glasses-forming metal alloys may have a high tendency to crystallize. For such materials, glasses are produced using fast cooling techniques such as splat quenching or melt spinning. In such cases, many authors attempt to derive kinetic data of the glass transition from the apparent heating rate dependence of the glass transition.

This contribution discusses the determination of kinetic parameters from cooling and heating measurements using DSC and fast DSC (FDSC) at consideration of the influence of the thermal inertia and its correction. It is shown that the use of heating measurements cannot provide meaningful kinetic data because the apparent heating rate dependence of the glass transition is essentially due to thermal inertia.

The materials of investigation cover a wide range of glass formers. They are a soda-lime silica glass, a palladium based metallic glass forming alloy and a non-crystallizing polymer (polystyrene).