Dynamic Mechanical Analysis Basics: Part 2 Thermoplastic Transitions and Properties

Introduction

The new PerkinElmer® DMA 8000 allows accuracy and precision measurements of the transitions seen in thermoplastics. These transitions, caused by molecular motions and free volume changes, define how a polymer will behave at a certain temperature. Dynamic Mechanical Analysis (DMA) is a powerful technique for studying these transitions.[1]

The thermal transitions in polymers can be described in terms of either free volume changes[2] or relaxation times. A simple approach to looking at free volume, which is popular in explaining DMA responses, is the crankshaft mechanism[3] where the molecule is imaged as a series of jointed segments. From this model, it is possible to simply describe the various transitions seen in a polymer. Other models exist that allow for more precision in describing behavior; for example, the Doi-Edwards Model.[4] Aklonis and Knight[5] give a good summary of the available models, as does Rohn.[6]

The Crankshaft Model

The Crankshaft Model treats the molecule as a collection of mobile segments that have some degree of free movement. This is a very simplistic approach, yet very useful for explaining behavior, as seen in Figure 1. As the free volume of the chain segment increases, its ability to move in various directions also increases. This increased mobility in either

Key Features

- The Crankshaft Model of polymer responses
- Review of various types of thermal transitions and their importance
- Overview of how DMA aides in the understanding of thermoplastic properties

PerkinElmer® precisely.

the side-chains or in small groups of adjacent backbone atoms results in a greater compliance (lower modulus) of the molecule. These movements have been studied and Heijboer[7] classified β, and α transitions by their type of motions. The specific temperature and frequency of this softening help drive the end use of the material.

Moving from very low temperature, where the molecule is tightly compressed, to a higher temperature, the first changes are the solid-state transitions. This process is shown in Figure 2. As the material warms and expands, the free volume increases so that localized bond movements (bending and stretching) and side chain movements can occur. This is the gamma transition, T_γ, which may also involve associations with water. As the temperature and the free volume continue to increase, the whole side chains and localized groups of 4-8 backbone atoms begin to have enough space to move and the material starts to develop some toughness.[8] This transition, called the beta transition T_β, is not as clearly defined as described here. Often it is the T_g of a secondary component in a blend or of a specific block in a block copolymer. However, a correlation with toughness is seen empirically.[9]

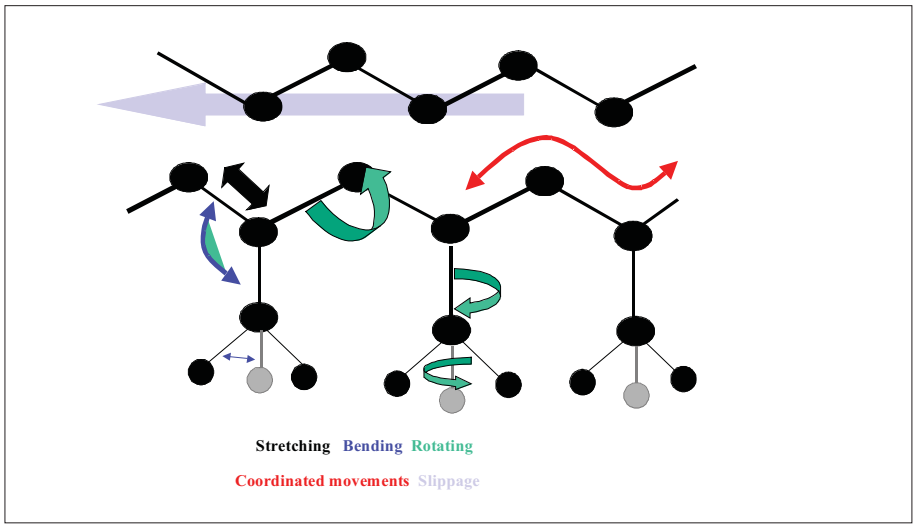

Figure 1. The Crankshaft Model shows the types of molecular motions detected in the DMA 8000.

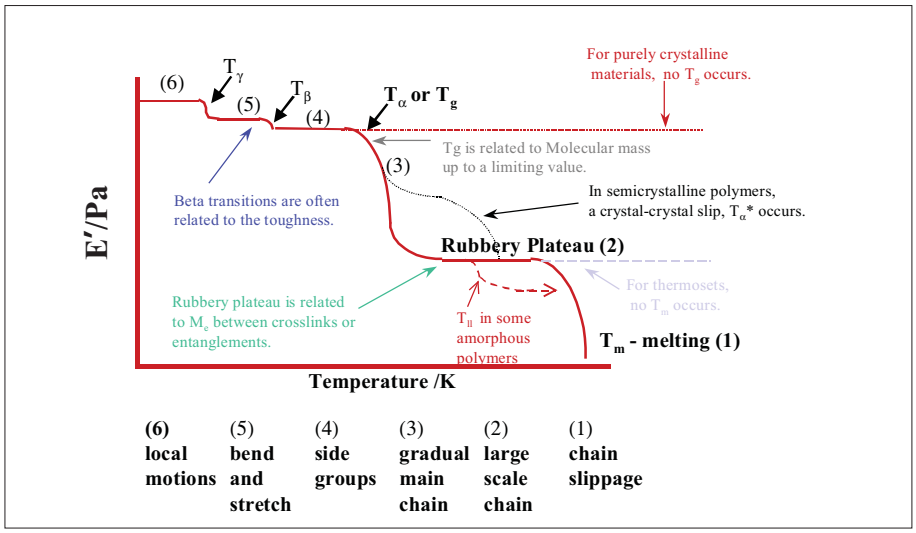

Figure 2. An idealized DMA scan showing the types of transitions seen in the DMA 8000.

As heating continues, the T_g, or glass transition, appears when the chains in the amorphous regions begin to coordinate large scale motions. One classical description of this region is that the amorphous regions have begun to melt. Since the T_g only occurs in amorphous material, in a 100% crystalline material there would not be a T_g. Continued heating drives the material through the T_α* and T_{ll}. The former occurs in crystalline or semi-crystalline polymer and is a slippage of the crystallites past each other. The latter is a movement of coordinated segments in the amorphous phase that relates to reduced viscosity. These two transitions are not universally accepted. Finally, the melt is reached where large-scale chain slippage occurs and the material flows. This is the melting temperature, T_m. For a cured thermoset, nothing happens after the T_g until the sample begins to burn and degrade because the crosslinks prevent the chains from slipping past each other.

This quick overview provides an idea of how an idealized polymer responds. Now a more detailed description of these transitions can be provided with some examples of their applications. The best general collection of this information can be found in McCrum's 1967 text.[3]

Sub-T_g transitions

The area of sub-T_g or higher order transitions has been heavily studied[10] as these transitions have been

associated with mechanical properties. These transitions can sometimes be seen by DSC and TMA, but they are normally too weak or too broad for determination by these methods. DMA, DEA, and similar techniques are usually required.[11] Some authors have also called these types of transitions[12] second order transitions to differentiate them from the primary transitions of T_m and T_g, which involve large sections of the main chains. Boyer reviewed the T_β in 1968[13] and pointed out that while a correlation often exists, the T_β is not always an indicator of toughness. Bershtein[14] has reported that this transition can be considered the "activation barrier" for solid-phase reactions, deformation, flow or creep, acoustic damping, physical aging changes, and gas diffusion into polymers as the activation energies for the transition and these processes are usually similar. The strength of these transitions is related to how strongly a polymer responds to those processes. These sub-T_g transitions are associated with the materials properties in the glassy state. In paints, for example, peel strength (adhesion) can be estimated from the strength and frequency dependence of the sub-ambient beta transition.[15] For example, Nylon 6,6 shows a decreasing toughness, measured as impact resistance, with declining area under the T_β peak in the tan δ curve. It has been shown, particularly in cured thermosets, that increased freedom of movement in side chains increases the strength of the transition. Cheng[16] reports in rigid rod polyimides that the beta transition is caused by the non-coordinated movement of the diamine groups although the link to physical properties was not investigated. Johari has reported in both mechanical[17] and dielectric studies[18] that both the β and γ transitions in bisphenol-A-based thermosets depends on the side chains and unreacted ends, and that both are affected by physical aging and postcure. Nelson[19] has reported that these transitions can be related to vibration damping. This is also true for acoustical damping.[20] In both of these cases, the strength of the beta transition is taken as a measurement of how effectively a polymer will absorb vibrations. There is a frequency dependence in this transitions like in the T_g, although its activation energy is only 30-40 J/g.

Boyer[21] and Heijober[7] showed that this information needs to be considered with care as not all beta transitions correlate with toughness or other properties. This can be due to misidentification of the transition, or that the transition does not sufficiently disperse energy. A working rule of thumb[22] is that the beta transition must be related to either localized movement in the main chain or very large side chain movement to sufficiently absorb enough energy. The relationship of large side chain movement and toughness has been extensively studied in polycarbonate by Yee[23] as well as in many other tough glassy polymers.[24]

Less use is made of the T_γ transitions and they are mainly studied to understand the movements occurring in polymers. Wendorff[25] reports that this transition in polyarylates is limited to inter- and intramolecular motions within the scale of a single repeat unit. Both McCrum[3] and Boyd[26] similarly limited the T_γ and T_δ to very small motions either within the molecule or with bound water. The use of what is called 2D-IR, which couples an FT-IR and a DMA to study these motions, is a topic of current interest.[27]

The glass transition (T_g or T_α)

As the free volume continues to increase with increasing temperature, the glass transition, T_g, occurs where large segments of the chain start moving. This transition is also called the alpha transition, T_α. The T_g is very dependent on the degree of polymerization up to a value known as the critical T_g or the critical molecular weight. Above this value, the T_g typically becomes independent of molecular weight.[28] The T_g represents a major transition for many polymers, as physical properties change drastically as the material goes from a hard glassy to a rubbery state. It defines one end of the temperature range over which the polymer can be used, often called the operating range of the polymer. For where strength and stiffness are needed, it is normally the upper limit for use. In rubbers and some semi-crystalline materials like polyethylene and polypropylene, it is the lower operating temperature. Changes in the temperature of the T_g are commonly used to monitor changes in the polymer such as plasticizing by environmental solvents and increased cross-linking from thermal or UV aging.

The T_g of cured materials or thin coatings is often difficult to measure by other methods and more often than not the initial cost justification for a DMA is measuring a hard to find T_g. While estimates of the relative sensitivity of DMA to DSC or DTA vary, it appears that DMA is 10 to 100 times more sensitive to the changes occurring at the T_g. The T_g in highly crosslinked materials can easily be seen long after the T_g has become too flat and broad to be seen in the DSC. This is also a problem with certain materials like medical grade urethanes and very highly crystalline polyethylenes.

The method of determining the T_g in the DMA 8000 can be a manner for disagreement as at least five ways are in current use (Figure 3). Depending on the industry standards or background of the operator, the peak or onset of the tan δ curve, the onset of the E' drop, or the onset or peak of the E" curve may be used. The values obtained from these methods can differ up to 25 °C from each other on the same run. In addition, a 10-20 °C difference from the DSC is also seen in many materials. In practice, it is important to specify exactly how the T_g should be determined. For DMA, this means defining the heating rate, applied stresses (or strains), the frequency used, and the method of determining the T_g. For example, the sample will be run at 10 °C min^{-1} under 0.05% strain at 1 Hz in nitrogen purge (20 cc min^{-1}) and the T_g determined from peak of the tan δ curve.

It is not unusual to see a peak or hump on the storage modulus directly preceding the drop that corresponds to the T_g. This is also seen in the DSC and DTA and corresponds to a rearrangement in the material to relieve stresses frozen in below the T_g by the processing method. These stresses are trapped in the material until enough mobility is obtained at the T_g to allow the chains to move to a lower energy state. Often a material will be annealed by heating it above the T_g and slowly cooling it to remove this affect. For similar reasons, some experimenters will run a material twice or use a heat-cool-heat cycle to eliminate processing effects.

The T_g has a pronounced sensitivity to frequency, shifting about 5-7 degrees for every decade jump in frequency. The ease of multiplexing with up to 100 frequencies per run makes it relatively easy to collect this information in the DMA 8000. Measuring the activation energy associated with a transition and finding it to be about 300-400 J/g is one way to assure the measured transition is really a T_g.

The rubbery plateau, T_α* and T_{ll}.

The area above the T_g and below the melt is known as the rubbery plateau and the length of it as well as its viscosity is dependent on the molecular weight between entanglements (M_e)[29] or crosslinks. The molecular weight between entanglements is normally calculated during a stress-relaxation experiment but similar behavior is observed in the DMA 8000. The modulus in the plateau region is proportional to either the number of crosslinks or the chain length between entanglements. This is often expressed in shear as:

$$G' \cong (\rho RT)/M_e$$

where G' is the shear storage modulus of the plateau region at a specific temperature, ρ is the polymer density, and M_e is the molecular weight between entanglements. In practice, the relative modulus of the plateau region shows the relative changes in M_e or the number of crosslinks compared to a standard material.

The rubbery plateau is also related to the degree of crystallinity in a material, although DSC is a better method for characterizing crystallinity than DMA.[30] Also as in the DSC, there is evidence of cold crystallization in the temperature range above the Tg (Figure 4). That is, one of several transitions that can be seen in the rubbery plateau region. This crystallization occurs when the polymer chains have been quenched (quickly cooled) into a highly disordered state. On heating above the T_g these chains gain enough mobility to rearrange into crystallites, which causes a sometimes-dramatic increase in modulus. Standard DSC and HyperDSC® or StepScan™ Differential Scanning Calorimetry, can be used to confirm this.[31] The alpha star transition, T_α*, the liquid-liquid transition, T_{ll}, the heat set temperature, and the cold crystallization peak are all transitions that can appear on the rubbery plateau. In some crystalline and semi-crystalline polymer, a transition is seen here called the T_α*[32].

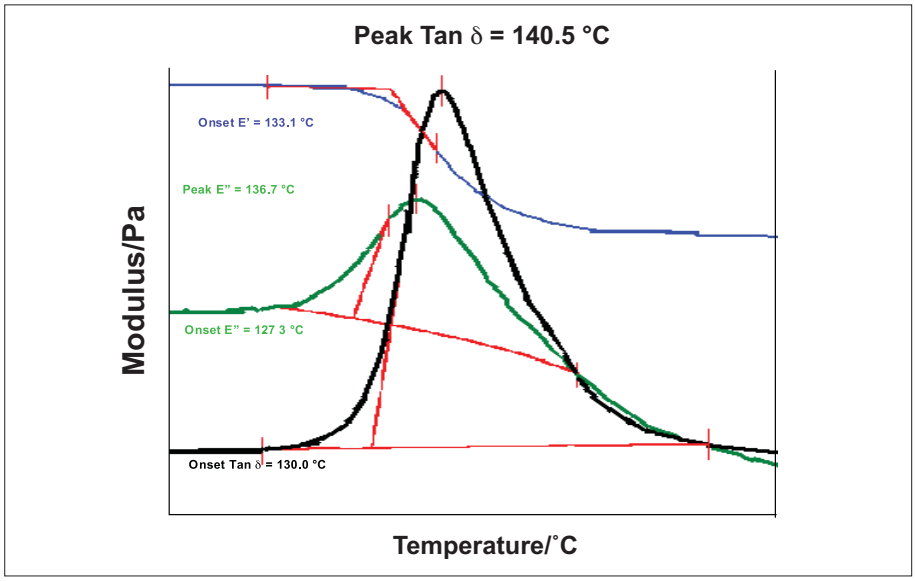

Figure 3. Methods of measuring the Tg in a DMA scan.

The alpha star transition is associated with the slippage between crystallites and helps extend the operating range of a material above the T_g. This transition is very susceptible to processing induced changes and can be enlarged or decreased by the applied heat history, processing conditions, and physical aging.[33] Hence, the T_α* has been used by fiber manufacturers to optimize properties in their materials.

In amorphous polymers, the T_{ll} transition is seen instead, which is a liquid-liquid transition associated with increased chain mobility and segment-segment associations.[34] This order is lost when the T_{ll} is exceeded and regained on cooling from the melt. Boyer[35] reports that, like the T_g, the appearance of the T_{ll} is affected by the heat history. The T_{ll} is also dependent on the number average molecular weight, M_n, but not on the weight average molecular weight, M_w. Bershtein[36] suggests that this may be considered as quasi-melting on heating or the formation of stable associates of segments on cooling. While this transition is reversible, it is not always easy to see, and Boyer[37] spent many years trying to prove it was real. It is still not totally accepted. Following this transition, a material enters the terminal or melting region.

Depending on its strength, the heat set temperature can also be seen in the DMA 8000. While it is normally seen in a TMA experiment, it will sometimes appear as either a sharp drop in storage modulus (E') or an abrupt change in probe position. Heat set is the temperature at which some strain or distortion is induced into polymeric fibers to change its properties, such as to prevent a nylon rug from feeling like fishing line. Since heating above this temperature will erase the texture, and polyesters must be heated above the T_g to dye them, it is of critical importance to the fabric industry. Many final properties of polymeric products depend on changes induced in processing.[38]

The terminal region

On continued heating, the melting point, T_m, is reached. The melting point is where the free volume has increased so the chains can slide past each other and the material flows. This is also called the terminal region. In the molten state, this ability to flow is dependent on the molecular weight of the polymer. The melt of a polymer material will often show changes in temperature of melting, width of the melting peak, and enthalpy as the material changes[39] resulting from changes in the polymer molecular weight and crystallinity.

Degradation, polymer structure, and environmental effects all influence what changes occur. Polymers that degrade by crosslinking will look very different from those that exhibit chain scission. Very highly crosslinked polymers will not melt as they are unable to flow.

The study of polymer melts and especially their elasticity was one of the areas that drove the development of commercial DMAs. Although a decrease in the melt viscosity is seen with temperature increases, the DMA is most commonly used to measure the frequency dependence of the molten polymer as well as its elasticity. The latter property, especially when expressed as the normal forces, is very important in polymer processing.

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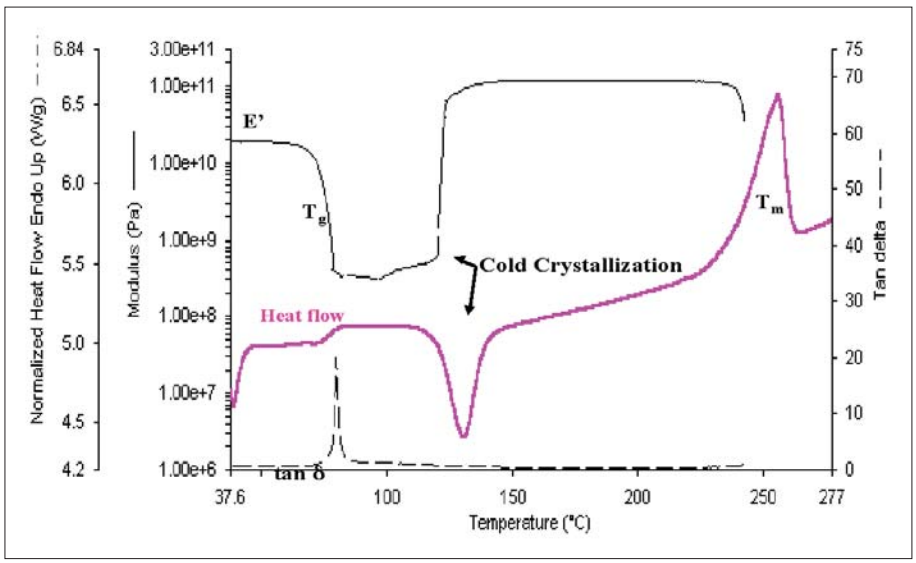

Figure 4. Cold crystallization seen in the DSC and DMA.

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PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
Phone: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

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