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Improved HyperDSC Method to Determine Specific Heat Capacity of Nanocomposites and Probe for High-Temperature Devitrification

Introduction

There has been tremendous interest in recent years in nanocomposites – using small scale particulate fillers – to improve the properties of thermoplastics and thermosets. For example, the effect of using such small scale filler particles is such as to toughen the plastics, reduce vapor transfer, and improve transparency. One rapid way to quantify the effect of a particular filler formulation is to measure its effect on the change in specific heat (C_p) that occurs at the glass transition (T_g). In this analysis, discussed by Christophe Schick,[1] the C_p of an amorphous nanocomposite can be usefully partitioned between three entities: (1) unaffected amorphous polymer whose properties are the same as that in the pure amorphous polymer, called the mobile amorphous fraction; (2) the C_p of the filler itself; and (3) the C_p of the polymer which is immobilized by its attachment to the nanoparticle, the rigid amorphous fraction (RAF). The properties of the composite can be related to the extent of these fractions. The chemical bonding – weak or strong – of the RAF to the nanomaterial filler may be an indicator of the performance of the nanocomposite, and it may be an indicator of how readily it will decompose in the environment. A second T_g – devitrification of the RAF – would indicate a relatively weak bond of the RAF to the nanomaterial filler.

Background

Christophe Schick demonstrated the use of the HyperDSC® technique to measure RAF and to look for evidence of devitrification of the RAF in the temperature region between the glass transition temperature (T_g) and the rate-suppressed onset of decomposition. He demonstrated how this C_p data, made accurate by corroborative use of StepScan™ methods, could be compared to the C_p function of neat polymer to further evaluate the degree of agglomeration of filler in a nanocomposite.[1]

The key relationship in his paper for quantifying the RAF in a composite is:

$$RAF = 1 - Filler\ Content - \frac{\Delta C_p}{\Delta C_p\ pure}$$

Where ΔC_p and ΔC_p pure are the changes in specific heat at the glass transition temperature, T_g, for the composite, and for the unfilled polymer, respectively.

This work suggests an alternative method for determining C_p that takes advantage of fast heating and cooling rates to obtain quantitative C_p in the upper temperature region without having to dwell in that high temperature region to establish an upper isothermal.

In the conventional method to measure C_p (ASTM® E1269), a sample is equilibrated at a low temperature and then heated at some rate to an upper temperature where the temperature is again held constant until there is full equilibration. The problem with the conventional C_p method – and with modulated temperature methods – is that the sample is likely to degrade when held at high temperatures, and this degradation compromises the accuracy of measurement.

In the method suggested here, the temperature program for the sample (and baseline) is that of heating at a very rapid rate (here 400 °C/min) to the upper temperature, then immediately cooling at the same rapid rate to a temperature sufficiently low with little or no sample decomposition. Figure 1 shows the raw data, including sensor temperature and heat flow.
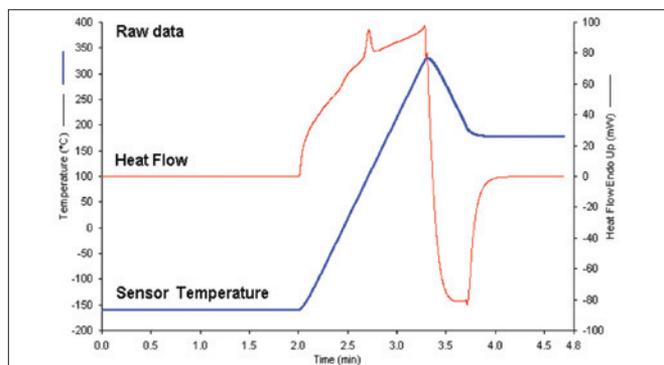

Figure 1. Raw data for thermoplastic polyurethane nanocomposite using the 400 °C/min heat-cool C_p method – analysis time: 5 minutes.

Experimental and Data Handling

The instrument employed for this analysis was the PerkinElmer® DSC 8500, a power-controlled, dual-furnace differential scanning calorimeter (DSC) with the ability to scan at rates up to 750 °C/min and achieve rapid equilibration, a requirement when using rapid scan rates. The purge gas was helium. The block heat sink temperature selected was -180 °C, with the cooling provided by the CLN₂ liquid nitrogen cooling accessory. Calibration used the two melting standards indium and lead. Encapsulation was with aluminum HyperDSC pans, which are low mass and provide optimum thermal coupling (Part No. N5203115).

When PerkinElmer Pyris™ software's AutoSlope function is selected in Preferences, all runs are automatically shifted and sloped to zero heat flow using the final heat flow points of the highest and lowest temperature isotherms. To convert to C_p units, one subtracts the iso-aligned baseline data and then selects Single Curve C_p from the Calculate/Specific Heat menu. The result is a specific heat data curve as a function of temperature tested that can be plotted, further analyzed, and saved (Figure 2).
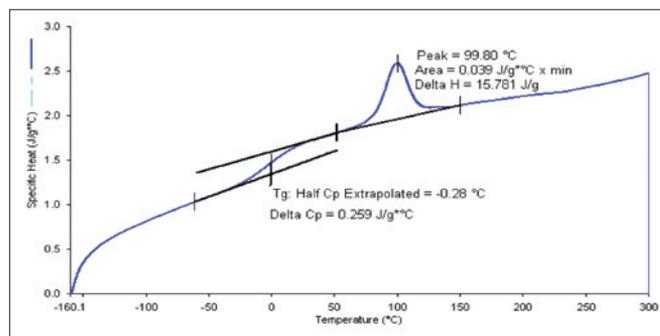

Figure 2. Specific heat capacity data for thermoplastic polyurethane composite using the 400 °C/min heat-cool C_p method, with T_g and peak calculations applied.

This method enabled the specific heat to be obtained up to 300 °C without appreciable error from decomposition. The data was delivered to the supplier of the nanocomposites in the form of tables created in Pyris and transferred into a spreadsheet (Figure 3).
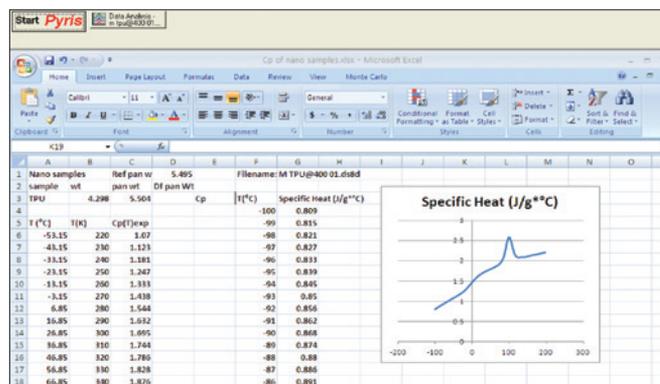

Figure 3. Microsoft® Excel® spreadsheet, for further analysis of C_p data, after transferring a table from Pyris software.

Assessing Method Accuracy

The goal of this project was to show generation of sufficiently accurate specific heat capacity data from HyperDSC – that the more time consuming StepScan analysis would not be required. To demonstrate accuracy, the same method that produced the above data was also used to analyze the smaller of the two sizes of sapphire specific heat standard in the PerkinElmer Specific Heat Kit (Part No. 02190136). The C_p results were then compared with those in the table that was provided with the kit. The 400 ˚C/min data were in agreement with literature values within 1% from -50 ˚C to 200 ˚C, and within 1.5% up to 320 ˚C. While this accuracy may be somewhat less when running plastics samples because of extraneous effects (e.g., sample inhomogeneity, moisture loss, sample movement, less than optimal thermal coupling), the sapphire test has proven that the new method can be highly accurate with proper sample preparation.
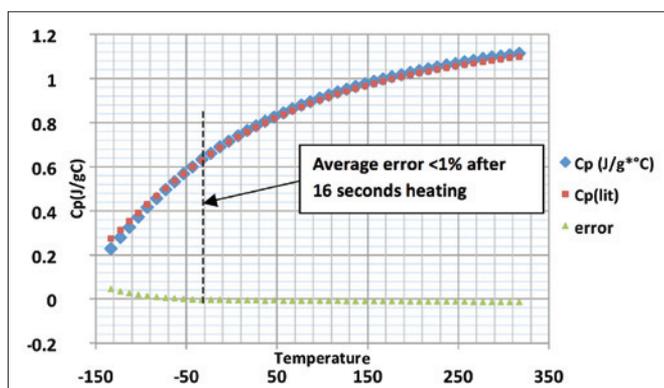
Figure 4. Specific heat capacity of sapphire using the 400 ˚C/min heat-cool method, showing Pyris data, literature data and error.

Looking for Evidence of Devitrification

The Schick et al. (2007) investigation was looking for evidence that, at higher temperatures, kinetic energy might free up the rigidly held polymer and reveal a second, but higher and weaker, glass transition attributed to devitrification of the RAF phase. This was the reason for using the HyperDSC technique to otain access to the high-temperature region as well as specific heat data, while kinetically delaying the onset of decomposition. He did not report any evidence
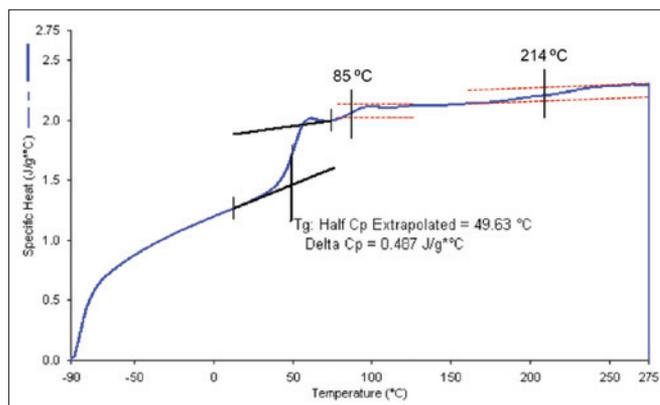
Figure 5. Specific heat capacity of uncured epoxy nanocomposite using the 400 ˚C/minute heat-cool method, showing possible second T_gs. One interpretation of this data is that the multiple T_gs are due to devitrification of RAF. Not all portions of this sample showed this effect. The sample for analysis was visibly inhomogeneous. ***Note:*** at normal DSC scan rates, or when using a modulated technique, decomposition would show additional thermal effects above 200 ˚C, which would mask evidence of devitrification.

of this devitrification effect in the formulation (PMMA and SiO_2) he investigated, but we wanted to provide a rapid method of assessing other formulations for this effect. In the (proprietary) nanocomposite samples we evaluated, we observed some evidence of increased C_p at higher temperatures, but further work would be required – including analyzing the unfilled plastics – to make any definitive statement about devitrification.

Conclusions

HyperDSC shows promise for elucidating nanocomposites. The use of a rapid heat-cool method, such as demonstrated here, extends the upper temperature range for which accurate specific heat capacity measurements are practical. This should help identify devitrification – loss of nanocomposite bonding – in the amorphous polymer system. This method further extends the utility of power-controlled DSC to investigate metastable states of polymer systems.

References

1. Sargsyan, A. Tonoyan, S. Davtyan, C. Schick, The amount of immobilized polymer in PMMA SiO_2 nanocomposites determined from calorimetric data, Eur. Polym. J. 43 (2007) 3113-3127.

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