

# Thermal Effects in Poly(hexamethylene Adipamide) and Polyoxymethylene at High Hydrostatic Pressures

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## Synopsis

The temperature changes as a result of rapid hydrostatic pressure applications are reported for poly(hexamethylene adipamide) (nylon 66) and poly(oxymethylene) (POM) in the reference temperature range from 298 to 423 K and in the pressure range from 13.8 to 200 MN/m<sup>2</sup>. The adiabatic temperature changes were found to be a function of pressure and temperature. A curve fitting analysis showed that the empirical curve  $(\partial T/\partial P) = ab(\Delta P)^{b-1}$  described the experimental thermoelastic coefficients obtained from the experiments. The data were analyzed by determining the predicted thermoelastic coefficients derived from the Thomson equation  $(\partial T/\partial P) = \alpha T_0/\rho C_p$ . The experimental and predicted Grüneisen parameter  $\gamma_T$  were also determined. The relationship between the thermal effects and the chain molecular motion is discussed by including dynamic mechanical analysis and DSC measurements for the nylon 66 and POM samples.

## INTRODUCTION

The adiabatic heating phenomenon that takes place during the rapid deformation of solids is important in understanding the thermodynamics of deformation. This adiabatic heating, also defined as the thermoelastic effect, has been found to be very useful in determining important thermodynamic variables for inorganic salts,<sup>1,2</sup> metals,<sup>3-5</sup> and organic polymers.<sup>6-10</sup> These thermal effects can be observed during rapid extension, rapid compression, or rapid applications of hydrostatic pressures. This is important because the sign and magnitude of the thermal effects are a function of the type of deformation imposed on the material. For instance, two classic examples can be found in rubber and steel. A rubber band warms up when it is stretched and cools down when it is released, whereas the opposite is found for steel.

Some technological applications of the thermoelastic effect are currently emerging. It is being used as a method of determining local stresses associated with stress concentrations in engineering materials.<sup>11,12</sup> Also, it has been pointed out that the use of hydrostatic pressures to measure the adiabatic heating phenomenon affords more advantages over uniaxial deformation because the internal friction of the material is substantially minimized.<sup>10,13</sup>

In this study we report the thermal effects in polyoxymethylene (POM) and poly(hexamethylene adipamide) (nylon 66) during rapid hydrostatic pressure applications. These two polymers are usually known to be crystalline. The

effect of the degree of crystallinity was not studied. Thermoelastic measurements were done over a range of reference temperatures. Data on the thermoelastic effect in polymers is very limited. No report has been issued on the thermoelastic effect in POM or nylon 66.

### EXPERIMENTAL

The polyoxymethylene and the poly(hexamethylene adipamide) were obtained from Cadillac Plastics and Chemical Company as Delrin-500 and Zytel nylon 66 rods, respectively, of 1/4 in. (0.635 cm) outside diameter. Samples were cut to 3.6 in. (0.22 cm) long. Delrin and Zytel nylon 66 resins are manufactured by DuPont Corp. The materials were of extrusion and injection molding grade. Polymer rods were used as received. The values of the heat capacity, the thermal expansion coefficient, and the density were supplied by Cadillac Plastics. These values were reconfirmed using data obtained from the literature.

The apparatus and evaluation procedure for obtaining the temperature changes resulting from the rapid application of pressure were described previously.<sup>13,14</sup> The polymer sample was contained in the center of the high pressure unit. Liquid mercury was used to transmit the pressure to the sample. Hydrostatic pressures were achieved by using a 1 HP air compressor and an air-driven, high-pressure reciprocating pump. The pressure was measured with two Bourdon gauges, each with a maximum of 345 MN/m<sup>2</sup> and sensitivity of 3.45 MN/m<sup>2</sup>. The temperature changes were recorded using two iron-constantan thermocouples. The measuring junction was located in the geometric center of the rubber sample, whereas the reference junction was located outside the high pressure unit. This arrangement allowed us to measure directly only the temperature differences generated by the pressure variations and with maximum sensitivity since, with both junctions at atmospheric pressure, the output of the differential thermocouple was virtually zero.

To record the thermal effects, the system was allowed to equilibrate to atmospheric pressure and to the reference temperature. Pressure was rapidly applied by opening a valve which caused the selected pressure to be transmitted instantaneously to the sample. An increase in temperature was recorded. The pressure was released by the rapid opening of a second valve to atmospheric pressure which resulted in a decrease in temperature in the plastic material.

Mercury, the pressure medium, shows a thermoelastic effect when pressure is applied.<sup>14</sup> To see the influence of this effect, a number of experiments were done. First, a sample of Delrin and nylon 66 were insulated with a layer of Teflon tape. A second sample was insulated with three layers: a layer of Teflon tape, a layer of stainless steel film of 0.001 in. ( $2.54 \times 10^{-2}$  mm), and a second layer of Teflon tape in that order. Third, other samples were not insulated. Using the same procedure, the temperature changes were measured. No differences were found in the thermal effects for the respective samples. These results indicated that the thermal heating of mercury during pressure application did not affect the temperature changes of the polymers. Previously we also discussed<sup>14</sup> that the thermal effects for mercury under hydro-

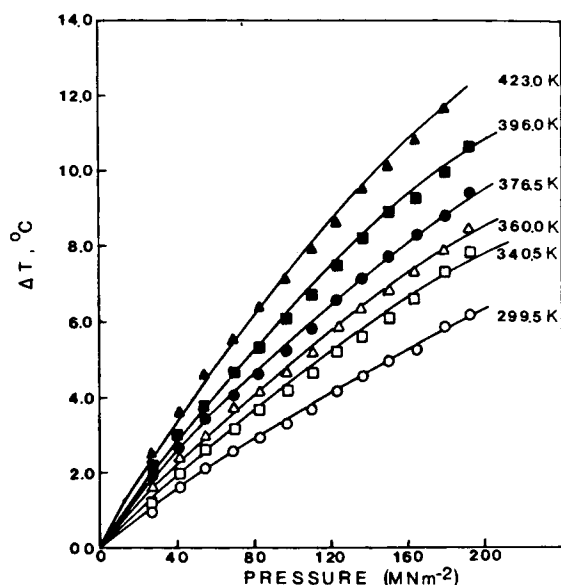


Fig. 1. Temperature changes as a function of applied pressure for POM at different reference temperatures.

static pressure occurred very rapidly, which is due to the high thermal conductivity of mercury. For polymers, the thermal conductivity is smaller than for mercury, therefore allowing accurate measurements of the thermal effects because the heat losses with the surroundings are substantially diminished.

The dynamic mechanical analysis was determined by using a mechanical spectrometer (Rheometrics Inc., RMS-605 Model) with torsional cylindrical fixtures. A differential scanning calorimeter, Model DuPont 1090, was used to determine the melting point of the thermoplastics.

## RESULTS AND DISCUSSION

Figures 1 and 2 show the temperature changes as a function of the applied pressure at different temperatures for POM and nylon 66, respectively. The data is presented only for positive  $\Delta P$ 's and thus positive temperature increases. The magnitude of the temperature changes were found to be relatively significant for both POM and nylon 66. Figures 3 and 4 show the temperature changes as a function of the reference temperature at selected pressures for POM and nylon 66, respectively. Figures 1-4 clearly show that the adiabatic temperature changes were a strong function of the reference temperature and the pressure applied.

A curve fitting analysis showed that the adiabatic temperature changes as a function of pressure could be described through the empirical equation  $\Delta T = a(\Delta P)^b$ , where  $a$  and  $b$  are constants.  $\Delta T = T - T_0$  and  $\Delta P = P - P_0$ , where  $T_0$  is the reference temperature and  $P_0$  is the atmospheric pressure. Table I shows the results of the curve-fitting analysis. The experimental thermoelastic coefficients ( $\partial T/\partial P$ ) were determined by differentiating on both sides the above empirical equation to obtain  $\partial T/\partial P = ab(\Delta P)^{b-1}$ . This equation shows

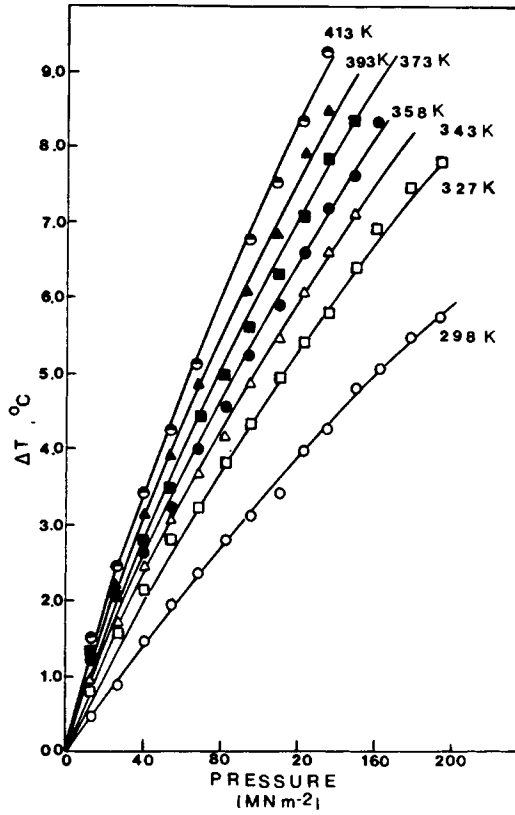


Fig. 2. Temperature changes as a function of applied pressure for Nylon 66 at different reference temperatures.

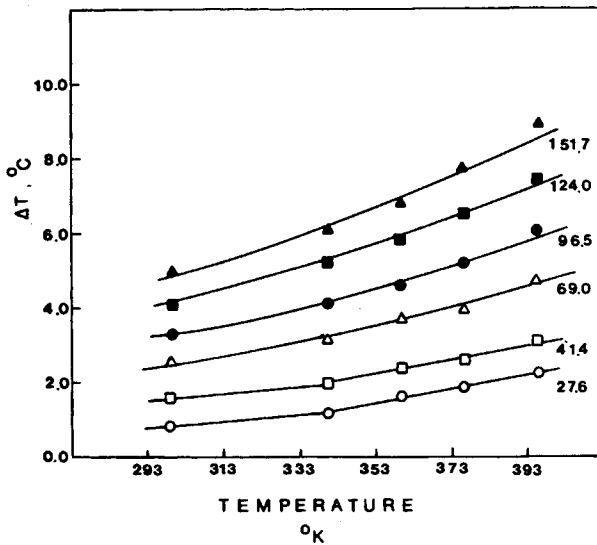


Fig. 3. Temperature changes as a function of the reference temperature for POM at selected applied pressures.

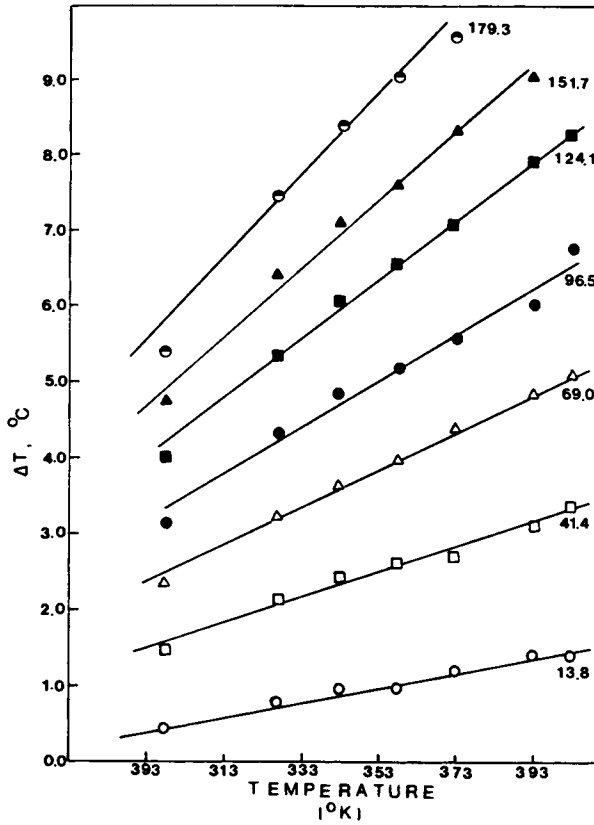


Fig. 4. Temperature changes as a function of the reference temperature for nylon 66 at selected applied pressures.

TABLE I  
Values for  $a$  and  $b$  in the Empirical Equation  $\Delta T = a(\Delta P)^b$   
Obtained from the Curve Fitting Analysis

Reference temp. (K)	$a$	$b$	Coefficient of determination, $R^2$
POM			
299.5	0.0445	0.9398	0.99
340.5	0.0573	0.9344	0.99
360.0	0.1057	0.8290	1.00
376.5	0.1090	0.8475	1.00
396.0	0.1259	0.8448	1.00
432.0	0.1640	0.8240	1.00
Nylon 66			
298.0	0.0393	0.9548	1.00
327.0	0.0884	0.8532	1.00
343.0	0.1030	0.8446	1.00
358.0	0.0999	0.0664	1.00
373.0	0.1333	0.8226	1.00
393.0	0.1573	0.8069	1.00
413.0	0.1606	0.8192	1.00

a dependence on the thermoelastic coefficients on the pressure applied. This equation is purely empirical, and no effort was given to correlate it with thermodynamic variables. Table II gives the numerical expressions for  $(\partial T/\partial P)$  at certain reference temperatures and shows the thermoelastic coefficients determined from selected pressures at the same reference temperature.

From thermodynamic relationships, it is possible to derive an expression that describes the temperature changes during adiabatic deformation. Thomson<sup>15,16</sup> proposed a general thermodynamic equation which describes the change in temperature as the result of rapid application of pressure. Later Joule<sup>17,18</sup> verified Thomson's equation with an investigation of some thermodynamic properties of solids by measuring the temperature changes produced by sudden stretching or compression a variety of materials at low stresses. Swalin<sup>19</sup> has shown a recent and modern derivation of the Thomson equation to describe the thermoelastic effect. It is important to define the type of deformation, that is, tension, compression, or volumetric (hydrostatic pressure) deformation. For hydrostatic pressure, the Thomson equation can be written as

$$\frac{\partial T}{\partial P} = \frac{\alpha_v T_0}{\rho C_p}$$

where  $\alpha_v$  is the volume thermal expansion coefficient,  $C_p$  is the specific heat at constant pressure, and  $\rho$  is the density. The term  $\partial T/\partial P$  is usually called thermoelastic coefficient.

The values for the thermal expansion coefficient, the specific gravity, and the heat capacity for POM and nylon 66 were taken from different sources, and they are shown in Table III. This data was confirmed by the table of physical properties provided by the Cadillac Plastics Co.

The pressure and temperature dependence of the thermal expansion coefficient, the heat capacity, and the density for POM and nylon 66 are unknown. The predicted thermoelastic coefficients were then determined at different temperatures and at atmospheric pressure, and they are shown in Table III. The experimental and predicted thermoelastic coefficients are comparatively shown in Figure 5. The experimental thermoelastic coefficients were found to be a function of pressure and temperature. From Figure 4, nylon 66 shows slightly higher thermoelastic coefficients, and therefore higher temperature changes with pressure applied than POM.

Examining Figure 4 and Tables II and III, good agreement was found between the theoretical thermoelastic coefficient and the experimental coefficients at atmospheric pressure and 298 K for both nylon 66 and POM. However, deviations were found at other pressures and temperatures. This confirms previous findings that certain properties of viscoelastic materials are very sensitive to pressure and temperature; therefore, care should be taken in applying thermodynamic variables that are well established for nonviscoelastic materials on reversible thermodynamics.

In addition, the pressure and temperature dependence found on the experimental  $(\partial T/\partial P)$  values clearly suggest that the term  $\alpha/\rho C_p$  in the Thomson

TABLE II  
Experimental Thermoelastic Coefficients ( $\partial T/\partial P$ ) Determined for POM and Nylon-66 at Selected Pressures

Reference temp. (K)	$\frac{\partial T}{\partial P} = ab(\Delta P)^{b-1}$	$\Delta P$ (MN/m <sup>2</sup> )	$\frac{\partial T}{\partial P}$ (K/MN m <sup>-2</sup> )
POM			
299.5	$0.0418 \times (\Delta P)^{-0.0602}$	0.1013	0.0480
		4.0	0.0385
		20	0.0349
		100	0.0317
340.50	$0.0535 \times (\Delta P)^{-0.0656}$	0.1013	0.0622
		4.0	0.0489
		20	0.0440
		100	0.0396
360	$0.0876 \times (\Delta P)^{-0.1710}$	0.1013	0.1296
		4.0	0.0691
		20	0.0525
		100	0.0399
376.5	$0.0924 \times (\Delta P)^{-0.1525}$	0.1013	0.131
		4.0	0.0748
		20	0.0585
		100	0.0460
396	$0.1064 \times (\Delta P)^{-0.1552}$	0.1013	0.1517
		4.0	0.0860
		20	0.0668
		100	0.0520
423	$0.1351 \times (\Delta P)^{-0.1760}$	0.1013	0.2022
		4.0	0.1060
		20	0.0798
		100	0.0601
Nylon-66			
298	$0.0375 \times (\Delta P)^{-0.0452}$	0.1013	0.0416
		4.0	0.0352
		20	0.0328
		100	0.0305
327	$0.0754 \times (\Delta P)^{-0.1468}$	0.1013	0.1060
		4.0	0.0615
		20	0.0486
		100	0.0384
343	$0.0869 \times (\Delta P)^{-0.1554}$	0.1013	0.1242
		4.0	0.0701
		20	0.0546
		100	0.0425
358	$0.0866 \times (\Delta P)^{-0.1336}$	0.1013	0.1380
		4.0	0.0719
		20	0.0580
		100	0.0470
373	$0.1097 \times (\Delta P)^{-0.1774}$	0.1013	0.1646
		4.0	0.0857
		20	0.0644
		100	0.0484
393	$0.1269 \times (\Delta P)^{-0.1931}$	0.1013	0.1975
		4.0	0.0971
		20	0.0712
		100	0.0522
413	$0.1316 \times (\Delta P)^{-0.1808}$	0.1013	0.1990
		4.0	0.1024
		20	0.0765
		100	0.0572

TABLE III  
 Physical Data for POM and Nylon 66

Specific gravity <sup>a</sup> (kg/m <sup>3</sup> )	Specific heat <sup>a</sup> (J/kg K)	Volumetric <sup>a,b</sup> thermal expansion (1/K)	Thermoelastic <sup>c</sup> coefficient $\partial T/\partial P$ (K/MN m <sup>-2</sup> )
POM			
$1.452 \times 10^3$ (20)	$1.465 \times 10^3$ (21)	$3.6 \times 10^{-4}$ (22)	$T_0 = 298 \text{ K } 0.0514$ $T_0 = 340 \text{ K } 0.0586$ $T_0 = 373 \text{ K } 0.0643$ $T_0 = 393 \text{ K } 0.0678$
Nylon 66			
$1.09 \times 10^3$ (23)	$1.419 \times 10^3$ (24)	$3.0 \times 10^{-4}$ (25)	$T_0 = 298 \text{ K } 0.0578$ $T_0 = 340 \text{ K } 0.0660$ $T_0 = 373 \text{ K } 0.0723$ $T_0 = 393 \text{ K } 0.0762$

<sup>a</sup>Reference numbers in parentheses.

<sup>b</sup> $\alpha_v \approx 3\alpha_L$ .

<sup>c</sup>Calculated from  $\partial T/\partial P = \alpha_v T_0/\rho C_p$ , at atmospheric pressure.

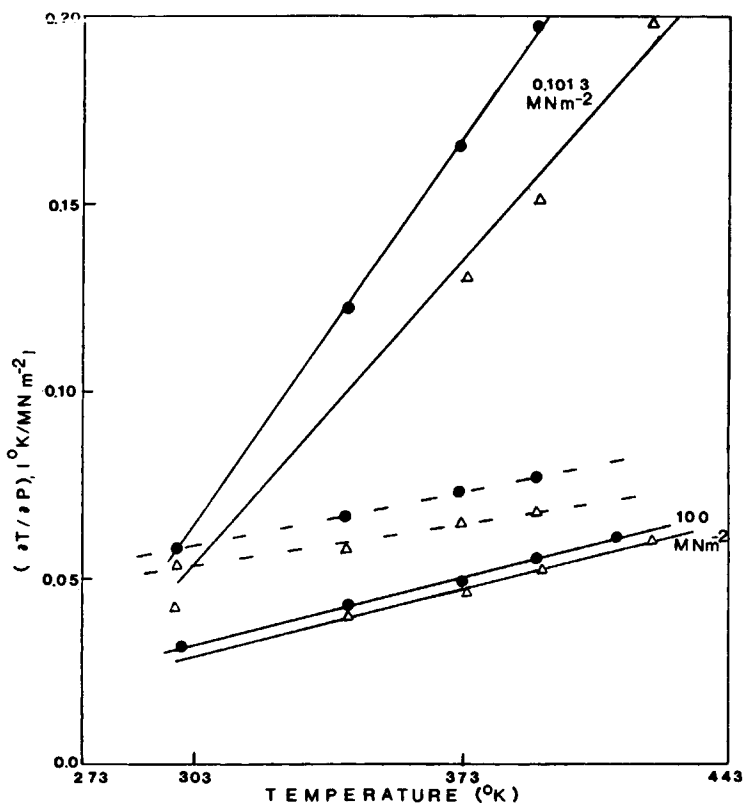


Fig. 5. Thermoelastic coefficients ( $\partial T/\partial P$ ) as a function of temperature for POM ( $\Delta$ ) and nylon 66 ( $\bullet$ ). Experimental values (—) at two pressures and predicted values (---) from the Thomson equation.



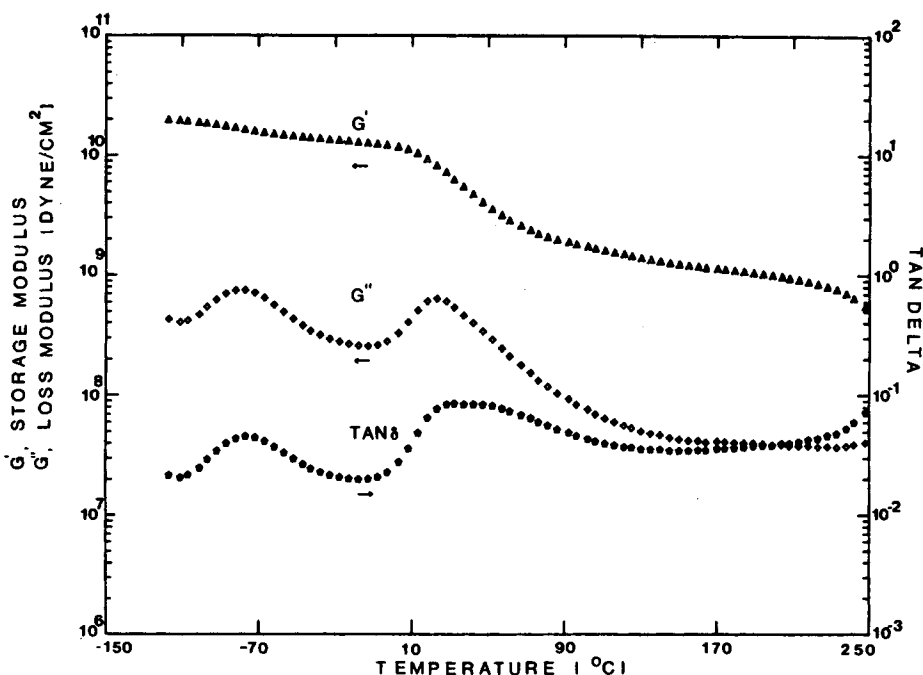


Fig. 6.  $G'$ ,  $G''$  and  $\tan \delta$  values for nylon 66 as a function of temperature at 1 Hz and 0.1% deformation.

equation is a strong function of both pressure and temperature. Similar results were found by other authors<sup>7</sup> in poly(methyl methacrylate), where the thermoelastic coefficients obtained from uniaxial tension and compression measurements were used to determine the pressure and temperature dependence on the  $\alpha_v$  and  $C_p$  coefficients.

To further evaluate our data, the dynamic mechanical analysis was conducted at 1 Hz frequency of forced vibration and at 0.1% deformation. The shear storage modulus  $G'$ , the shear loss modulus  $G''$ , and the dissipation factor  $\tan \delta$  were determined. They are shown in Figures 6 and 7 for nylon 66 and POM, respectively.

For nylon 66 (Fig. 6) two transitions were identified from approximately  $-82$  to  $-62^\circ\text{C}$  and from  $23$  to  $67^\circ\text{C}$ . These two loss peaks can be labeled as  $\beta$  and  $\alpha$  peaks, respectively. The glass transition for nylon 66 is about  $50^\circ\text{C}$ , which corresponds to the  $\alpha$ -transition in our measurements.<sup>26</sup> For POM, one transition was identified from approximately  $-76$  to  $-52^\circ\text{C}$ , which corresponds to the  $\alpha$ -peak or the glass transition. Other authors determined the glass transition for POM in the range from  $-75$  to  $-85^\circ\text{C}$ , which agrees well with our findings.<sup>27,28</sup>

The melting measured for POM was  $181^\circ\text{C}$ , whereas for nylon 66 it was  $265^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$  in a nitrogen flow of  $30\text{ mL}/\text{h}$ . Figure 8 shows the DSC scan for both POM and nylon 66. Wilski<sup>29</sup> reported a melting point of  $181^\circ\text{C}$  for POM whereas DuPont Co.<sup>30</sup> reports a melting range of  $250$ – $265^\circ\text{C}$  for nylon 66.

Thermoelastic measurements were conducted from  $25^\circ\text{C}$  to approximately  $150^\circ\text{C}$  for both nylon 66 and POM. The values of the storage modulus

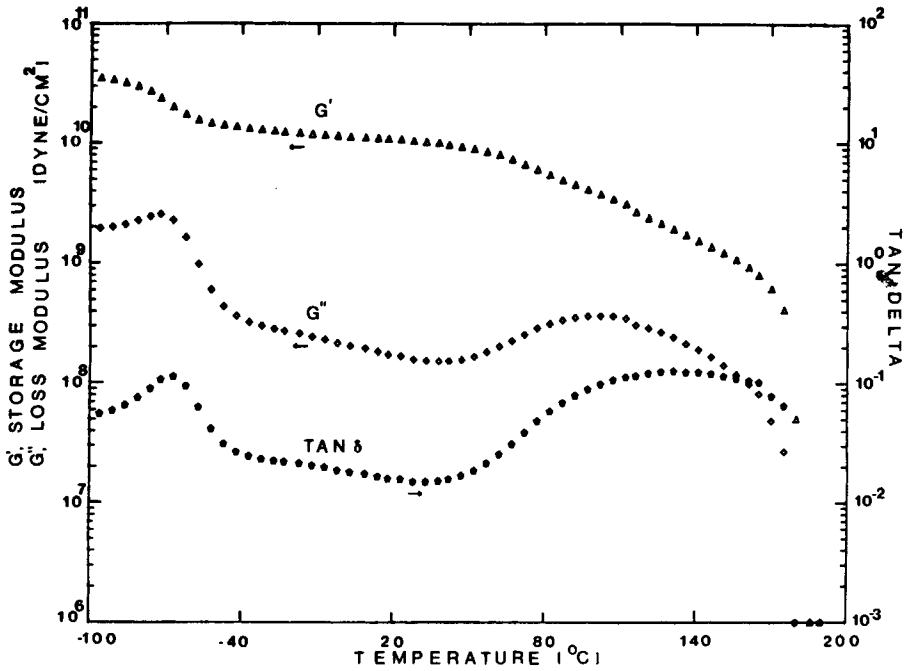


Fig. 7.  $G'$ ,  $G''$  and  $\tan \delta$  values for POM as a function of temperature at 1 Hz and 0.1% deformation.

indicated that within this temperature range POM showed higher storage modulus and lower dissipation factors than nylon 66. This is important because, from Figure 5, the thermoelastic coefficients ( $\partial T/\partial P$ ) were found to be higher for nylon 66 than for polyoxymethylene. Therefore, the thermoelastic effect is related to the  $\alpha$ -transition of polymers where higher temperature changes are found with an increase in the flexibility ( $T_g$  or  $\alpha$ -transition) of the material.

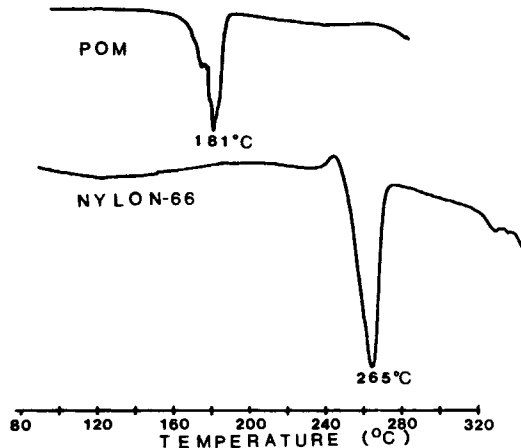


Fig. 8. DSC scan for POM and nylon 66 at 10 deg/min in nitrogen flow at 30 mL/min.

The thermoelastic method (adiabatic heating) has been used to determine important thermodynamic properties. For example, Bottani et al.<sup>3,4</sup> measured the Grüneisen parameter and the thermal diffusibility coefficient in metals using the temperature increments obtained from rapid compression. Haward and Trainor<sup>7</sup> reported the values of the linear coefficient of expansion and the Grüneisen coefficient constant at different stresses and temperatures in poly(methyl methacrylate) from thermoelastic experiments. Similar calculations have also been conducted for glassy polymers.<sup>8,9</sup>

The macroscopic or the thermodynamic of Grüneisen relationship  $\gamma_T$  can be estimated from the thermoelastic coefficient ( $\partial T/\partial P$ ) through the equation

$$\gamma_T = \frac{\partial T}{\partial P} \frac{B_s}{T} = \frac{\partial T}{\partial P} \frac{1}{T} B_T \frac{C_v}{C_p}$$

where  $B_s$  is the adiabatic bulk modulus,  $B_T$  the isothermal bulk modulus,  $C_v$  the specific heat at constant volume, and  $C_p$  the specific heat at constant pressure. The derivation of these relationships can be found in the literature.<sup>9,19</sup>

The ratio  $C_v/C_p$  can be determined from reversible the thermodynamics equation

$$\frac{C_v}{C_p} = 1 - \frac{T\alpha_v^2 B_T}{\rho C_p}$$

therefore allowing the determination of the Grüneisen coefficient.

For nylon 66 the isothermal bulk modulus reported in the literature is  $8.1 \times 10^3 \text{ MN/m}^2$ .<sup>31-33</sup> The isothermal bulk modulus has not been reported for POM. It was estimated through the equation  $B_T = E/3(1 - 2\nu)$ , where the elastic modulus  $E = 2.828 \times 10^3 \text{ MN/m}^2$  and the Poisson ratio  $\nu = 0.42$ . Therefore, for POM  $B_T$  is approximately  $6.0 \times 10^3 \text{ MN/m}^2$ . Using the experimental values and the predicted values from the Thomson equation for the thermoelastic coefficients, the Grüneisen parameter was calculated, and the results are shown in Tables IV and V for nylon 66 and POM, respectively. The Grüneisen parameter was found to be a function of both pressure and temperature. In general, the value of the Grüneisen parameter decreases with pressure at constant temperature and increases with temperature at constant pressure. The predicted  $\gamma_T$  values obtained via the Thomson equation were slightly dependent on the reference temperature. The low values for  $\gamma_T$  (for example, 0.565 for POM) indicate relatively large thermal effects and high values of  $\gamma_T$  (for example, 0.856 for POM) indicate small thermal effects under the application of hydrostatic pressure. Thus, the Grüneisen coefficient gives an estimation between mechanical and heat effects in material.<sup>19</sup>

Warfield<sup>34</sup> reported the Grüneisen constant of polymers using pressure dependence of the bulk modulus. The lattice Grüneisen constant  $\gamma_L$  is usually measured in this type of experiment which relates to the polymer chains moving in relation to each other (interchain motion). In our case the thermoelastic experiments are related to the thermodynamic Grüneisen constant  $\gamma_T$ , which is an average over all vibrations. Warfield<sup>34</sup> reported  $\gamma_L = 5.6$  and  $\gamma_T = 0.51$  for POM. Thus differences were found between our  $\gamma_T$  values obtained from thermal effects under rapid pressure applications and the ones reported in the literature. The differences found between the values for the Grüneisen parameters may be related to the differences in the material used in

TABLE IV  
Values of the Grüneisen Constant for Nylon 66

Temp. (K)	$C_v/C_p^a$	From experimental thermoelastic coefficients		Predicted values from the Thomson equation, $\gamma_T$
		$\Delta P$ (MN/m <sup>2</sup> )	$\gamma_T$	
298	0.86	0.1013	0.972	1.351
		4	0.823	
		20	0.767	
		100	0.713	
343	0.84	0.1013	2.464	1.309
		4	1.391	
		20	1.083	
		100	0.843	
373	0.82	0.1013	2.931	1.287
		4	1.526	
		20	1.147	
		100	0.862	
393	0.81	0.1013	3.297	1.272
		4	1.621	
		20	1.189	
		100	0.871	

<sup>a</sup>Determined from  $C_v/C_p = 1 - T\alpha_c^2 B_T / \rho C_p$ .

TABLE V  
Values of the Grüneisen Constant for POM

Temp. (K)	$C_v/C_p^a$	From experimental thermoelastic coefficients		Predicted values from the Thomson equation, $\gamma_T$
		$\Delta P$ (MN/m <sup>2</sup> )	$\gamma_T$	
299.5	0.89	0.1013	0.856	0.921
		4	0.686	
		20	0.622	
		100	0.565	
340.50	0.87	0.1013	0.954	0.898
		4	0.750	
		20	0.675	
		100	0.607	
376.5	0.86	0.1013	1.795	0.873
		4	1.025	
		20	0.802	
		100	0.630	
396	0.85	0.1013	1.954	0.866
		4	1.108	
		20	0.860	
		100	0.670	

<sup>a</sup>Determined from  $C_v/C_p = 1 - T\alpha_c^2 B_T / \rho C_p$ .

the experiments and in the different  $\alpha_p$ ,  $C_p$ , and  $\rho$  values used in the calculations. Experimental studies on the Grüneisen constant for nylon 66 have not been reported in the literature.

To conclude, thermoelastic experiments dealing with adiabatic heating under rapid application of hydrostatic pressures afford a different approach to determine, and perhaps further understand, the thermal properties of viscoelastic materials. The simplicity of the experiment reported here may suggest a quick way to evaluate important thermodynamic variables for viscoelastic materials.

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