CHARACTERIZATION OF METASTABLE POLYMERS BY FSC TAKING INTO ACCOUNT (RE)ORGANIZATION PROCESSES

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ABSTRACT

It is well known that many crystallizable materials and substances, and especially polymer systems, are capable to adjust their crystallization behaviour – and by that their morphology and resulting end properties – to the conditions imposed. In doing so, they switch from an existing to another metastable state related to the actual dimensions and (im)perfections of the nano-to-sub-micrometer sized structures developing, and as related to the operating interactions of constituting macromolecules.

A dominant one amongst these conditions, given a specific molecular architecture, is the thermal history, specifically the temperature - time ramps the system experienced, during which treatment the system passes many metastable states On one hand metastability facilitates the realization of various, and sometimes quite different properties, on the other hand it poses a problem for characterization because the analytical techniques applied often interact with the system studied, for example by contributing to the thermal history themselves, causing changes in the system during the measurement. In industrial characterization usually a standard measuring set of fixed temperature - time ramps is applied and the results for samples are compared on the basis of such a set. However, by this just a snapshot of the metastability spectrum is obtained, which is not necessarily the relevant one in case a problem is at hand.

To arrive at a profound understanding of the possible metastable states of a polymer system and related properties, a full evaluation changing the thermal conditions – specifically cooling and heating rates – is very helpful in order to enable interpretation by using knowledge of the relations between thermal history and states of different metastability. It is anyhow a necessary precursor of the development of a specific protocol for a useful 'quick and dirty' standard measurement set.

However, in the past, at least two reasons obstructed such an evaluation. Firstly, such an evaluation asks for expertise in the field of crystallization and morphology. Moreover, it is time consuming. Both pose a sincere problem for industrial research laboratories, while the expertise needed asks for higher-level skills and knowledge of the researchers involved than before. Secondly, up till recently, such an extended characterization also appeared to be impossible because of inadequate capabilities of the instrumentation available.

In the field of thermal analysis the second reason – inadequate capabilities of instrumentation – has been remedied in the last decade by the appearance of Fast Scanning Calorimeters (FSC), see www.scite.eu for references. Specifically the introduction of High Performance DSC [HPer DSC; and its commercial equal: HyperDSC]; the RHC and the Chip-Calorimeters in recent years has a profound impact on the capabilities of thermal analysis. Characterization by thermal analysis especially demonstrates the presence and impact of metastability through the (re)organization phenomena encountered on a daily basis like – well known to thermal analysts – supercooling, amorphization, 'hot' crystallization, cold crystallization, (re)crystallization, (re)melting, annealing etc. Another reason to apply FSC in addition to Standard DSC is that, in practice, quite some physical and chemical processes occur at much higher scan rates than realizable using Standard DSC. The necessity of accounting for the influence of (re)organization effects in the research efforts using analytical characterization techniques will be shown and discussed for polymers. Examples will be presented as obtained by Standard DSC, HPer DSC and by the recently introduced Flash DSC 1, a power compensation twin-type, chip-based ultra-fast calorimeter.