APPLICATIONS OF THERMAL ANALYSIS IN POLYMER AND COMPOSITES CHARACTERIZATION

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Abstract

Thermal Analysis is the generic name for a series of measurement techniques traditionally used to determine changes in material properties with temperature. No other techniques have proved more useful than thermal analysis in the material characterization. The observation of the behavior of materials and the quantitative measurement of the change on heating deliver a great deal of useful information on the nature of the material. As a result, thermal analysis has been used in many areas of basic and applied research, production, and quality control in the material science, especially polymer and polymer composites. This paper describes the application of thermal analysis techniques in the design, optimization, technical support, and QA/QC of polymer and polymer composites. The results illustrate the value of thermal analysis for characterizing polymeric materials.

Introduction

Temperature dependent variations in the physical and mechanical properties of a giving polymeric material significantly affect its application and end-use performance. In attempts to develop predictive capabilities processing properties for a giving polymeric material, a number of questions may be raised: (1) at what temperature does the polymeric material undergo a rapid loss of modulus? (2) at what temperature should the polymer be processed; (3) how rapidly does the polymer solidify as it is cooled; (4) how much does the polymeric material expand/contracted when heated/cooled. All these questions can be answered by thermal analysis, which is defined as "A group of techniques in which a physical property of a substance and/or its reaction products is measured as a function of temperature whilst the substance is subjected to a controlled temperature program"[1]. Common thermal analysis techniques include: (1) Differential Scanning Calorimetry (DSC), the most widely used thermal analysis technique, which measures the heat flow in materials and provides information about phase changes (amorphous and crystalline transitions) as well as chemical changes (degradation and reactions); (2) Thermogravimetric Analysis (TGA), which measures weight changes associated with thermal events. While TGA is most commonly used to determine compositional analysis, it is also valuable for determining thermal stability. In addition, by analyzing multiple TGA curves obtained under different heating rates, it is possible to predict long-term as well as short-term thermal stability; (3) Dynamic Mechanical Analysis (DMA), which measures the storage or elastic modulus and the loss or viscous modulus of materials subjected to sinusoidal or static stresses; (4) Thermomechanical Analysis (TMA), which measures the dimension changes (length or volume) as a function of temperature while it is subjected to a constant mechanical stress; (5) Dielectric Analysis (DEA), which measures the two fundamental electrical characteristics of a material - capacitance and conductance - as a function of time, temperature and frequency. Both capacitance and conductance can be correlated to changes in the molecular and/or structural state of the material. Due to its high sensitivity to small changes in material internal structures, DEA is more sensitive to low energy transitions, such as the glass transitions of filled epoxy systems, than are other thermal analysis techniques.

Experimental Setup

DSC experiments were conducted on a TA Q1000 DSC. The Q1000 DSC incorporates a sensor system that measures and compensates for thermal lags using a uniquely positioned, independent, null point (Tzero) thermocouple in addition to ΔT thermocouples.[2] After an initial calibration of thermal characteristics of the sensor, the recorded temperature signal corresponds to the temperature of the sample pan, not to a sensor embedded in the DSC, which is normally all that is available. Moreover, the heat flow signal is compensated to minimize the smearing (peak broadening) effects caused by cell and capsule capacitance. The Q1000's heat flow signal is the output of a four-term heat flow equation that takes into account the specific thermal characteristics of the DSC cell and capsule being used.[3]

DMA experiments were performed on a TA Q800 DMA featuring Combined Motor and Transducer (CMT) technology that provides controlled stress

capability. Based on the CMT design, DMA Q800 utilizes state-of-art, non-contact, linear drive technology to provide precise control of stress, and air bearings for low friction support. Strain is measured using optical encoder technology that provides unmatched sensitivity and resolution.

TMA experiments were conducted on a TA Q400EM TMA featuring both Dynamic TMA and Modulated TMA™. In modulated thermomechanical analysis (MTMA™), the sample experiences the combined effects of a linear ramp, and a sinusoidal temperature of fixed amplitude and period.[4,5] After Fourier transformation of the raw data, the net signals can be resolved into the reversing and non-reversing signal. Coefficient of thermal expansion is observed in the reversing signal and stress relaxation, softening and heat shrinking are observed in the nonreversing signal. As a result, both expansion and contraction can be measured simultaneously by MTMA.

TGA experiments were conducted in a TA Q500 TGA and DEA experiments were performed in a TA 2970 DEA.

Results & Discussion

1. *Characterization of a Polyester Resin/Catalyst System by TGA, DSC, and DMA*

Figure 1 demonstrates how DSC, TGA, and DMA were used to characterize the curing behavior of a polyester resin/t-butyl perbenzoate catalyst system. For the system to cure, the inhibitor must be removed from the sample. As the sample is heated, TGA detects the weight loss associated with the loss of inhibitor between room temperature and 75°C. Immediately after the loss of inhibitor, DSC detects an exothermic event (at 75°C) associated with the cross-linking/cure reaction. When a material cross-links there is a significant change in the mechanical properties of the sample. DMA easily detects the rapid increase in storage modulus at the later stages of cure as shown in Figure 1. Because DMA measures the physical and mechanical changes in a material, this technique is inherently more sensitive to the final stages of cure compared to DSC. This example shows how data from multiple thermal analysis techniques can be correlated to better understand the thermal properties of a sample.

2. *Characterization of Epoxy Reinforced Glass by DSC and DMA*

Figure 2 shows how DSC and DMA can be used to characterize the properties of an epoxy reinforced glass sample. Both DSC and DMA can be used to determine the Tg. DMA, because of its inherent sensitivity to the glass transition, is an ideal technique for identifying the Tg of highly filled systems. Absolute modulus numbers, both below and above the glass transition temperature, can be determined by plotting the storage modulus signal as a function of sample temperature. The storage modulus above Tg is related to the degree of cure (cross-link density) of the material: the higher the storage modulus above Tg, the higher the degree of cure. Tg is also an indication of degree of cure: the higher the glass transition temperature, the higher the degree of cure. Noise and vibration damping performance can be assessed by looking at the tan delta signal.

3. *Characterization of Resin Curing by DSC and Modulated DSC (MDSC)*

DSC provides quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes, or changes in heat capacity. Figure 3 demonstrates the DSC's ability to detect the glass transition temperature and residual cure in a thermosetting resin. The two most common means of analyzing degree of cure are: 1) quantifying residual cure in the as-received material and 2) measuring the shift in the glass transition temperature. By knowing the heat of reaction of the 100% unreacted material, the degree of cure of the sample can be calculated based on curing exothermic peak. The solid curve represents the data for the material exhibiting optimum physical properties. By quantifying the residual cure (79J/g) and the Tg (-5°C) of this material, the optimum cure level is established. The dashed curve, on the other hand, is the same material cured differently (75%). The dashed curve is easily identified as an "under cured" material because of the lower Tg (-12°C) and higher residual cure (145J/g).

MDSC is an enhanced DSC technique which subjects a material to a linear heating method which has a superimposed sinusoidal temperature oscillation (modulation) resulting in a cyclic heating profile. Deconvolution of the resultant heat flow profile during this cyclic heating provides not only the total heat flow obtained from conventional DSC, but also separates that total heat flow into its heat capacity-related (reversing) and kinetic (nonreversing) components.[3,6] The reversing signal contains heat capacity events such as the glass transition and melting. The non-reversing signal contains kinetic events such as crystallization, crystal perfection and reorganization, cure, and decomposition. Figure 4 shows an MDSC experiment on a sample of an epoxy resin compound. Clearly, analysis of the glass transition temperature and the curing exotherm using the total heat flow signal (conventional DSC) is difficult because of the overlapping enthalpic relaxation at the glass transition temperature and a

decrease in heat capacity during the curing process. The MDSC data, however, shows the glass transition temperature and overlapping enthalpic relaxation events can be separated into the reversing and non-reversing heat flow signals. The decrease of heat capacity during the cure is vitrification. This is the point where the crosslinking networks are established. With this network established, the reaction essentially shuts down due to a decrease in molecular mobility and the reaction becomes a diffusion-controlled process. In addition, the decrease in the sample heat capacity, as expected during the curing process, is shown in the reversing heat flow signal. Analysis of these transitions by conventional DSC is difficult because the sum of all thermal events is shown in the total heat flow signal. Transition analysis is simplified by taking advantage of the ability of MDSC to separate heat capacity and kinetic related events into more easily analyzed signals.

4. Separation Overlapping Transitions in a Thermoset Composite Printed Circuit Board by MTMA™

The total, reversing and nonreversing signals for the thermal curve of a thermoset composite printed circuit board (PCB) are shown in Figure 5. The total dimension (the blue short dash curve), which is identical to that from standard TMA, shows the masking effect on the glass transition by the enthalpic recover transition typical of aged thermoset material. The enthalpic recovery causes the test specimen to shrink as it gains mobility upon passing through the glass transition. That is, the sample contracts (due to the enthalpic recovery) and expands (due to the glass transition) at the same time with the total length change reflecting the sum of these two events. The green solid curve in Figure 5 shows the reversing expansion of the sample as a result of the increase in the coefficient of linear thermal expansion. The dark red long dash nonreversing curve contains the shrinkage information resulting from the enthalpic recovery. Clearly, MTMA signals can separate the actual Tg from the stress relation event induced by non-optimum processing of the PCB.

5. Characterization of Phenolic Fiberglass Resins by DEA

Automotive phenolic components are generated through a molding process in which the phenolic resin undergoes a chemical crosslinking reaction as the material is heated to high temperatures. Figure 6 shows the log of the conductivity as a function of sample temperature. The glass transition event of the phenolic matrix occurs at approximately 110°C as reflected by the small peaks observed in the data in this temperature region. As the temperature increases above the Tg of the phenolic resin, the conductivity shows an increase. This increase occurs because the resin becomes a viscous liquid at temperature above Tg and ionic mobility (due to trace ionic impurities) becomes an important factor in the electrical response of the material. As the resin viscosity continues to decrease with increasing temperature, it becomes easier for the trace ions to migrate through the resin, and the conductivity shows an increase. At a temperature of approximately 150°C, a small peak or inflection is observed in the conductivity data. This represents the onset of a polymerization reaction. This reaction occurs with the evolution of water and apparently results in the development of a material which has an intermediate molecular weight (i.e., non-crosslinked). As the sample temperature continues to increase, the conductivity data, after showing the inflection at 150°C, also continues to show a general increase. This behavior indicates that the resin matrix continues to exhibit a decrease in its viscosity with respect to temperature. If the material were fully cured, or crosslinked, at this point, a decrease would be obtained in the conductivity data. A maximum is observed in the conductivity data at a temperature of 240°C. This maximum generally corresponds to the point of minimum resin viscosity. As the temperature continues to increase, the conductivity shows a sharp decrease which is due to the development of a crosslinked polymer network. As the resin undergoes crosslinking, its viscosity greatly increases, and ionic mobility is hindered. This process is reflected as a drop in the conductivity data above 240°C. In summary, the DEA data demonstrates that dielectric analysis is a valuable technique for characterizing the properties of filled (or unfilled) phenolic resins. The following key parameters are obtained using DEA: (1) glass transition temperature; (2) initial polymerization reaction; (3) point of minimum resin viscosity; (4) onset of crosslinking.

Summary

Thermal analysis is an acknowledged technique in both R&D and QA/QC of materials. Valuable information can be obtained on such properties as: softening or Tg, degree of cure, rate of cure, onset of crosslinking, degradation temperatures for stability assessment, coefficients of thermal expansion, modulus (stiffness) and damping properties. The ability to measure and characterize the critical thermal, physical, degradation and mechanical properties of material in the different ways make thermal analysis well suited to handle the diversity of materials including polymer and polymer composites. The results are highly useful for research & development as well as quality assurance applications.

Reference

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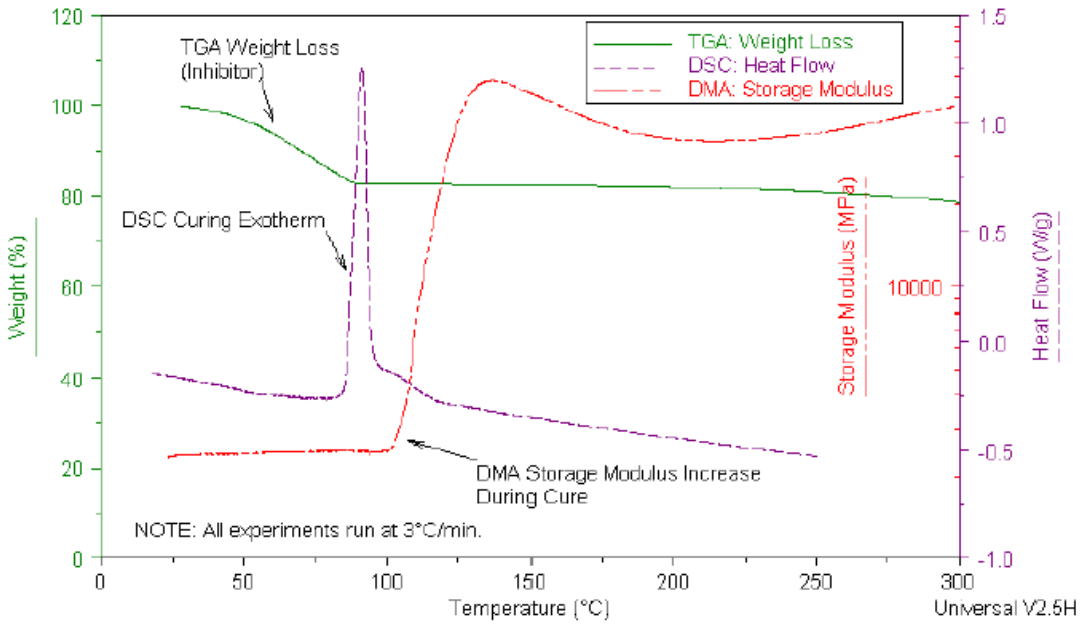

Figure 1. Overlay TGA, DSC and DMA curves of a polyester resin/t-butyl perbenzoate catalyst system.

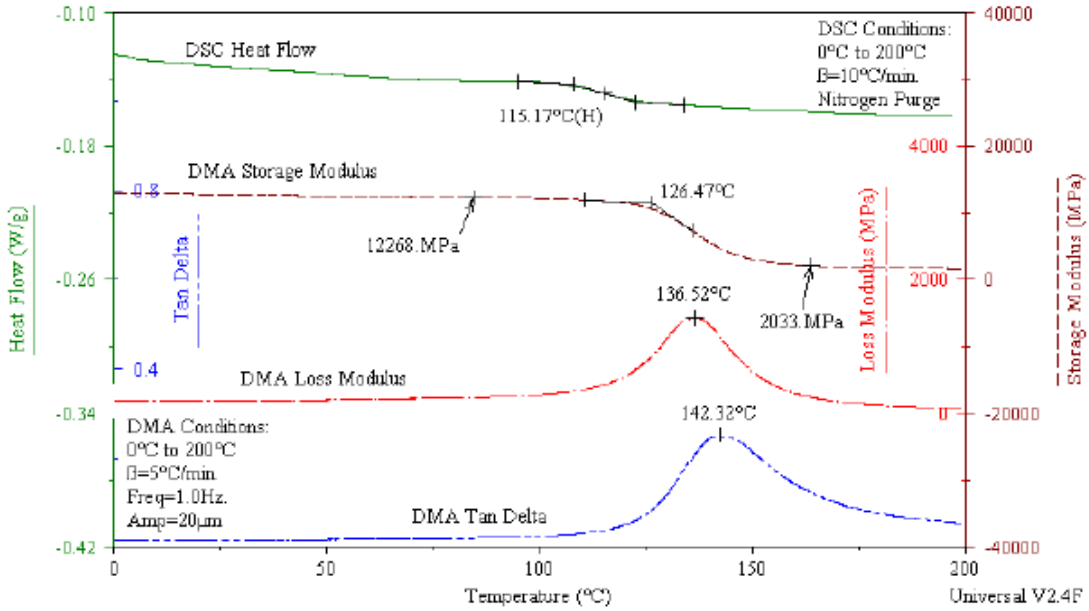

Figure 2. Overlay DSC and DMA curves of an epoxy reinforced glass sample.

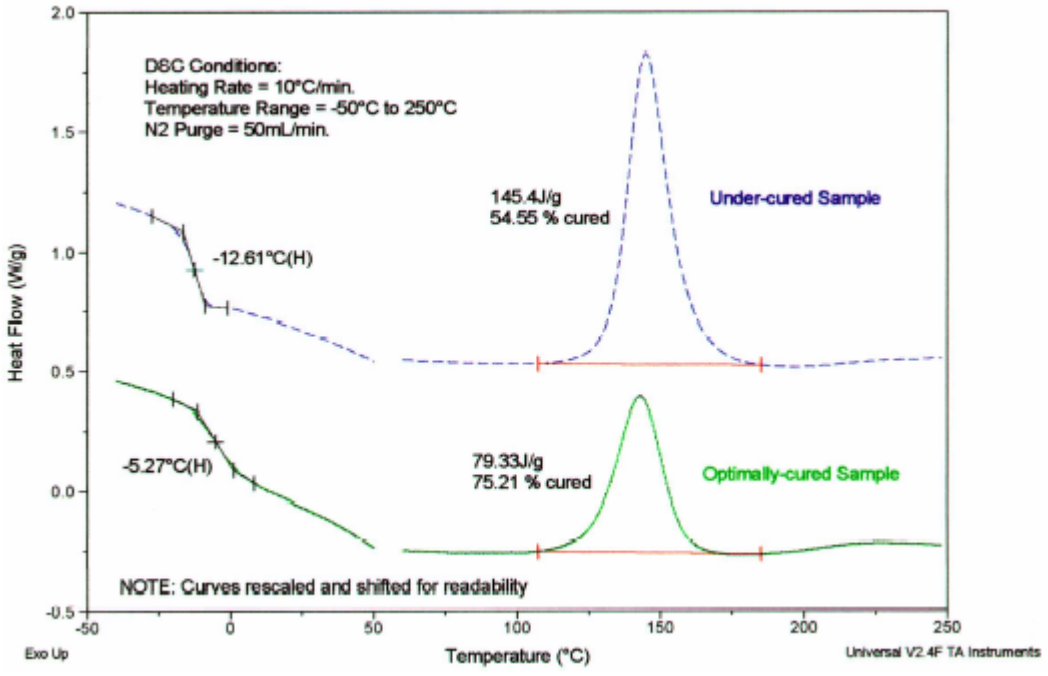

Figure 3. Characterization of the Degree of Cure of Thermosetting Resin by DSC.

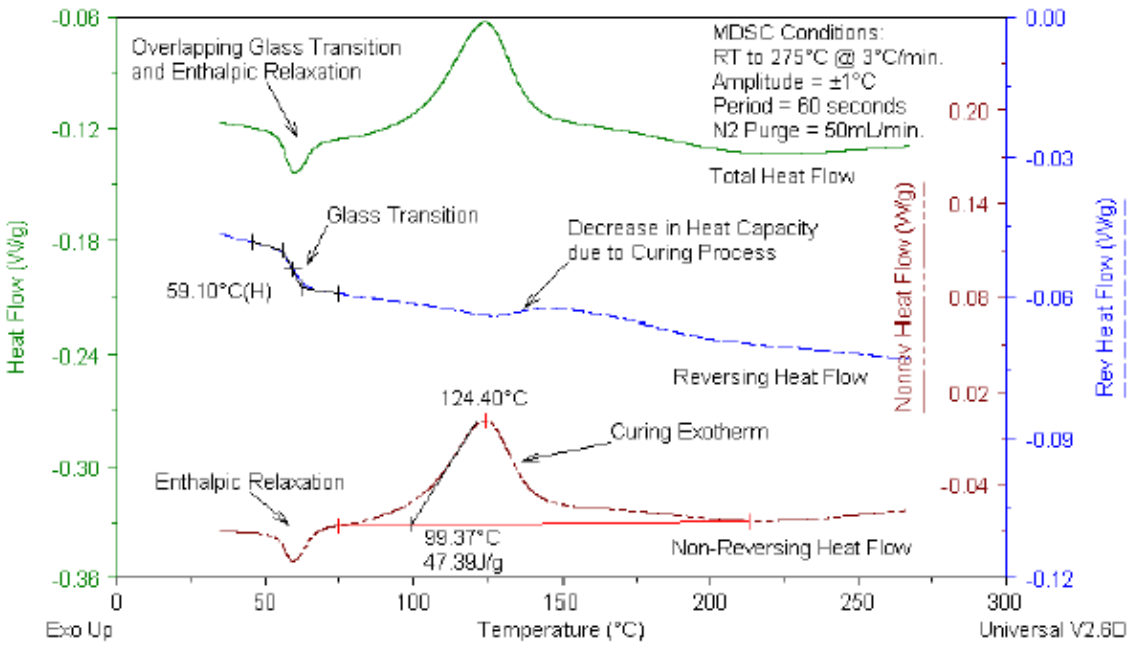

Figure 4. Characterization of an epoxy resin compound by MDSC.

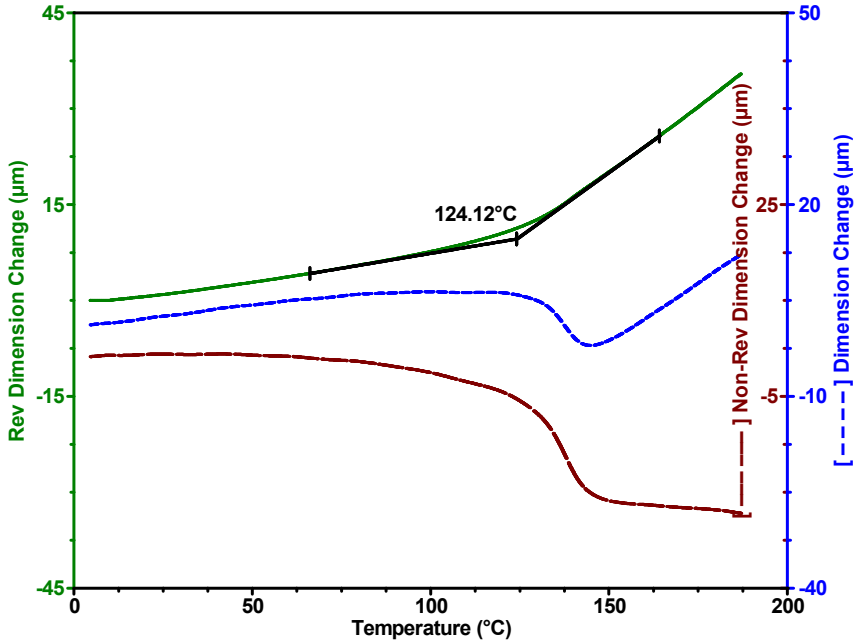

Figure 5. MTMA results of thermoset composite printed circuit board.

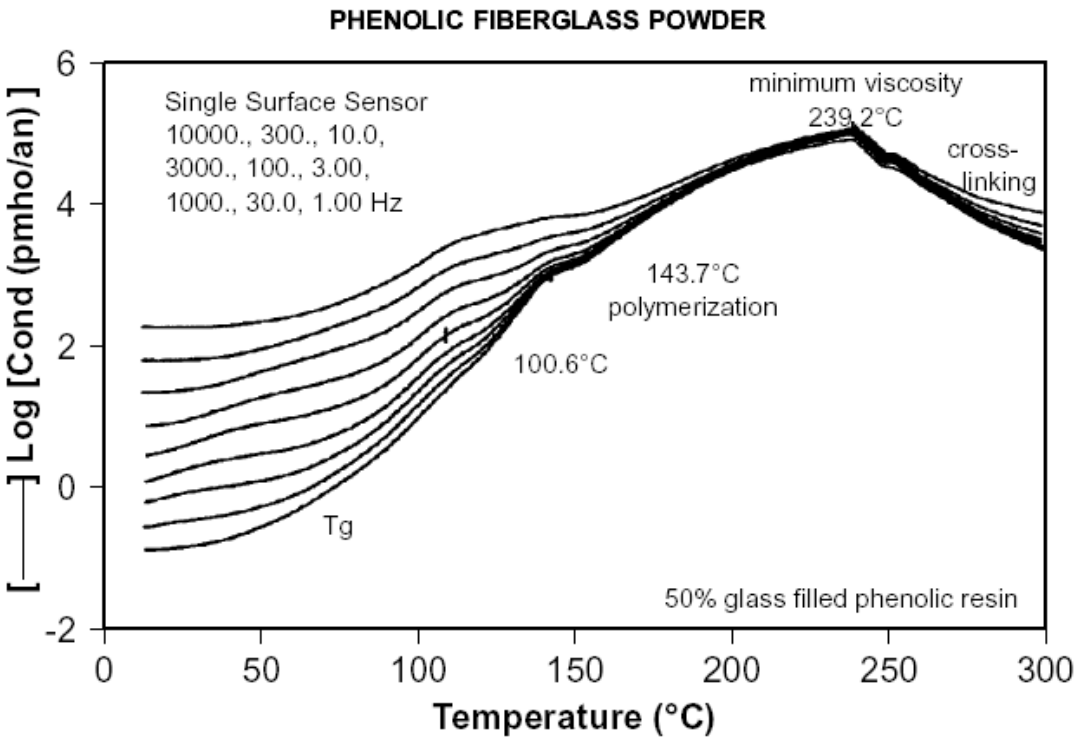

Figure 6. DEA result of a Phenolic Fiberglass Resin.