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A Differential Scanning Calorimetry Method for Determining Strain-Induced Crystallization in Elastomeric Fibers

Investigations of the thermodynamics of rubber elasticity are numerous, pre-dating, in fact, the mathematical development of thermodynamics itself (1). As early as 1925 it was observed that natural rubber crystallizes when stretched (2). This is a consequence of the reduction in entropy associated with deformation. Traditionally, measurements of strain-induced crystallinity (SIC) in rubbers involved methods such as observing the decrease in force at constant elongation (3), x-ray scattering (4), and birefringence (5). However, direct measurements of the thermodynamic transition energy associated with SIC are not often reported in the literature. This is undoubtedly due to the difficulty of performing calorimetric measurements on samples maintained in an elongated state.

Indirect methods do exist for estimating enthalpies of fusion associated with SIC. One method involves simultaneous measurement of work and heat during elongation of samples in a specially designed deformation calorimeter (6). The difference between these quantities is a general measure of the enthalpy of crystallization according to the first law of thermodynamics. However, since the deformation process is a nonequilibrium one, this relationship is not expected to be satisfied exactly, and kinetic effects are observed. Others have suggested that SIC enthalpies can be approximated by integrating equilibrium force-versus-temperature intercepts at various elongations (7).

In our laboratory we are evaluating segmented elastomeric fibers as potential working substances in rubber heat engines (8). To this end we have developed a simple and quantitative DSC method for determining the enthalpy of fusion for SIC. The method involves winding of an elongated elastomeric fiber onto a specially designed holder, securing the ends to prevent contraction of the sample, and scanning the sample in a standard differential scanning calorimeter (DSC). Similar measurements, based on this technique, have been made by other workers (9-13). This technique in conjunction with deformation calorimetry and force-temperature measurements should enable us to construct a complete thermomechanical energy balance on the fibers.

Experimental

Holders for stretched fiber samples were machined from brass to the geometry shown in Figure 1. Final spool weights averaged 530 mg $\pm$ 1%. Brass was chosen due to its high thermal diffusivity, high melting point, and low expansion coefficient. The dimensions are such that the spools fit snugly inside the sample and reference compartments of a DSC-2 Perkin-Elmer differential scanning calorimeter with platinum compartment covers in place. The center hole is 0-80 threaded to facilitate automatic windup at low linear velocity using a motor-driven windup apparatus.

Sample preparation is relatively simple. The spool is first threaded onto the

Fig. 1. DSC sample spool.

Fig. 2. Effect of heating rate on transition temperature. Comparison of sample spool and standard aluminum DSC pan.

motor-driven shaft and a 25-50-mg fiber sample is secured to the spool at one end. The remaining end hangs freely and is dead-weight loaded to obtain the desired elongation. After creep is complete, the equilibrium final length is measured and the elongated sample is wound onto the spool. Ends are then secured by tying them together to prevent contraction of the sample during the DSC scan. Maintaining the sample in the elongated state is critical, as no SIC peak is observed if the sample is allowed to contract during the scan (11-13). The spool containing the sample is then placed opposite a reference spool in the DSC-2 and the experiment is conducted in the normal manner.

Fig. 3. DSC scans of elastomeric fiber at various fixed extension ratios.

To optimize DSC operating conditions it was necessary to determine the heat transfer characteristics of the sample/spool system. To this end a small piece of indium metal calibration standard ($T_m^0 = 429.78$ K) was inserted under the upper lip of the spool and held in place by a fiber sample under low tension. This procedure locates the indium at maximum distance from the sample chamber heating surface. This configuration was scanned at 5-mcal/s sensitivity in the vicinity of the indium transition to determine temperature lag of the transition due to thermal gradients within the spool.

Results and Discussion

Observed transition temperatures versus heating rate for indium are plotted in Figure 2 for comparison of the spool and standard aluminum DSC pan sample environments. Data are normalized to $T_m^0 = 0$ -K/min heating rate. It is seen that both environments show linearity over the entire range of heating rates tested.

A lumped thermal diffusivity of 4×10^{-4} cm²/s is calculated for the system as compared with 4.25×10^{-4} and 0.33 cm²/s for the fiber and brass, respectively. This would indicate that radial heat conduction through the fiber is limiting, conduction through the brass spool being rapid by comparison. Considering the spool as an extended heat transfer surface, this geometry shows a heating surface-to-volume ratio advantage of 2.5X over the standard aluminum pans for equal sample weight. It is this large sample/surface contact area that minimizes thermal lag problems observed in oversized DSC samples (14).

Calibration peak areas for the melting endotherm of indium in the spool and standard sample pan agree within experimental error. Sensitivity of the sample spool is 75% of the standard pan as determined from peak height ratios.

Data obtained by this method are shown in Figures 3 and 4. Curves are DSC heating scans at 20 K/min, 5-mcal/s sensitivity. Samples are 25 mg of a seg-

Fig. 4. First and second DSC scans of elastomeric fiber at $\lambda = 4$.

Fig. 5. DSC scans of elastomeric fiber at $\lambda = 5$ with ends restrained and unrestrained during the scan.

mented elastomeric fiber having poly(tetramethylene oxide) (PTMO) soft segments of 2000 molecular weight, stretched to the indicated extension ratio ($\lambda = L/L_0$).

Figure 3 is a composite of DSC scans for fibers stretched to $\lambda = 1, 2, 3$, and 4. Note the growth of the SIC endotherm at 330 K with increasing extension indicative of the higher-melting extended-chain crystalline morphology formed at high elongations. In the relaxed state ($\lambda = 1$) only thermally induced folded chain crystals are observed (15), while evidence of a mixed morphology at intermediate extensions is indicated by the broad endotherm near room temperature.

Fig. 6. Percent strain-induced crystallinity versus extension ratio for elastomeric fibers: (—) distribution function fit to data points, (---) calculated first derivative.

This is in agreement with theory (16). Preliminary x-ray diffraction data confirm the presence of crystallinity at high elongation with a unit cell comparable to the extended-chain equilibrium crystal. Note also the changing form of the glass transition for PTMO with increasing extension. Previous DSC studies of the melting behavior and crystallization kinetics of stretched natural rubber (9-12) and highly drawn polyethylene (13) have also differentiated between thermal- and strain-induced crystallization.

Figure 4 shows first- and second-scan data of the same fiber at $\lambda = 3$. Note the reforming of the SIC peak at lower temperature following the initial melting. This would indicate recrystallization in a more relaxed state and is consistent with our force-versus-temperature results.

The importance of maintaining the sample at constant length is clearly demonstrated in Figure 5 for the PTMO soft segment fiber at $\lambda = 5$. It is seen that when the sample ends are not restrained during the DSC scan that the high-temperature endotherm is completely absent.

Weight percent strain-induced crystallinity calculated from the endotherms of Figure 3 are plotted in Figure 6 as a function of extension ratio. A value of 2.88 kJ/mol was used as the heat of fusion of extended chain PTMO (15). A distribution function is empirically fit to the data and its first derivative is also plotted. This may give information about nucleation frequency distribution and critical extension when more data are available. The formation of most crystallinity at intermediate elongations is in agreement with dynamic mechanical and deformation calorimetry measurements by other workers (17).

In conclusion, we have shown that this relatively simple method of maintain-

ing elastomeric samples at constant length during quantitative DSC studies can yield valuable information on thermodynamic phenomena associated with deformation. This direct measurement of the enthalpy of strain-induced crystallization should facilitate decomposition of the energy and entropy processes contributing to rubber elasticity at high elongations. Future work will focus on the relationships of these quantities to polymer chain architecture.

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