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MEASUREMENT OF SPECIFIC HEAT AND ENERGETIC CHARACTERIZATION OF MATERIALS UP TO HIGH TEMPERATURES

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A new DSC system has been developed which not only allows quantitative results in the temperature of −160°C to 700°C, but also allows the quantitative determination of a variety of material properties up to 1500°C. For example, the specific heat of materials can be measured to at least 1400°C, while enthalpies, etc. can be measured to 1500°C.

Introduction

DTA and DSC have been used for many years for the study of the thermal behavior of various materials. Conventional DSC systems generally yield good results in the temperature range from approximately −160° to 700°. In this temperature range the heat transfer is essentially comprised of conduction and convection. However, at temperatures above 700° problems arise with the baseline characteristics and reproducibility of results due to radiation effects.

Experimental

Materials

The low-temperature studies were conducted using a commercial grade low- and high-density polyethylene (LDPE and HDPE) and amorphous polystyrene (PS). The high-temperature studies were carried out on AXM5Q1 Poco graphite, commercial alumina (Al_2O_3) and hafnium carbide (HfC). The test samples were cut from larger pieces of the material. The dimensions of all test samples were 6 mm diameter and 1 mm thick.

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Instrumentation

A Netzsch model 404 DSC equipped with a low-temperature furnace and a NiCr-CuNi (Type E) measuring head was used for all low-temperature measurements. The high-temperature measurements were carried out using a high-temperature platinum furnace and a Pt10%RH-Pt (Type S) measuring head. The instrument allows measurements to be conducted under vacuum or in a static or dynamic gas atmosphere. A schematic of the DSC 404 measuring part is shown in Fig. 1. Temperature control of the DSC is accomplished using a Netzsch model 413 programmer and controller. The analog signals representing sample temperature and differential temperature are processed by various Netzsch amplifiers. Data acquisition and instrument control are provided by a 16/32 bit computer system with peripheral units and the appropriate software.

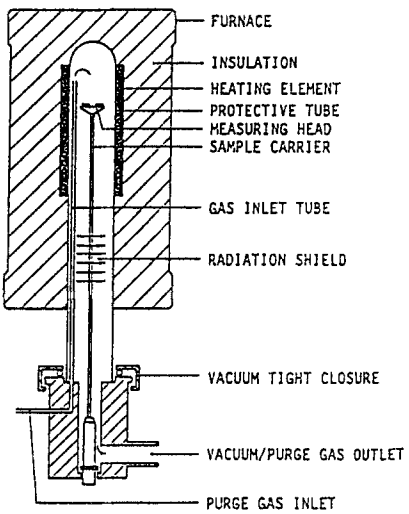

Fig. 1 Schematic of DSC 404

Procedure

The low-temperature measurements were conducted with aluminum crucibles and lids, while the high-temperature tests were carried out with platinum-rhodium crucibles and lids. Helium and argon were used for the low- and high-temperature tests, respectively. The measurements on LDPE and PS were conducted at heating rates of 10 and 5 deg/min, respectively, while all high-temperature tests were carried out at 20 deg/min. Baseline,

standard runs using sapphire and sample runs were required to obtain the necessary data to compute the specific heat. Utilizing these experimental data the specific heat was computed using the well-known ratio method. The method has been described in detail by Henderson, Emmerich and Wassmer [1].

Results and discussion

Figure 2 depicts the specific heat as a function of temperature from -150° to 375° for both HDPE and LDPE. It must be pointed out here that the peaks in the specific heat curve for both materials are a result of melting. Therefore, the values in this region represent the apparent specific heat. That is, a combination of the specific heat and melting enthalpy. As would be expected the specific heat of the low-density polyethylene below the melting point is higher than that for the high-density polyethylene. The reason for this behavior is the increased molecular motion of LDPE as compared to HDPE. As a consequence of the practically identical liquid phases (i.e. at temperatures above approximately 160°) the specific heat of both materials is almost the same. The specific heats computed for both matrials are in good agreement with literature values.

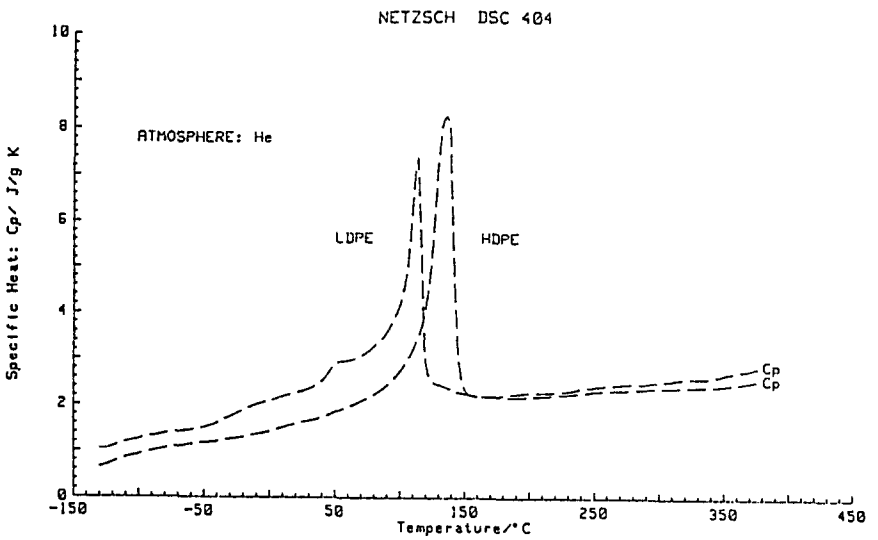

Fig. 2 Specific heat of HDPE and LDPE

Figure 3 shows the heat flow in milliwatts for low-density polyethylene in the temperature range of 0 to 200°. Clearly shown is the onset of side chain melting at approximately 42°. The onset of the main chain melting occurs at approximately 82° with a peak temperature of about 114°. The enthalpy of the melting process was computed as 96.7 J/g. Using this enthalpy and the enthalpy for 100% crystalline polyethylene (293 J/g) the degree of crystallinity was computed as approximately 33%.

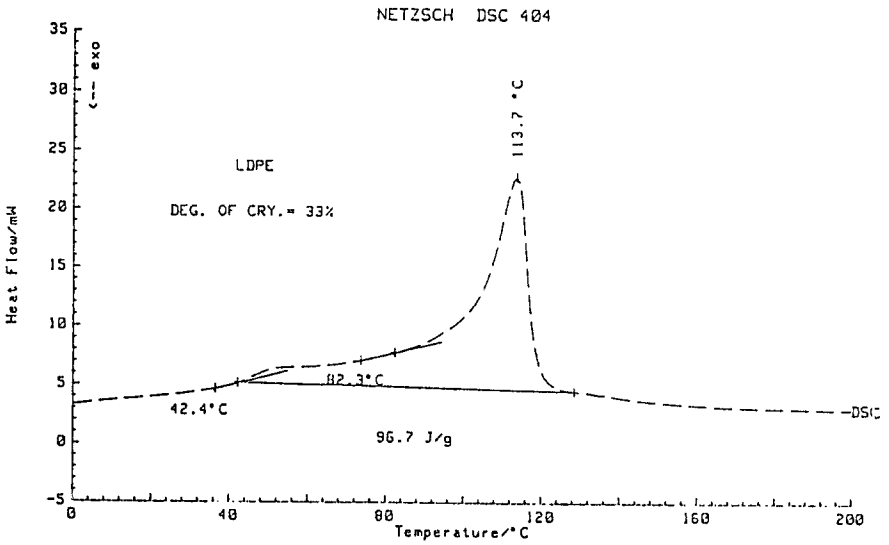

Fig. 3 Melting enthalpy of LDPE; Sample: LDPE, 21.09 mg; Reference: 0.00 mg; Atmosphere: He; Crucible : Al

The melting characteristics of LDPE presented here are generally in agreement with the literature values (e.g. see reference [2]), however it must be stated that the degree of crystallinity is lightly lower than those published for this material. In order to clarify this, several samples were run with both first and second heatings. All measurements gave degrees of crystallinity in the range of 32–36%. One could speculate that these differences are due, in part, to impurities, etc., however this cannot be verfied.

The specific heat of polystyrene for the first and second heating in the temperature range of −150 to 300° is presented in Fig. 4. To obtain these results the sample was first heated to approximately 20° above the glass transition point, then cooled to −150°, then immediately reheated to 300°. It is clear that the specific heat both above and below the glass transition temperature is almost identical for the first and second heating. This was the

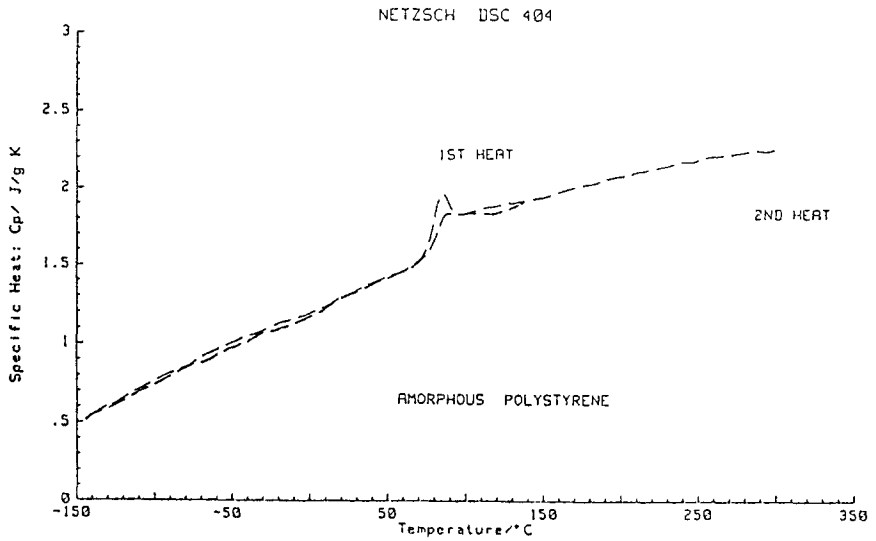

Fig. 4 Specific heat of PS for first and second heating; Sample: PS, 28.80 mg; Standard: Sapphire, 55.61 mg; Atmosphere: He; Crucible: Al

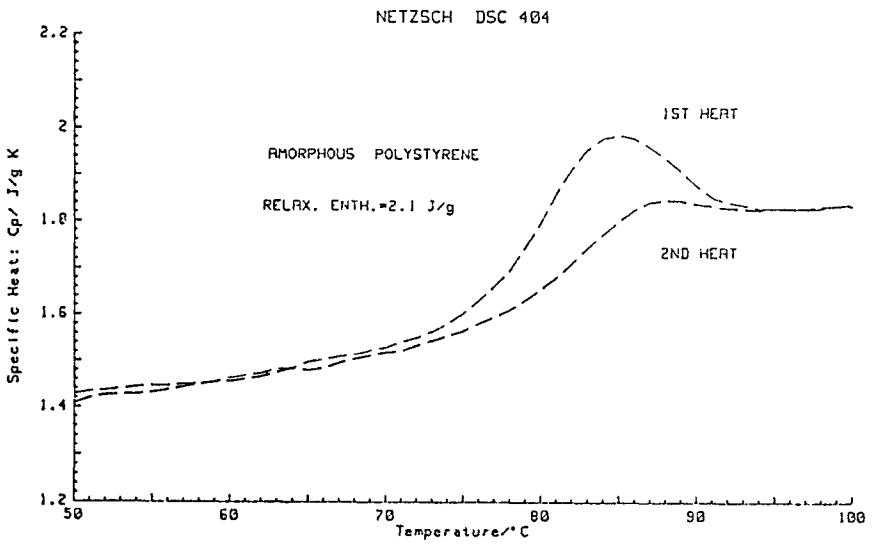

Fig. 5 Specific heat and relaxation enthalpy of PS; Sample: PS, 29.00 mg; Standard: Sapphire, 55.61 mg; Atmosphere: He; Crucible: Al

expected behavior. The major difference in the specific heat values is in the region of the glass transition. Clearly, the relaxation enthalpy during the first

heating is quite large. Again, this was expected since the sample had been aged approximately 6 years below the glass-transition temperature.

Figure 5 is an expanded plot of Fig. 4 in the glass transition region. Here the difference between the first and second heating is more clearly visible. By integrating the area between the two curves the relaxation enthalpy was computed as 2.1 J/g. In the near future additional studies will be undertaken to determine the relaxation enthalpy for polystyrene aged for various amounts of time below the glass-transition temperature.

Figure 6 shows the results of specific heat measurements for Poco graphite, alumina and hafnium carbide over the temperature range of 50 to 1400°. The results depicted in this figure for all three materials are in good agreement with published values. The specific heat of Poco graphite, Al_2O_3, and HfC is within ±2, ±1.5, and ±1.5%, respectively. Literature values for Poco graphite can be found in [3], while the values for Al_2O_3 and HfC are published in Ref. [4].

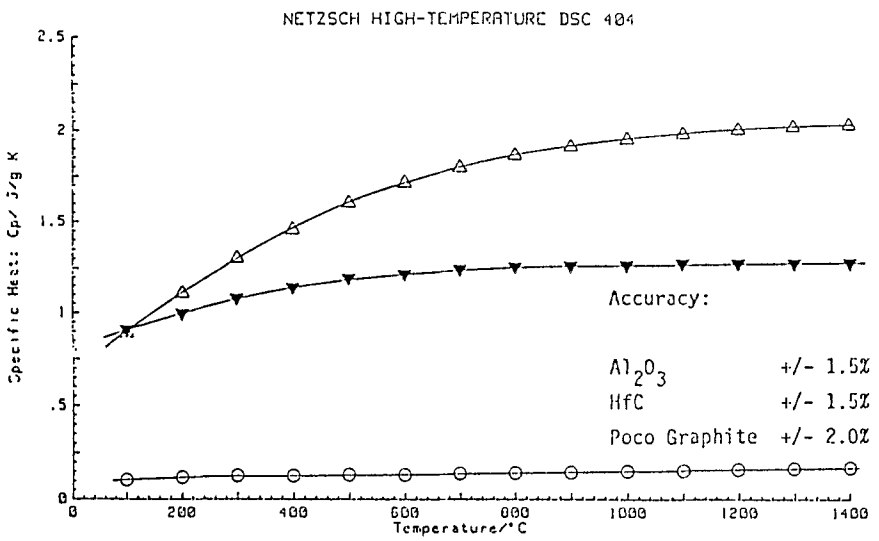

Fig. 6 Specific heat of Poco graphite, Al_2O_3 and HfC; Δ Poco graphite; ▼ Alumina; O Hafnium carbide

Concluding comments

The results presented in this paper for both the polymeric and high-temperature materials clearly demonstrate the accuracy and sensitivity of the Netzsch DSC 404 from −150 to over 1400°. It is clear that glass transition

temperatures, melting enthalpies, degreed of crystallization and specific heats of polymeric materials, as well as the specific heat, etc. of high-temperature materials can easily be determined using this instrument.

References

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Zusammenfassung – Ein neuartiges DSC Messystem (Netzsch DSC 404) wurde entwickelt, das sich durch hohe Reproduzierbarkeit der Basislinie, grosse Empfindlichkeit und breiten Temperaturanwendungsbereich (−160°C bis 700°C resp. bis 1500°C) auszeichnet. Die Messanordnung ermöglicht die Verwendung von unterschiedlichen Gasatmosphären als auch Messungen im Vakuum. Es werden Beispiele der Bestimmung von Schmelzvorgängen, der Glasumwandlungstemperatur, der Kristallinität und der spezifischen Wärme, sowohl für Polymere als auch für anorganische Materialien dargestellt und diskutiert.