found various values for this temperature, or have provided data which can be used to estimate it. These results are summarized in *Table 2*.

Comparing the data of *Table 1* and *Figure 1* with like data obtained in tetrahydrofuran[1,2] shows that $[M]_e$ is smaller in cyclohexane, supporting previous findings[4,6,7] that equilibrium monomer concentrations are lower in less polar solvents (see Introduction). These data also permit the calculation of ΔH and ΔS^0 for this polymerization, from equation (1). The values obtained from the present work, plus those reported in the literature for polymerization in other solvents, are summarized in *Table 3*.

Table 2 'Absolute' ceiling temperature for the anionic polymerization of α-methylstyrene

Solvent	Absolute T_c(°C)	Reference
Tetrahydrofuran	51*	1
Tetrahydrofuran	61	2
Neat monomer	~55	4
Neat monomer	57	7
Cyclohexane	54	This work

*Extrapolated from data for polymerizations from 0° to –40°C

Table 3 Enthalpy and entropy for the anionic polymerization of α-methylstyrene

Solvent	Counterion	$-\Delta H$ (kcal/mol)	$-\Delta S^0$ (cal/mol/°C)	Reference
Tetrahydrofuran	Na^+	6.96	24.8	2
Tetrahydrofuran	Na^+	7.47	26.5	3
Tetrahydrofuran	Na^+	10.8	35.4	5
p-Dioxane	K^+	10.6	–	6
Cyclohexane	Li^+	11.4	39.0	This work

It was noted in all polymerizations that the deep-red colour of the α-methylstyryl anion faded as the reactions proceeded. This has been described by others, who have attributed it to a variety of possible reactions leading to termination of the 'living' polymer[4,12]. The higher the reaction temperature, the more rapidly the colour faded. It was found in this work, however, that the colour was more persistent when the ether modifiers were present; some colour always remained in the polymerization mixtures up to at least 264 h reaction time. Since maximum polymer yield was reached in 24–72 h, it is felt that a true equilibrium was attained, i.e. the $[M]_e$ values were not the result of premature termination of the polymerization. This was not the case when unmodified sec-butyllithium was the initiator. It gave such slow polymerizations that equilibrium was never reached, and colour faded almost completely in these runs after several days. Hence no results from them are included in the data reported here.

ACKNOWLEDGEMENTS

The author wishes to thank the Goodyear Tire & Rubber Company for permission to publish these results, and Professor Maurice Morton of the University of Akron for helpful discussions. Gas chromatographic analyses were carried out by R. D. Kovalak and K. E. Getzinger. This is Contribution No. 591 from the Research Laboratories of the Goodyear Tire & Rubber Company.

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Letter

Thermomechanical study of the hysteritic behaviour of natural rubber networks

Introduction

The deformation of a rubber-like material can be described in a simple way using thermodynamic state functions. At constant pressure and temperature the following state equation can be written:

$$\Delta H = \Delta W + \Delta Q \qquad (1)$$

where ΔH is the enthalpic change, ΔW the elastic work, and ΔQ the heat transferred from or to the sample.

All the terms of the equation (1) can be referred to the volume unit.

The elastic work ΔW, in elongational deformation, is given by the integration of the function τ vs. α, where τ is the force on the unit of undeformed cross-sectional area, and α is the strain ratio defined as L/L_0, L and L_0 being the deformed and undeformed sample length. The integration, which can be performed graphically, gives the numerical value of the integral:

$$\int_1^\alpha \tau \mathrm{d}\alpha$$

It follows that:

$$\int_1^\alpha \tau \mathrm{d}\alpha + \Delta Q = \Delta H \qquad (2)$$

If equation (2) is used to analyse the hysteretic behaviour of a sample that is stretched and relaxed in a cyclic manner, going through a maximum value of the strain, it can be rewritten:

$$\oint \Delta W + \oint \Delta Q = \oint \Delta H \qquad (3)$$

0032–3861/78/1906–0731$01.00

That is, the algebraic sum of the cyclic integrals of the functions ΔW and ΔQ is equal to the cyclic integral of the enthalpic term. In a previous paper[1] we have used equation (3) in an approximate manner to calculate $\oint \Delta H$ for a sample stretched and relaxed step by step, plotting continuous curves through experimental points detected discontinuously. Experimental results indicate a negative value for the term $\oint \Delta H$, and this datum is discussed in terms of possible aggregation phenomena induced by the stretching.

In the present paper we have used equation (3) in a corrected form by continuously detecting the force and the heat for a sample deformed in continuous way. This experimental analysis gives a thermodynamic quantitative picture of the hysteretic behaviour of an elastomeric sample. In particular we have analysed the hysteretic behaviour of a natural rubber network.

The hysteretic behaviour was investigated at two different temperatures and changing the maximum value of the strain, the deformation rate and the storing time at zero load between two successive hysteretic cycles.

Results obtained confirm a negative value for $\oint \Delta H$ and suggest the possibility that aggregation phenomena can take place during the deformation in a quasireversible way in the time scale of the experiment under all the conditions used.

Experimental

Materials. The natural rubber network was obtained using dicumyl peroxide as vulcanization initiator at 145°C for 45 min. The initiator concentration was 0.3%.

The average molecular weight, M_c, between two successive crosslinking points was 11 000. This datum was obtained by analysing the stress–strain behaviour of the sample[2] in terms of the Mooney–Rivlin equation.

Method. Figure 1 shows a schematic illustration of the apparatus we used. It is mainly based on a Calvet microcalorimeter. The use of this kind of calorimeter in the thermomechanical analysis has been previously described[1,3].

In this paper, as shown in *Figure 1* the calorimetric cell is equipped with a motor system that makes it possible to deform the sample at constant rate in a continuous way and to detect the stress by a force transducer. At the same time the heat exchanged during the deformation is given by the calorimetric cell. In our experiments the sample is deformed in a cyclic manner giving rise to a hysteretic loop.

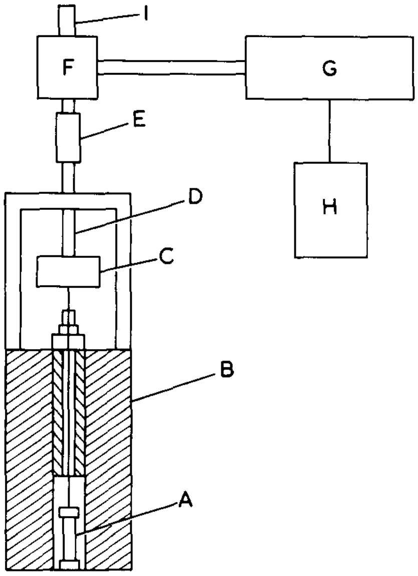

Figure 1 Schematic illustrations of the apparatus used: A, sample; B, microcalorimetric cell; C, force transducer; D, microscrew; E, joint; F, revolution speed reducer; I, revolution counter; G, motor; H, revolution speed controller

A typical force plotting is given in *Figure 2* where the area A is proportional to $\oint \Delta W$. In *Figures 3a* and *b* we report two typical calorimetric signals, the first at low deformation rate, and the second at high deformation rate. In the first case $\oint \Delta Q$ is proportional to the difference between the areas A and B, while in the second case $\oint \Delta Q$ is proportional to the area A. The possibility of calculating $\oint \Delta W$ and $\oint \Delta Q$ is related to the force and heat calibrations.

The force transducer can easily be calibrated using a set of reference weights, while the calorimeter cell can easily be calibrated using a calibration cell based on the Joule effect. Considering that the sensitivity limit in the microcalorimetric measurement is 8 μJ/cm^3, the error in the function $\oint \Delta Q$ is mainly due to the experimental error in the volume, and can be evaluated in the range ±5%. An estimation of the error in the function $\oint \Delta W$, gives a value under the limit ±10%.

Results

In *Table 1* we report all the experimental thermodynamic data regarding the hysteretic behaviour of a natural rubber elastic network. Data refer to hysteretic cycles carried out at two different temperatures (25°, 40°C), at two different strain rates (0.40, 1.46 min^{-1}), up two different maximum strain values, 2 and 3 In this way, we have eight different working conditions.

For each condition we report two values for each thermodynamic function. The first value refers to the first hysteretic run, the second refers to a second hysteretic run carried out 30 seconds after the first. The second hysteretic run was carried out even 24 h after the first, but we do not report the experimental data because they are very similar, within the range of the experimental error, to the data obtained in the first run.

Discussion

First we should point out that our studies were carried out in a temperature and strain range in which extensive crystallization phenomena cannot be present. In fact we are up in the temperature scale, and down in the strain range[4,5]. On the other hand we have not observed a sensitive creep of the sample length after each hysteretic cycle. Therefore we are considering a material which, under all the investigated conditions, behaves as a rubber-like material.

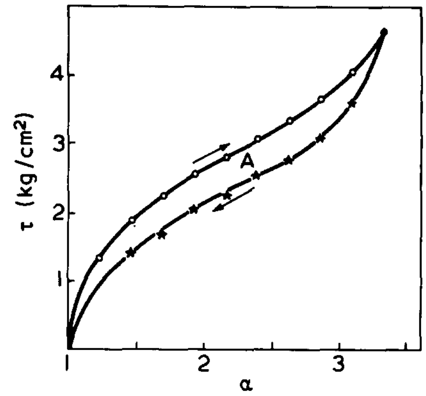

Figure 2 Typical force hysteretic loop. The stress τ is reported vs. the strain α The area A is proportional to $\oint \Delta W$

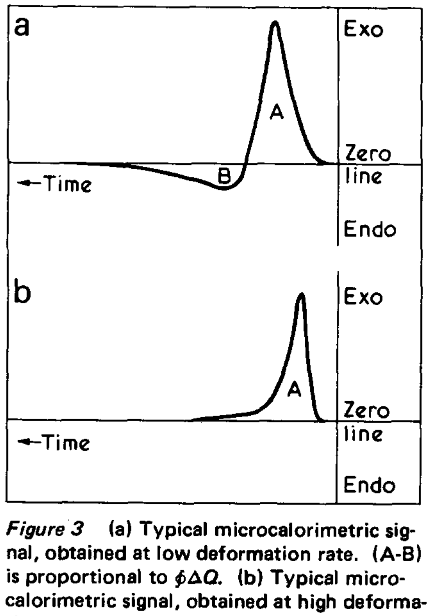

Figure 3 (a) Typical microcalorimetric signal, obtained at low deformation rate. (A-B) is proportional to $\oint \Delta Q$. (b) Typical microcalorimetric signal, obtained at high deformation rate. The area is proportional to $\oint \Delta Q$

Table 1 Thermomechanical results

Temperature[a] (°C)	α_{max}[b]	Strain rate (min^{-1})	$\oint \Delta W$[c]	$-\oint \Delta Q$[c]	$-\oint \Delta H$[c]
25	2	0.40	0.020	0.055	0.035
			0.016	0.048	0.032
		1.46	0.023	0.068	0.045
			0.017	0.059	0.042
40	2	0.40	0.012	0.034	0.022
			0.015	0.035	0.020
		1.46	0.015	0.044	0.029
			0.020	0.047	0.027
25	3	0.40	0.073	0.175	0.102
			0.058	0.131	0.073
		1.46	0.104	0.153	0.049
			0.079	0.140	0.061
40	3	0.40	0.062	0.114	0.052
			0.056	0.106	0.050
		1.46	0.053	0.120	0.067
			0.043	0.101	0.058

[a] Work temperature in the calorimetric cell, [b] maximum strain value in the hysteric loop; [c] thermodynamic functions are given in J/cm^3

This is an important point in our discussion. Turning our attention to the data of *Table 1* we can underline some evident features.

The sample is more hysteretic at 25°C where $\oint \Delta W$ and $\oint \Delta Q$ are always greater than at 40°C. The sample is more hysteretic in the first run than in the second one. Moreover the $\oint \Delta H$ term is always negative, that is, the enthalpy in the final state is less than that in the initial state. The observed behaviour of the two functions $\oint \Delta W$ and $\oint \Delta Q$ can be explained taking into account some molecular relaxation modes, like the entanglements slipping and the chain orientation. In fact the entanglements slipping has been described by many authors[2], and it has been demonstrated[7] by spectroscopic methods that an increase of the chain orientation takes place during the mechanical relaxation process. This means that some residual orientation can be present after the first hysteretic run. This residual orientation is possible in the temperature and strain range in which the thermomechanical analysis has been carried out, as observed in a photomechanical study[8].

The third molecular factor affecting the hysteretic behaviour is related to chain orientation. We believe that the third factor could be related to the possibility that some degree of order is present in the amorphous state. This order could be present before the stretching, or it could be induced or increased by the monodirectional deformation. The opinion that the amorphous state is characterized by a low degree of order, but not by the complete absence of it, was first suggested by Kargin[9]. The possible effects on the mechanical behaviour of an elastomer has been considered more recently by Dušek and Prins[10].

In our previous papers, in particular on the mechanical and photomechanical behaviour of ethylene–propylene copolymers[11,12], we have direct evidence of these phenomena and of their effects on the physical behaviour. Very recently all the matter has been discussed during a Symposium on the Physical Structure of the Amorphous State[13]. We believe that our results, and in particular the observed trend of the function $\oint \Delta H$, can agree with this opinion.

It is well known that an ordering phenomenon, like a crystallization, is characterized by a negative enthalpic change. It is therefore reasonable to believe that a negative value for $\oint \Delta H$ could support aggregation phenomena induced by the strain. We say aggregation and not crystallization for the explained reasons, and if crystallization takes place, the values of $\oint \Delta H$ imply only about 0.1% more crystallization at the end of the experiment than at the beginning.

Of course our data do not prove directly the aggregation or, in general. ordering phenomena, but we can support such a hypothesis without dispute.

To conclude, we want to underline that the three suggested molecular relaxation modes, can be memorized by the sample only for a short time, because, as reported, a second hysteretic run, carried out after 24 h, does not give evidence of any memorization phenomenon. Anyway we consider the obtained results very preliminary and more work is required in this area, in particular going up to strain values where a crystallization process takes place.

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*(Received 11 July 1977;
revised 27 February 1978)*

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