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Several Kinds of Thermal Analysis Technologies of Measuring Glass Transition Temperature

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ABSTRACT
Thermal analysis technology is a general term of a set of techniques that can measure the material's performance varying with temperature. The thermal property, volumetric property, mechanical property and electrical property of polymer exist obvious difference through glass transition, tracking these properties' variation with temperature changes can determine its GTT (glass transition temperature). According to different measuring principles, these thermal analysis technologies of testing GTT are divided into following several categories, they are differential scanning calorimetry (DSC), differential thermal analysis (DTA), modulated differential scanning calorimetry (MDSC), thermo-mechanical analysis (TMA), dynamic thermomechanic analysis (DMA) and dielectric thermal analysis (DEA). The article introduces their testing methods, characteristics and influencing factors, in order to provide a reference for choosing appropriate technique to measure the glass transition temperature.
Key words- Thermal analysis technology, Polymer, GTT

I. INTRODUCTION

Glass transition is the inherent nature of amorphous polymer materials, is the macro-reflection of the transformation of polymer's molecular motion form. The structure of macromolecular is much more complex than micro-molecular, so its molecular motion presents more complexity and diversity. According to the different moving force of macromolecular, the vast majority of polymer materials usually situate in following four physical states (or mechanical states): glassy state, viscoelastic state, high-elastic state (rubbery state) and viscous state. Polymer's glass transition is the transformation between glassy state and high-elastic state. When molten polymer slowly cools off it always reaches a temperature range below which the whole chain and chain segment of macromolecular can hardly move, then we call this state glassy state and name this temperature range glass transition temperature (T_g).

Glass transition can be divided into two types, one is traditional glass transition temperature and another one is called dynamic glass transition temperature. The former can be gained by traditional DSC, DTA or TMA, and it is mainly affected by cooling speed. The latter is mainly restrained by frequency and can be measured by DSC, DMA or DEA. Actually, the dynamic glass transition temperature is always higher than traditional glass transition temperature.

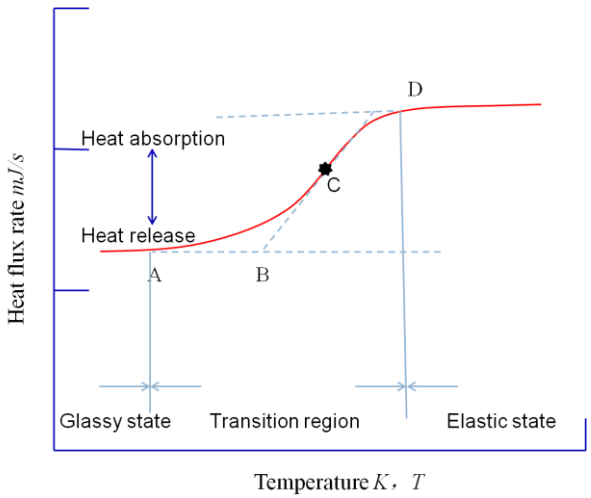
Glass transition temperature (T_g) is one of polymer's characteristic temperature, it is used as technical index of polymer. Take T_g as a boundary, polymer demonstrates different physical properties. When temperature is higher than T_g the polymer was rubber, yet when temperature is lower than T_g the polymer becomes plastic. Measuring T_g is meaningful for researching polymer material's application performance and processing property.

II. Testing methods of different thermal analysis technology to determining Tg

2.1 DSC/DTA/MDSC

When temperature changes across the T_g, the specific heat of polymer material often changes, too. And that differential scanning calorimetry (DSC), differential thermal analysis (DTA) and modulated differential scanning calorimetry (MDSC) all can detect this kind of thermal effect. At lower temperature, the freeze of molecular rearrangement results in lower specific heat. This change was relatively small, it is a stage in the direction of heat absorption on the DSC/DTA/MDSC curve when the temperature rises at constant speed. Generally, the front and back extrapolated baseline of the stage and the tangent line through the curve's inflection respectively intersect at two temperature points, the average value of two points is appointed to be T_g. Take DSC curve as an example, as is shown in Fig.1.

Figure 1 Typical DSC curve of glass transition



The measuring parameter of DSC/DTA equipment: inert gas (such as nitrogen), the flux is about 50mL/min, effective specimen quality is between 5mg and 20mg, heating rate is usually 20℃/min, start scanning from the temperature lower than the expectant T_g of 50℃ and stop it when temperature goes over the extrapolated terminated temperature. As for partially crystallized sample, it should be heated to the point higher than the sample melting peak end temperature of 30℃.

If the material is reactive, or needs to evaluate the performance of the current sample, only a one-time heating scanning is needed. On condition that material thermal history requires elimination, it can be shock cooled to a low enough temperature after first heating scanning then secondary heating can go on. If devitrification temperature, liquid crystal temperature or crystallization temperature needs to be noticed in the cooling process, an appropriate cooling rate should be adopted.

The measuring parameter of MDSC equipment: take traditional DSC linear heating as basis then superpose a sinusoidal oscillation so that we can get MDSC. It can not only give out total heat flux signal of traditional DSC, but also get the reversible heat flow signal related to material's specific heat and the irreversible heat flow signal associated with dynamics. It has a slower heating speed, generally 5℃/ min or less, the period is 40~100s, the amplitude is ±(0.03~3)℃. The determination of heating rate and period generally follows the principle that there are at least four periodic oscillation in the transformation temperature range.

2.2Thermomechanic analysis (TMA)

TMA refers to analyzing the function relationship between strain and temperature when material bears compression, tension, bending, shear and so on, under the condition of procedures controlling temperature. Molecular rearrangement needs more space under rubber state (elastic state) than under glassy state, so that the glass transition temperature (T_g) can be measured by TMA using the theory that the expansion coefficient of material changes above and below the T_g.

The effect of volume change is much more sensitive than the effect of specific heat change. In a certain temperature region on TMA curve, the strain will change intensely and this part of curve is shown as an arc, and the intersection of the arc's front and back tangent (temperature ONSET) is designated as T_g .

The measuring parameter of TMA equipment: inert gas, the flux is 50mL/min, under the expansion mode the sample is a 3-millimeter diameter cylinder or a 3-millimeter square block and its thickness is generally 0.5~3mm, insure two bottom surface keep smooth and parallel. Heating speed is usually 3℃/min, and starting temperature is set to at least 15℃ lower than the predicted glass transition temperature while the terminate temperature is generally 20℃higher than the predicted T_g.

Install the sample and then adjust the furnace temperature to the starting temperature, next load the probe on the sample with 0~5mN force and heat it linearly after keeping for 15min. If there is a deformation of TMA curve due to the influence of thermal history, remove the probe and cool the furnace until its temperature drops to the starting one, the second test can get normal smooth curve

2.3 Dynamic thermomechanic analysis (DMA)

Dynamic thermomechanic analysis is a technique that measures the dynamic modulus or damping of material changing with temperature under oscillating load when procedure controls the temperature. High polymer is visco-elastic material, so under the function of alternating force its elastic part and viscous part all have their own reaction and this kind of reaction changes with temperature. Polymer's dynamic mechanical behavior can simulate actual usage and it is very sensitive to glassy transition, therefore, TMA is a useful method of measuring glass transition temperature.

DMA curve generally includes the curves of storage modulus *E'*, loss modulus *E"* and loss factor tgδ this three kinds of signal. In the glass transition region, storage modulus decreases sharply to a stable platform, loss modulus and loss factor form peaks. The determination of T_g can be done by three corresponding methods, they are *E'*

curve's ONSET temperature and the peak temperature of *E"* curve and tgδ curve. The DMA has so high sensitivity that can detect very weak secondary relaxation process, especially appropriate for the determination of the T_g of high crystallization and high cross linked composite material or filling material.

The measuring parameter of DMA equipment: different manufacturers and fixtures requires different sample size, in the case of single cantilever clamp, the sample is usually rectangular strips which are flat and have no defects (no crack or bubble). The samples that come from same series require uniform size. The samples with low modulus have bigger thickness while samples with high modulus are requested to be thinner, ensure the ratio between length and thickness larger than 10 as far as possible. In inert gas or air atmosphere, heating rate is generally 1~5℃/min, the frequency is 1hz commonly, set amplitude according to the type of material and keep the deformation of sample constant (usually less than 1%). Start from 30℃ below expected glass transition region and end at 20℃ higher than transition region.

2.4 Dielectric thermal analysis (DEA)

Because of the increase of polymer chain segment motion in the glass transition process, the dipole or ions in materials is influenced by electric field and going to rearrange and consume energy, great changes of material's dielectric properties will take place, so determining the glass transition temperature can be achieved by dielectric thermal analysis (DEA).

A sinusoidal voltage is applied to two electrodes which hold the specimen and to measure current variation. Through the frequency of the excitation voltage, the change of the amplitude of responsive electric current and the phase Angle can be converted into three parameters of dielectric properties: dielectric constant *ε'*, loss factor *ε"* and dielectric loss *tgδ*. In the glass transition process, dielectric constant curve and dielectric loss curve will appear a meteoric rise, while the loss factor curve will form a peak. Draw tangents of curve's flat part and steep part, and the intersection point is designated as ONSET temperature of *ε'* and *tgδ*, and the peak value of *ε"* is determined as glass transition temperature.

The measuring parameter of DEA equipment: the sample can be solid, liquid and colloid, choose sensors according to different samples, flat-plate sensor is generally used, heating speed is 3℃/min, frequency is usually 1hz.

III. Conclusion

Measurement of glass transition temperature is usually influenced by internal and external factors, as for high polymer flexibility of molecular chain, intermolecular forces as well as copolymerization, blending, cross-linking, plasticizing, etc are important internal factors that affect the T_g. And external factors mainly refer sample (such as sample size, sample history, etc.), heating speed and frequency and so on.

In terms of sensitivity, the order of these is six kinds of thermal analysis technology is DMA >DEA > TMA > MDSC > DSC > DTA. If same sample can get assessment from the several techniques at the same time, more comprehensive information could be achieved.

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