

# Characterization Methods for Polymer Systems

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**Abstract:** In this paper, new method for determining Rigidity temperature applying cooling curve analysis. The determined values of Rigidity temperatures for three AlSi8Cu3 alloys with different contents of Strontium using thermal analysis technique have been compared with Rigidity temperatures obtained using mechanical technique (viscosity measurement). It was established that there is good correlation between measured values of Rigidity temperatures determined using both above mentioned techniques. Thermal analysis is a useful tool for investigating the properties of polymer/clay nanocomposites and mechanisms of improvement of thermal properties. This review work presents examples of applications of differential scanning calorimetry (DSC), modulated temperature differential scanning calorimetry (MT-DSC), dynamic mechanical thermal analysis (DMA), thermal mechanical analysis (TMA), thermogravimetric analysis (TG) and thermoanalytical methods.

**Keywords:** Polymer, Characterization , Rigidity, Thermal

## I. INTRODUCTION

Several, recent, revolutionary advances in combinatorial (or high throughput, HT) polymer science have appeared in the literature, which significantly accelerate the rate of data generation. Although these new HT approaches may in part have been inspired by the similar application of HT concepts in the catalyst field, the development of these methods for polymer. research required new techniques be created specifically for the unique issues associated with polymers. These elegant advances are a challenge placed before the polymer community to create new more efficient analytical, synthetic, processing, and characterization methods useful for the study of other polymer problems. The goal of our research program is the development of a system of HT methods for rapid, detailed study of polymer nanocomposites. Whenever possible we attempt to keep the cost of the approach in mind and use standard commercially available equipment.

An additional goal of our research focuses on the development of fundamental structure-property relations for polymer nanocomposites. Our primary interest is to develop an understanding of the governing, fundamental, mechanisms behind the enhanced mechanical properties and improved flammability properties of nanocomposites. Polymer nanocomposites are prepared by mixing a polymer (or monomer) with some dissimilar material, or additive, that has one or more dimensions on the nanometer scale. Over the last few decades, a wide variety of materials and synthesis approaches have been developed that allow molecular-level control over the design and structure of nanocomposite materials. Nanocomposites have been prepared by sol gel methods [1], by in situ polymerization routes, and by using simple compounding methods. All of these approaches share a common theme; the intermingling, on the nanometer scale, of dissimilar materials for the purpose of creating new materials with properties not available from either of the component pure materials. Forexample, simple organic polymers modified with layered silicates have been

prepared with improved heat distortion temperatures, twice the modulus, a factor of ten lower permeability of gases and solvents, improved thermal stability, a 4-fold lower flammability enhanced ablative performance, and reduced rates of degradation in space. All these attributes derive from incorporation of only 5 to 10% (mass fraction) of the layered silicate, and only occur if the surface-area between the two phases is very high, i.e., the particle size of the additive is on the nanometer scale and the degree of phase mixing is homogeneous on the nanometer scale.

In other words, the fraction of material in an "interphase" must be high. During the last decade there has been steadily increasing interest in the field of polymer/clay nanocomposites since the modification of polymer matrix with small amounts of nanoparticles proved to be effective in enhancing the mechanical, thermal, fire retardant, barrier and optical properties of a variety of polymers. Thermal analysis methods were widely applied to characterize the thermal behavior of polymeric nanomaterials. The rich bibliography on polymer/clay nanocomposites shows that the effect of montmorillonite (MMT) on thermal properties of polymer is complex and many factors contribute to the enhancement, such as MMT dispersion, the strength of inter-facial interactions, catalytic effects induced by organomodifier and/or montmorillonite itself, type of polymer matrix, preparation method, etc [2].

## II. THERMAL ANALYSIS METHOD

Differential scanning calorimetry (DSC) has been widely applied in investigations of numerous phenomena occurring during thermal treatment of organoclays and polymer-clay nanocomposites, involving melting, crystallization, curing and glass transition. In a work of Tian and Tagaya DSC method was used to investigate the influence of preparation route of nanocomposite material on polymer morphology. The melting enthalpy of

poly(lactic acid)/montmorillonite (PLA/MMT) nanocomposites changed with an increase of nanoadditive content, depending on the method of nanocomposite preparation [1]. The changes of melting enthalpy,  $H$ , of the PLA/MMT system prepared by the melt extrusion were considerably higher than those obtained by solvent dissolution method. It was considered that the binding force between PLA and inorganic compound in the composite prepared by melt extrusion method was higher than in those prepared by solvent dissolution method. The automotive industry makes frequent use of the cast multicomponent hypoeutectic AlSiCu alloys. These alloys have been characterized by presence of two Al–Si and Al–Si–Cu eutectics, which are primarily responsible for defining the microstructure and mechanical properties of these alloys. Comprehensive understanding of solidification paths of these alloys is of paramount importance for metallurgical engineers. This knowledge also enable the process, quality and simulation engineers as well as designers to ensure that the casting will achieve the desired properties for its intended application after corresponding melting, liquid metal processing, mold filling and heat treatment procedure. In order to ensure that cast components have good mechanical properties their as-cast microstructures must be closely monitored.

The solidification path of AlSiCu alloys can be studied using thermal analysis technique. Application of the thermal analysis technique in the ferrous and non-ferrous casting industry has been already many years successfully employed. Cooling curve analysis has been used for many years to determine binary phase diagrams and for fundamental metallurgical studies. In using this technique, binary alloys of varying composition were studied as they cooled and the arrest points were recorded and plotted on a temperature – composition (phase) diagram. The cooling curve method is useful for commercial applications for a number of reasons: it is simple, inexpensive and provides consistent results. This technique is a good choice for determining fundamental relationships between cooling curve characteristics and as cast structure [3].

### III. PREDICTION OF THE COMPLETE LIQUID–SOLID PHASE TRANSITION CURVE

The enhancement of bioavailability of poorly water-soluble drugs is one of the most challenging problems in pharmaceutical science. Drug–polymer solid dispersion can markedly improve the dissolution rate of drugs and lead to higher bioavailability (Chiou and Riegelman, 1971, Leuner and Dressman, 2000 and Yu, 2001). However, due to the lack of miscibility between most of the insoluble drugs and commonly used hydrophilic polymers, drug tends to crystallize out of the initially homogeneous drug/polymer solution during storage, especially at high drug loading and/or when exposed to moisture (Serajuddin, 1999, Vasconcelos et al., 2007, Rumondor et al., 2009a and Marsac et al., 2010). Besides drug crystallization, amorphous phase separation may also take place (Friesen et al., 2008 and Janssens and Van den Mooter, 2009) and generate drug-rich and polymer-rich

amorphous domains, which are still thermodynamically unstable in comparison with drug crystal. Hence, crystallization may start from these amorphous domains instead of the homogeneous drug/polymer solution (Six et al., 2003, Vasanthavada et al., 2005 and Rumondor et al., 2009c). In addition, both crystallization and amorphous phase separation may be interrupted by the glass transition (Cheng, 2008 and Qian et al., 2010). Therefore, for an apparently simple drug–polymer two-component system, it can go through multiple phase separation pathways and kinetically trapped in different metastable points in the temperature-composition phase diagram. Consequently, the drug dispersion structures may vary depending both on the composition and the thermal treatment history of the solid dispersion systems. Therefore, it is highly desirable to construct a complete phase diagram as a map where the possible phases of a solid dispersion system can be located, including the liquid–solid phase transition curve (i.e., the crystallization curve, along which drug crystals coexist with a drug/polymer glass solution in equilibrium), the amorphous phase separation curves, and the glass transition curve. The multi-dimensional parameter space for polymernanocomposites, such as “polymer” and “nano-additive.” All of these materials must be miscible with one another so that a nanocomposite can form, and so that there is a strong stabilizing interaction at the interphase between the two dissimilar materials. This is essential both for the phase stability of the nanocomposite, and for optimal physical properties. These requirements introduce the next parameter, “surface chemistry.” Control of surface chemistry is most often accomplished, in layered silicate nanocomposites, by modification of the inorganic surface with an organophilic reagent, such as an alkyl ammonium, or a chelating agent. In POSS materials, many different functionalities can be incorporated directly into the structure. While this means that no additional “surface” treatment is required, there are still a large number of possible POSS materials which need to be evaluated to obtain the optimal property improvement for a specific application.

### IV. DYNAMIC MECHANICAL THERMAL ANALYSIS

One of the basic ideas of modifying polymers with nanoplates of clays is to enhance the material's mechanical properties. DMA was frequently used in nanocomposites characterization since it allows the measurement of two different moduli of the nanocomposites, a storage modulus ( $E'$ ) which is related to the ability of the material to return or store mechanical energy and a loss modulus ( $E''$ ) which is related to the ability of the material to dissipate energy as a function of temperature. DMA data show significant improvements in the storage modulus over a wide temperature range of a number of polymer nanocomposites with MMT, such as PVDF, PP and PMMA. For all aluminum cast alloys, the transformation from liquid to solid state is accompanied by a decrease in volume in the ranges between 4% and 8%, dependent on the type of alloy. In order to fulfill the

volume deficit, the cast parts during solidification need to be fed with extra volume of liquid melt. The main intention in this case is to prevent shrinkage formation by maintaining a path for fluid flow from the higher heat mass and the pressure of the riser to the isolated liquid pool. Campbell [8] summarized the five characteristic feeding mechanisms that can occur during solidification of aluminum cast alloys. They are: liquid feeding, mass feeding, interdendritic feeding, burst feeding and solid feeding. Among these mechanisms liquid and mass feeding are relatively uncomplicated because of the low viscosity and wide active feeding path. After mass feeding resistance to melt flow increased considerably [4].

The crystallization process of aluminum cast alloys begins with the development of primary  $\alpha$ -aluminum dendrite network. A dendrite is a characteristic tree like structure of crystal growing as molten metal freeze. Dendrites normally grow from a single nucleus both forwards (primary) and sideways (secondary) which may be only a few  $\mu\text{m}$  in diameter. During the early stages of the aluminum alloy solidification dendritic crystals are separate and move freely in the melt.

However, as the melt cools, the dendrite tips of the growing crystals begin to impinge upon one another until a coherent dendritic network is formed. The temperature at which this occurs is called Dendrite Coherency Temperature (DCT) and is very important feature of the solidification process. After coherency point solidification mode has been changed in favor of growth and coarsening of secondary dendrite arms. The impingement of  $\alpha$ -aluminum crystals at dendrite coherency temperature lead to sharp decrease in the flow of the residual melt. Furthermore this temperature marked the moment when the "mass" feeding transferred to interdendritic feeding [5].

## V. CONCLUSION

The Rigidity point of AlSi8Cu3 alloy has been studied using cooling curve analysis. It was found that the Rigidity point/temperature can be identified on the  $\Delta T$  curve as the second minimum, immediately after AlSi eutectic nucleation. Experimental results have demonstrated pretty fair agreements between results obtained using cooling curve technique compared with rheological measurements. We used a felodipine/PAA system to illustrate how the proposed method is used. The results predicted that the equilibrium solubility of felodipine in PAA is below 0.1 wt%. It should be noted that equilibrium solubility of drug in polymer at temperature below the glass transition temperature could not be experimentally determined, and this method provided a way to predict them.

In addition, our method predicted that the felodipine/PAA system, if amorphous phase separated, would form a phase of almost pure drug and the other phase of almost pure polymer. This prediction was consistent with the two  $T_g$ s measured in experiments.

## REFERENCES

- [1] Hickner, M. A., Ghassemi, H., Kim, Y. S., Einsla, B. R., & McGrath, J. E. (2004). Alternative polymer systems for proton exchange membranes (PEMs). *Chemical reviews*, 104(10), 4587-4612.
- [2] Ray, S. S., & Okamoto, M. (2003). Polymer/layered silicate nanocomposites: a review from preparation to processing. *Progress in polymer science*, 28(11), 1539-1641.
- [3] Groppo, E., Lamberti, C., Bordiga, S., Spoto, G., & Zecchina, A. (2005). The structure of active centers and the ethylene polymerization mechanism on the Cr/SiO<sub>2</sub> catalyst: A frontier for the characterization methods. *Chemical reviews*, 105(1), 115-184.
- [4] Mino, G., & Kaizerman, S. (1958). A new method for the preparation of graft copolymers. Polymerization initiated by ceric ion redox systems. *Journal of Polymer Science*, 31(122), 242-243.
- [5] Wingender, J., Neu, T. R., & Flemming, H. C. (Eds.). (2012). *Microbial extracellular polymeric substances: characterization, structure and function*. Springer Science & Business Media.