DSC as Problem Solving Tool: Characterization of Consistency of PFA Resins

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Problem

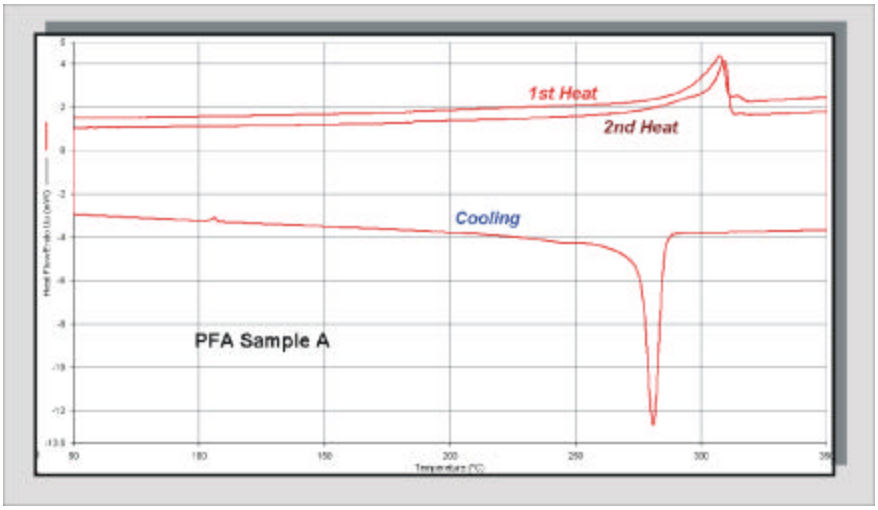
An engineer at a polymer processing facility has a need to characterize incoming feedstocks of PFA (perfluororalkoxy) polymer to ensure that the polymer will yield the desired end-use mechanical properties. The company manufactures tubing from the PFA polymer and needs to ensure that the tubes have uniform properties. There is concern that some of the lots of feedstock polymer may contain higher than expected levels of recyclates, which may yield significantly different end-use property characteristics. The need for an easy-to-perform characterization test is important to the processing facility to ensure consistency of the final PFA tubing materials.

Solution

Differential scanning calorimetry (DSC) provides a sensitive and easy-to-use means of characterizing polymeric materials, including PFA. DSC measures heat flow into or from a sample as it is heated, cooled or held isothermally.

PerkinElmer offers a number of high performance DSC instruments to accommodate a wide variety of testing needs, temperature ranges and applications. The DSC system from PerkinElmer features the user friendly Pyris for Windows software, which permits the easy set-up and analysis of DSC experiments.

Figure 1. Complete DSC results (heat-cooled-reheat) on PFA tubing sample A.



Analysis of FA Tubing Samples

In this study, the thermal properties of two different PFA tubing products were measured using DSC. Two tubes (Samples A and B), which exhibited significantly different mechanical properties, were analyzed by DSC. The samples were heated at a rate of 10 C/min from 25 to 360 C, cooled back to 25 C at 20 C/min and then reheated at 10 C/min from 25 to 360 C. The heat-cool-reheat conditions provide very valuable information on a polymer material. Cooling and reheating allows the original thermal history of the sample to be replaced by a standard and more controlled thermal history thereby providing a more sensitive means of making distinctions between two polymeric materials. For many polymer products, little difference may be seen during the 1st heating segment, but significant differences are often observed during cooling and reheating.

Displayed in Figure 1 is the complete set of DSC results generated for PFA Sample A. The plot shows the DSC heat flow as a function of sample temperature and an endothermic response (heat absorbed

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Figure 2. 1st heating segment results (as received) for PFA tubing sample A.

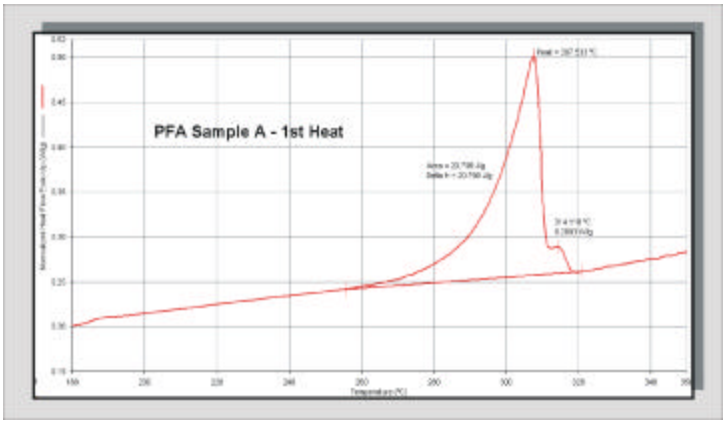


Figure 3. Cooling results obtained on PFA Sample A.

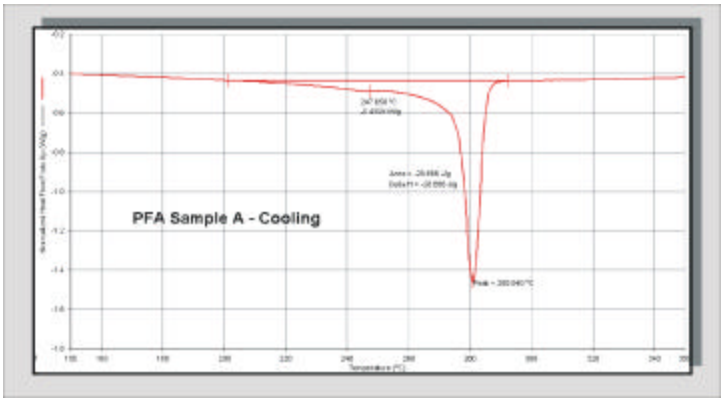
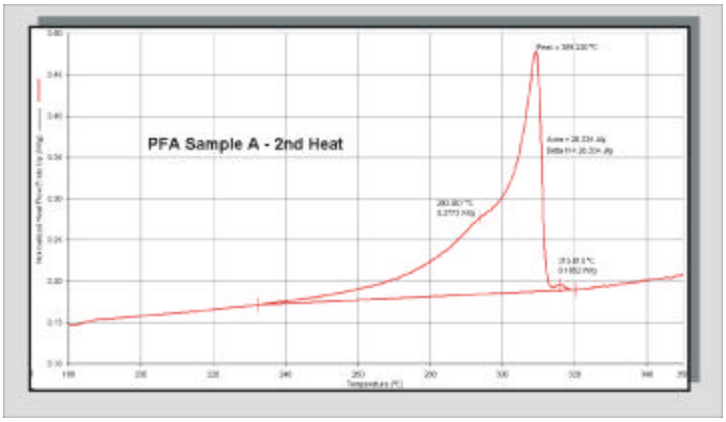


Figure 4. 2nd heating segment results on PFA sample A.



by sample) is oriented towards the top of the graph.

Shown in Figure 2 are the DSC results for the 1st heating segment for Sample A and this represents the thermal properties for the as-received material. The PFA undergoes melting at 307.5 C with a total heat of melting of 20.8 J/g. The heat of melting is an important quantity as it is directly related to the percent crystallinity of a semi-crystalline thermoplastic material such as PFA. A small, high temperature shoulder is observed on the main melting peak at 314 C.

After heating the PFA polymer through its melt, the sample was cooled, at a rate of 20 C/min, back to ambient conditions and the DSC results are displayed in Figure 3.

During cooling, the PFA resin undergoes crystallization at 280.8 C as reflected by the exothermic peak. The total heat of crystallization is 28.7 J/g for Sample A. A secondary crystallization peak occurs at significantly lower temperatures at 247.7 C. The occurrence of the lower temperature crystallization peak indicates that the resin contains a component that undergoes a distinctly separate crystallization transformation.

After cooling back to ambient conditions, PFA Sample A was reheated with its new thermal history and these results are displayed in Figure 4.

During the 2nd heat, sample A now yields its main melting peak at 309.0 C with a pronounced low temperature peak at 293.8 C. The low temperature

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Figure 5. 1st heating segment results (as received) for PFA tubing Sample B.

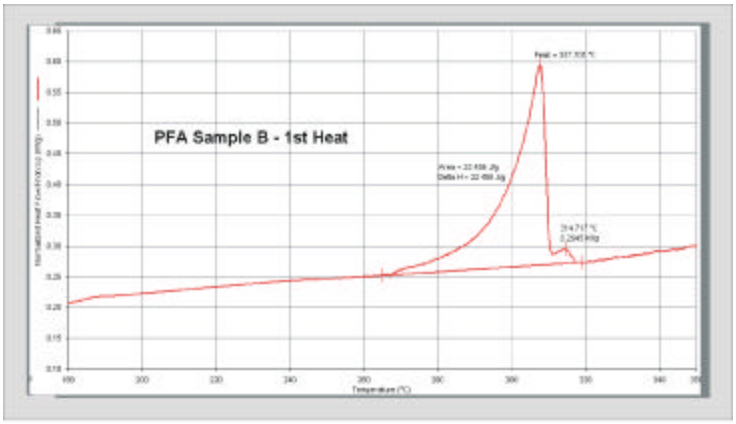


Figure 6. Cooling results on PFA Sample B.

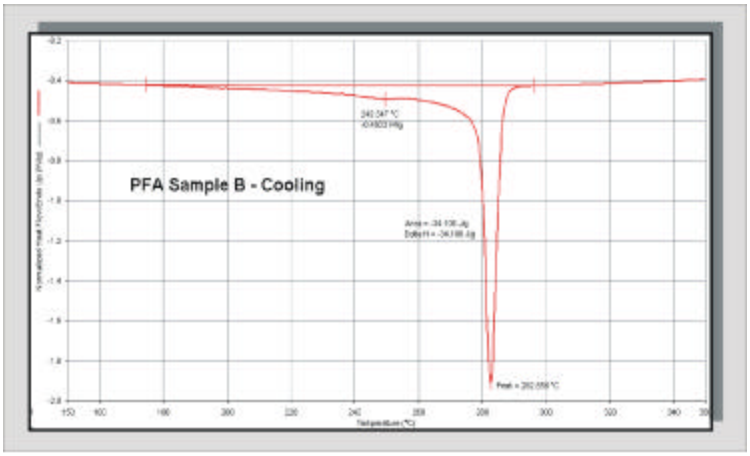
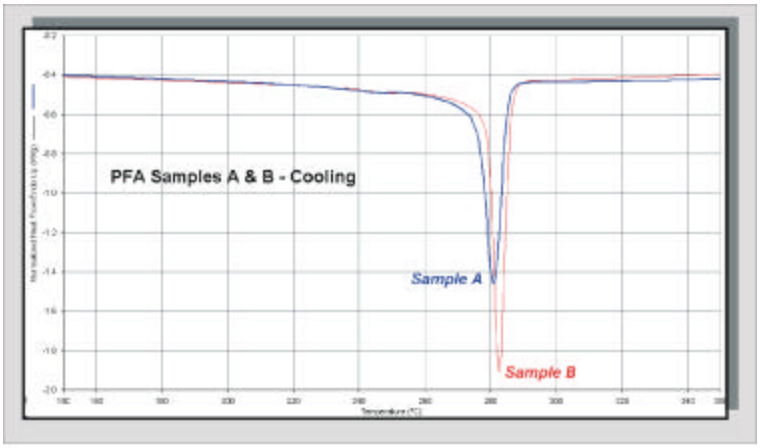


Figure 7. Cooling results for PFA Samples A and B.



melting transition reflects the component or phase that crystallized out at the lower temperature during the cooling segment. A comparison of the 1st heat results (Figure 1) with those of the 2nd heat reveal the impact and importance of thermal history on a polymer's physical properties. It is always recommended to perform a heat-cool-reheat experiment on a thermoplastic material as this cyclic approach provides more complete characterization information.

The other PFA tube (Sample B) was analyzed under identical experimental conditions as those used to characterize Sample A. The DSC results of the 1st heating segment (as received) are displayed in Figure 5 for Sample B. In order to make differences between Samples A and B more apparent, B was cooled back to ambient conditions at a rate of 20 C/min and then reheated. The results of the cooling segment are displayed in Figure 6.

The cooling data for PFA Sample B reveals that the resin undergoes rapid crystallization over a narrow temperature range as evidenced by the relatively intense exothermic peak at 282.7 C. Sample B undergoes additional crystallization at 249.3 C as reflected by the smaller peak. The total heat of crystallization is 34.1 J/g which significantly greater than the 28.7 J/g value obtained for Sample A.

An overlay of the cooling data for Samples A and B provides a direct visual comparison of the differences between the two resins and this is displayed in Figure 7. The DSC results have been normalized with regards to the sample mass for comparative purposes.

These overlaid results demonstrate that Sample B undergoes crystallization at a higher temperature

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Figure 8. 2nd heating segment results for PFA Sample B.

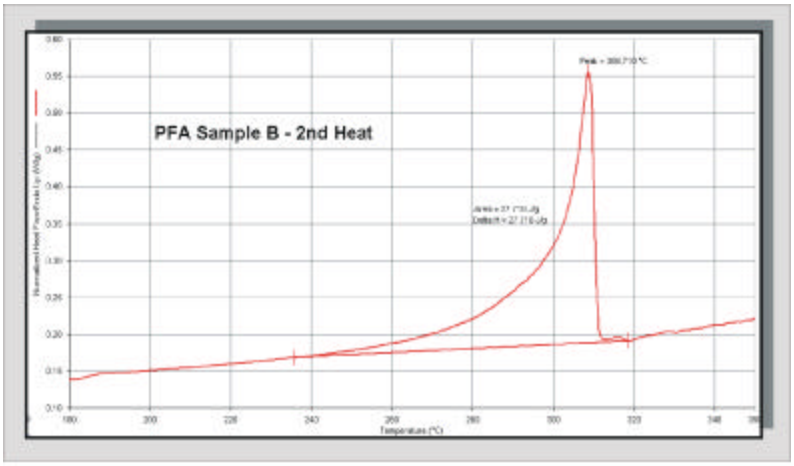
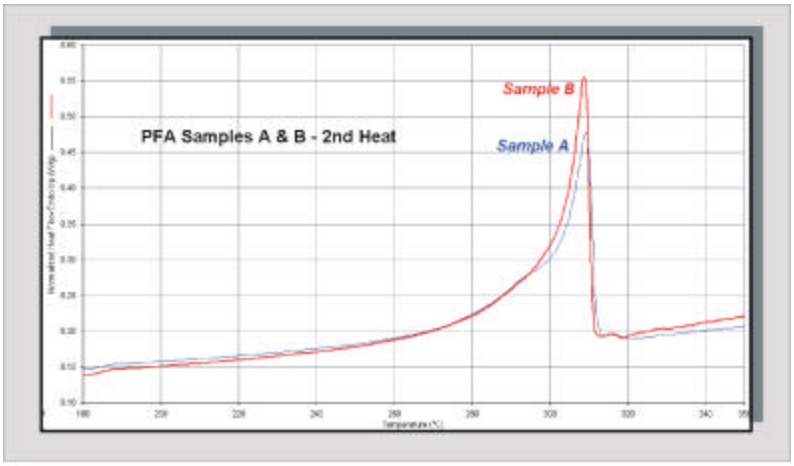


Figure 9. Overlay of 2nd heating results for PFA Samples A and B.



and much more intensely than does Sample A. This demonstrates that the properties of the two PFA feedstocks are significantly different with regards to their make-up. The crystallization of resin A is slowed down as compared to B and this may be indicative of a higher molecular weight component in A.

Sample B was cooled back to ambient conditions and then reheated through the melt with its new thermal history. The 2nd heating segment results are displayed in Figure 8 for Sample B.

During its reheat, Sample B melts at 308.7 C with a heat of melting of 27.7 J/g. In contrast with Sample A (Figure 4), B does not yield a pronounced low temperature peak in its melting endotherm. B does exhibit a low temperature 'tail', but not a clear peak. This is consistent with the fact that the cooling results showed significant differences between Samples A and B. A direct overlay of the 2nd heating segment results for Samples A and B is displayed in Figure 9.

These results demonstrate the resin B melts with a greater peak intensity as compared to Sample A, revealing that the two PFA feedstocks are significantly different with regards to their respective thermophysical properties.

Summary

The thermophysical properties of two PFA (perfluoroalkoxy) feedstock resins (used for the manufacture of polymeric tubes) were characterized with the PerkinElmer DSC. PerkinElmer offers a number of different research grade, high performance DSC instruments to accommodate a wide variety of materials, temperature ranges and applications. Oftentimes, the most valuable characterization information on polymer materials comes from performing heat-cool-heat experiments. The DSC results revealed that the two PFA resins were significantly different in terms of their crystallization and reheat melting properties. Sample B, which yielded distinctly different tensile properties as compared to A, crystallized more intensely and at a slightly higher temperature. During its 2nd heating, Sample B melted with a greater peak intensity and did not exhibit a lower temperature melting peak, as did resin A. The DSC data indicates that

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Sample A may have a different molecular weight distribution profile as compared to B and this may be due to the presence of recyclates or other chemical compositional variables.

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