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POLYMER CHARACTERIZATION USING THERMOMECHANICAL ANALYSIS

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The purpose of the work was to characterize the thermomechanical behaviour of two well-known and widely-used thermoplastic polymers. Both dynamic and constant load measurements were made for high-density polyethylene (HDPE), low-density polyethylene (LDPE) and amorphous polystyrene (PS). The results of these measurements yield valuable information which can aid in both design applications and material processing.

Introduction

Thermal analysis has proven a useful group of techniques for characterizing a wide range of materials serving both as a means to directly quantify certain properties and as an aid in morphological examinations. Due to the high sensitivity of thermal analysis instruments, they have been widely used for the investigation of polymeric materials and their composites which generally display a high correlation between the properties and the processing parameters, presence of dopents, impurities, aging, etc. In particular, thermomechanical analysis (TMA) and dilatometry readily yield data which can be used to determine linear and volumetric expansion coefficients, elasticity, glass transition temperatures, softening and melting points, volume relaxation, etc. An excellent review of the instrumentation and the measurement techniques in the area of polymers has been presented by Wendlandt and Gallagher [1], among others and therefore will not be repeated here.

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Experimental

Materials

The materials studied were HDPE, LDPE, and PS. Test samples approximately 6 mm in diameter and 2 mm thick were cut from long rods. The polystyrene samples had been aged approximately 6 years below the glass transition temperature.

Instrumentation

A Netzsch model 402 TMA equipped with a furnace capable of operation from −180 to 500° was utilized for all tests. The sample temperature was monitored with a Chromel-Constantan (Type E) thermocouple. The instrument is capable of operating in the dynamic mode at frequencies ranging from 0.03 to 5.0 Hz with a maximum load of 30 g or in the static mode with a variety of attachments to allow the measurement of expansion of fibers, large samples, waxes, etc. The maximum load in the static mode is 200 g. A high-temperature furnace capable of operation to 1000° is also available. A schematic of the measuring part is shown in Fig. 1.

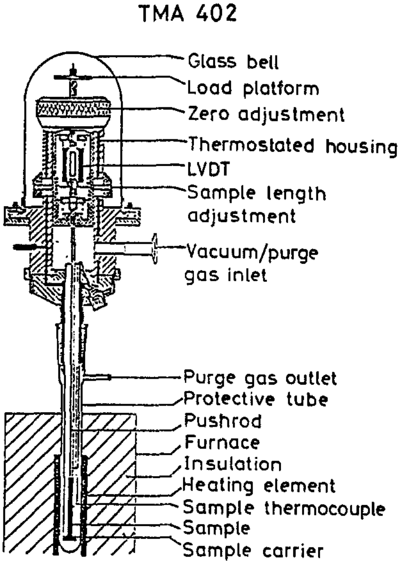

Fig. 1 Schematic of TMA measuring part

Temperature control of the TMA is provided by a Netzsch model 413 programmer and controller. The analog signals representing temperature and length change are conditioned by various Netzsch amplifiers. The data acquisition and evaluation, as well as instrument control are accomplished using a 16/32 bit computer system with peripheral units and the appropriate software.

Procedure

The HDPE and LDPE samples were tested in the dynamic mode with a frequency of 0.03 Hz and a load of 10 g. The PS sample was tested in the static mode with a load of 0.5 mg. The polyethylene and polystyrene samples were tested at heating rates of 10 and 5 deg/min, respectively. All measurements were carried out in an air atmosphere.

Results and discussion

Figure 2 shows the dimensionless expansion ($\Delta L/L_0$) of the HDPE and LDPE samples over the temperature range of −190 to about 140°. It is clear from the amplitude of the signal that the elasticity of the LDPE sample is greater over the entire temperature range. It is also obvious from the absolute magnitude of $\Delta L/L_0$ that LDPE possesses a higher expansion coefficient. More important, however, is the behaviour of both samples between approximately 40 and 140°. The slope of the LDPE expansion curve begins to change at about 45°, and in fact undergoes a slight contraction over the temperature range of 45 to about 80°. Finally at 113° the probe penetration is so deep that the signal goes out of range. The reason for this behaviour can be explained as follows. At 45° melting of the side chains occurs in LDPE resulting in an increase in the signal amplitude (elasticity) and a

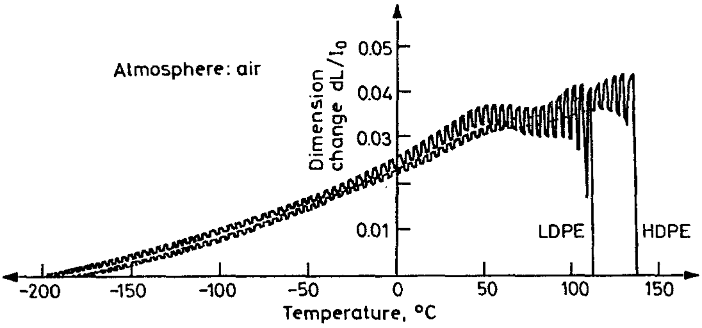

Fig. 2 $\Delta L/L_0$ for HDPE and LDPE

change in slope. Further at about 82° the onset of main chain melting is observed, resulting in an even greater change in the signal amplitude and another change in the slope. Finally at about 113° the melting peak is reached and the sample becomes so soft that the penetration is complete.

The behaviour of the HDPE sample on the other hand is quite different. It is clear that the HDPE possesses a higher degree of thermal stability. The first evidence of a change in slope of $\Delta L/L_0$ for HDPE is seen at about 60° and not until about 92° do the amplitude and the slope undergo a significant change. At about 138° the probe completely penetrates the sample. The temperatures of 92 and 138° correspond to the onset and peak melting temperatures for HDPE. This has been confirmed by DSC measurements, which show onset and peak melting temperatures of 92 and 135°, respectively. These data have been discussed by Henderson *et al.* [2].

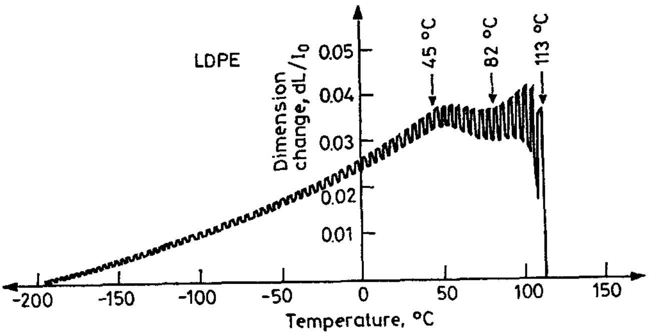

Fig. 3 $\Delta L/L_0$ for LDPE

The expansion of LDPE along with the appropriate temperatures has been replotted in Fig. 3. Here the dynamic behaviour of the sample is more clearly visible. Although the general behaviour of LDPE has already been discussed, a few additional comments are in order. First it is clear that the shape of the dynamic signal is slowly deformed from a square wave. This indicates a change from the purely elastic state to a visco-elastic state. Also the increase in amplitude of the signal as a function of temperature clearly demonstrates the temperature dependence of elasticity. Finally, the temperatures of 45 and 60° for LDPE and HDPE, respectively, correspond roughly to the vicat softening point. The vicat point is the temperature at which a polymer appreciably softens, under a well-defined set of test conditions. A description of this method can be found in ref. [3]. It must be clearly stated here that the authors do not imply that the vicat test can be replaced by dynamic TMA measurements. In this case, however, the two techniques develop similar results.

Plotted in Fig. 4 is the dimensionless specific volume $\Delta v/v_0$ of atactic polystyrene over the temperature range of −190 to approximately 120° for the first heating. As can be seen, the expansion is almost a linear function of temperature until the glass transition temperature (T_g) onset is reached at about 80°. At T_g the volume increase is about 17%. This volume relaxation is quite large and is due to the long aging time below T_g. Also of interest are the coefficients, α.. The two values are 8.1×10^{-5} $^{\circ}C^{-1}$ and 5.83×10^{-5} $^{\circ}C^{-1}$ for the temperature ranges of 0 to 50° and −185 to 50°, respectively. The value of α for the temperature range of 0 to 50° agrees well with the published values [4]. No expansion coefficients were found for the other temperature range. Although not shown here, the second heating (i. e. no aging time below T_g) of the same sample showed only a change in slope at the glass transition. That is, no volume relaxation was present, which of course is the expected behaviour for this case.

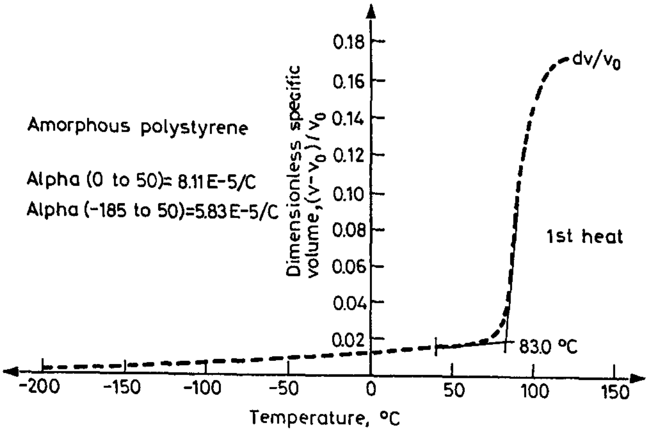

Fig. 4 $\Delta v/v_0$ for PS

Figure 5 shows a comparison of the specific heat (C_p) and $\Delta v/v_0$ for the first heating of PS over the temperature range of −150 to approximately 120°. The high degree of correlation between the volume and enthalpy relaxation is clearly shown in this plot. As can be seen, the T_g temperature is in good agreement for the specific heat and specific volume measurements. Data for the second heating of PS are not presented here due to space limitation, however, the reader is referred to the work of Wassmer, Emmerich and Henderson [5] for a discussion of the $_p$ and enthalpy relaxation in atactic polystyrene.

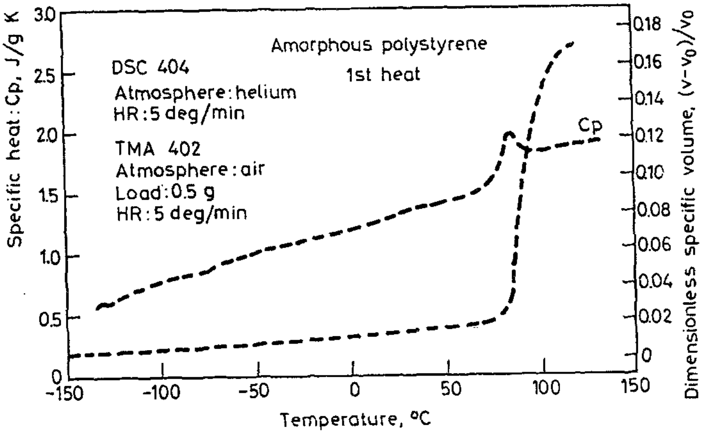

Fig. 5 C_p and $\Delta v/v_0$ for PS

Concluding comments

The results of the studies on polyethylene and polystyrene clearly demonstrate the utility of TMA for the characterization of polymeric materials. Valuable information such as glass transition, melting temperatures, expansion coefficients, etc. which can aid in optimization of processing, material selection, and quality control can be quickly and easily obtained. If the TMA technique is coupled with other thermal analysis methods such as thermogravimetry and differential scanning calorimetry, an even more complete evaluation of material properties can be made.

References

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Zusammenfassung — Die Thermomechanische Analyse (TMA) wurde zur Untersuchung der thermoplastischen Polymere HDPE, LDPE und PS angewandt. Die Messungen an HDPE und LDPE wurden dynamisch im Temperaturbereich von -90°C bis ca. +140°C durchgeführt. PS wurde von -190°C bis ca. +130°C statisch gemessen. Die Ergebnisse dieser Messungen zeigen deutlich die hervorragende Eignung der TMA bei der Bestimmung von Glasübergangs- und Schmelztemperaturen, der Charakterisierung der elastischen Eigenschaften sowie der Ausdehnungskoeffizienten. Zur Charakterisierung können weitere thermoanalytische Methoden (z. B. TG, DSC) herangezogen werden, wodurch zusätzliche Informationen erhalten und die TMA-Ergebnisse erhärtet werden können.