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THERMODYNAMIC CHARACTERIZATION OF CARBON BLACK-FILLED RUBBERS

*V. P. Privalko, V. P. Azarenkov, A. V. Baibak and Y. G. Yanovsky**

Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, 253160 Kiev, Ukraine
*Institute of Applied Mechanics, Russian Academy of Sciences, 117334 Moscow, Russia

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Abstract

Unfilled and carbon black-filled samples of synthetic isoprene- and butadiene-methylstyrene-based rubbers were characterized by precise heat capacity measurements in the temperature interval 4.2–300 K. Both unfilled samples proved to behave in an essentially fracton-like way in the temperature interval 6–30 K. The excess thermodynamic quantities derived from the smoothed data suggested that the thermodynamic state of the elastomeric phase in the filled rubbers was intrinsically unstable.

Keywords: excess thermodynamic quantities, filled rubbers, fracton-like vibration regime, heat capacity, thermodynamic stability

Introduction

The incorporation of high-modulus, disperse solid fillers into a low-modulus, continuous elastomeric phase has long been (and still is) an obvious pragmatic approach to improvement of the mechanical performance of rubbers. In the majority of documented cases (e.g. [1–3], either a large (in the case of 'reinforcing' fillers) or a small (in the case of 'inert' fillers) 'overshoot' of the experimental elasticity moduli above the estimates based on various hydrodynamic theories was almost invariably observed, as if the apparent volume content of the disperse phase, φ^*, exceeded its nominal content, φ. A seemingly reasonable explanation of this empirical finding was that a 'bound' rubber (BR) structurally different from the remainder of a continuous elastomeric matrix formed concentric shells of reduced thickness $\Delta r/r = (\varphi^*/\varphi)^{1/3}-1$ around the filler particles of size $2r$ (assuming, for simplicity, the spherical shape of the latter). In spite of many attempts to evaluate the structure and 'partial' properties of BR (e.g. [4–6]), its thermodynamic stability has so far not been characterized.

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It is therefore the purpose of the present communication to provide the first direct experimental data on the thermodynamic state of BR in carbon black-filled rubbers.

Experimental

Flat specimens (thickness 1–3 mm) of synthetic isoprene rubber SKI-3 and synthetic butadiene-dimethylstyrene rubber SKMS-30 filled with furnace carbon black TU P-234 (specific surface area about 240 $m^2 g^{-1}$) were prepared by hot-pressing at 350–370 K. Sample codings and compositions are shown in Table 1.

Table 1 Sample coding and composition (in parts by weight)

Ingredient	Sample coding				
	M340	M342	M344	D200	D240
SKI-3	200	200	200	–	–
SKMS-30	–	–	–	200	200
Stearic acid	2	2	2	4	4
Altax	1.2	1.2	1.2	–	–
Diphenylguanidine	6	6	6	–	–
Zinc oxide	10	10	10	10	10
Carbon black	0	40	80	0	80
Sulfur	2	2	2	4	4
Sulfeneamide	–	–	–	3	3

The heat capacity C_p in the temperature interval 4.2–300 K was measured in steps of 0.2–0.6 K in the interval 4.2–50 K, 0.6–1.5 K in the interval 50–150 K and 1.5–5 K at higher temperatures, with the aid of an automated adiabatic calorimeter [7]; the estimated maximum errors in the indicated temperature intervals did not exceed 2%, 1% and 0.5%, respectively.

Results and discussion

Heat capacity in the solid state

The raw values of the heat capacity C_p for all studied samples in the entire temperature interval of the solid (i.e. glassy) state below about 200 K varied smoothly with temperature T (Fig. 1). As can be seen from the $\log C_p$ *vs.* $\log T$ plots (Fig. 2), the experimental data for both unfilled samples M-340 and D-200 below 20 K may be reasonably well fitted to the Stockmayer-Hecht (SH) model [8], assuming $T^*=370$ K for the characteristic temperature, $\nu^*=255$ cm^{-1}

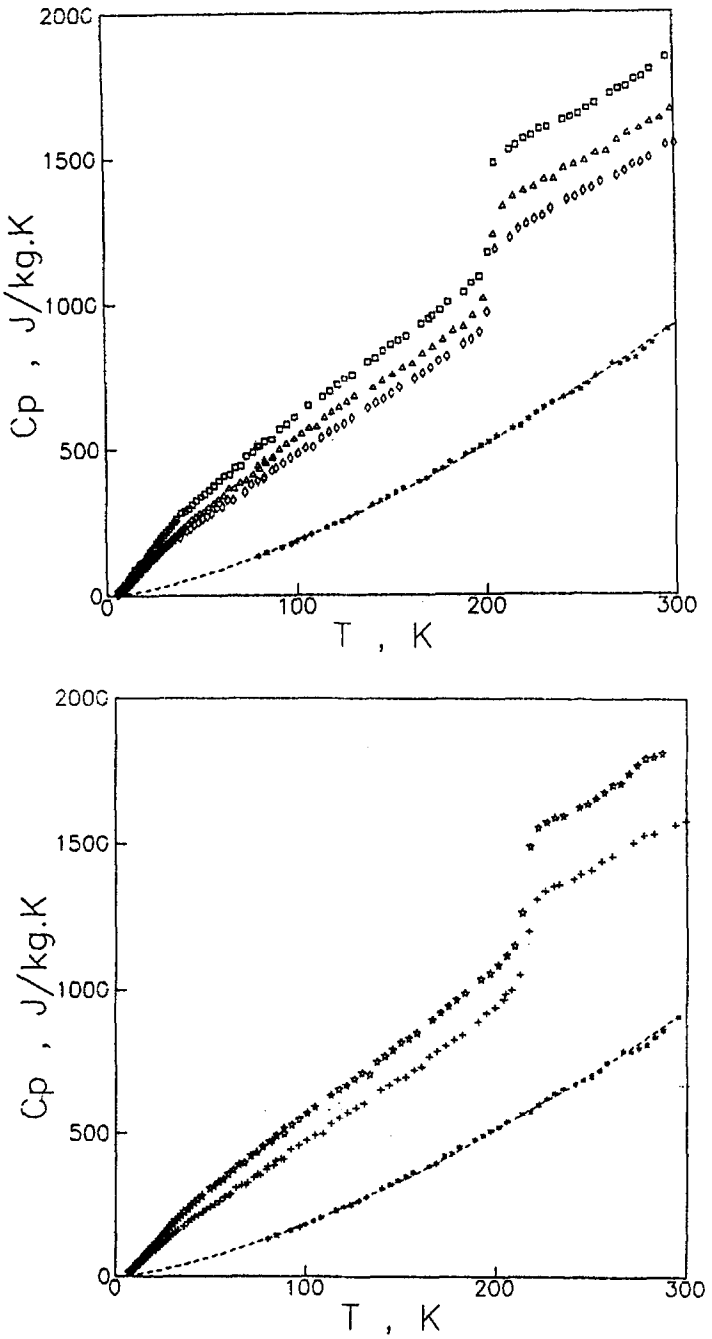

Fig. 1 Temperature dependence of the raw heat capacity of M-340 (squares), M-342 (triangles), M-344 (diamonds), D-200 (stars), D-240 (crosses) and carbon black (asterisks)

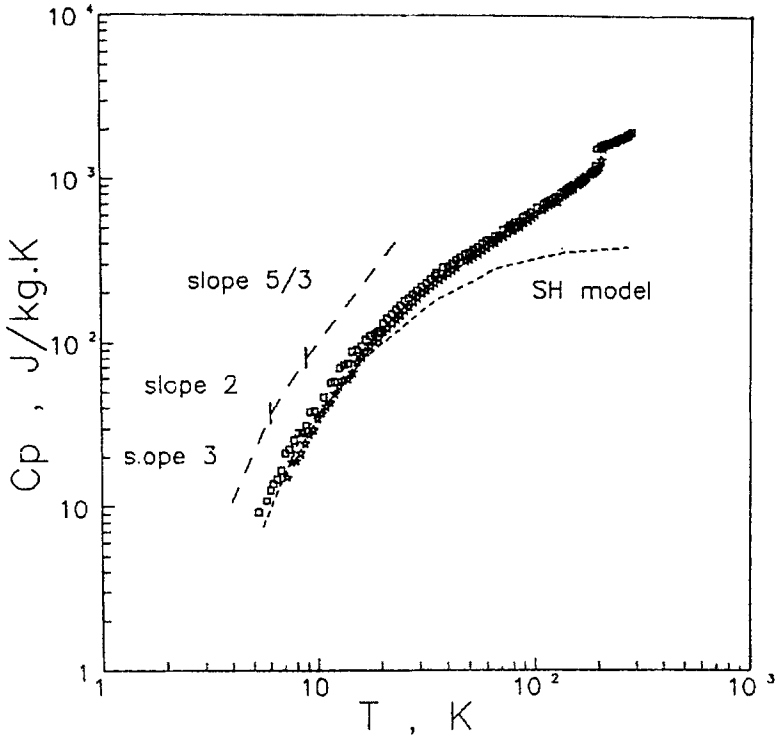

Fig. 2 LogC_p *vs.* log$T$ plots for M-340 and D-200

for the characteristic frequency of vibrations, and $m^*=40$ g mol^{-1} for the effective mass of the chain vibrating unit (regarding the observed variation in these parameters with the polymer nature [9] as unessential). It is pertinent to remark here, however, that the SH model, in a strict sense, was developed for polymer crystals; therefore, one should look for a different approach explicitly accounting for a disordered structure of the studied rubbers in the glassy state.

There is experimental evidence suggesting that polymer glasses behave essentially fractal-like in the frequency interval from about $\omega'=20$ to $\omega''=80$ cm^{-1} [10–13]; therefore, one should expect a cross-over of the vibration density of the states, $\rho(\omega)\sim\omega^{d-1}$ (where $d=D/a$, D is the mass fractal dimensionality and a is the low-frequency scaling exponent), to the fracton-like vibration regime [14, 15] in the temperature interval from $T'=h\omega'/k=5$ K to $T''=h\omega''/k=20$ K. In fact, analysis of the experimental $C_p\sim\int\rho(\omega)\,d\omega\sim T^d$ data for several polymers in the indicated temperature interval [16] revealed a surprisingly good agreement of the experimental exponents d with the theoretical $d=D=2$ and 5/3 (below and above 10 K, respectively) predicted on the assumption that $a=1$ (i.e. the high conductivity limit). The raw values of C_p for both unfilled rubbers apparently exhibit similar behavior in the temperature intervals of roughly 8–10 K and 10–30 K, respectively (Fig. 2).

At higher temperatures, the heat capacities of glassy rubbers could be approximated to by another scaling law, $C_p \sim T^{\alpha}$, with $\alpha \approx 0.9$. Empirically, the low value of the exponent α may be regarded as an indication of a cross-over to a high-temperature vibration regime with a dominant contribution of one-dimensional, intramolecular excitations to the total vibrational density of the states.

As could be expected, the absolute values of C_p and the slopes of the corresponding C_p *vs.* T plots for filled samples decreased, the higher the filler content (Fig. 1); however, a quantitative discussion of these trends as outlined above ought to be postponed until the low-temperature values of C_p for carbon black become available.

Glass transition region

As can be seen from Fig. 1 the glass-rubber transitions at $T_g = 202 \pm 2$ K (SKI-3) and 215 ± 2 K (SKMS-30) manifest themselves as sudden heat capacity jumps [$\Delta C_p(O) = 0.360 \pm 0.010$ J g^{-1} K^{-1} and 0.350 ± 0.010 J g^{-1} K^{-1}, respectively]. Within the limits of experimental uncertainty, the values of T_g for filled and unfilled samples were the same; moreover, the apparent heat capacity jumps for filled samples, $\Delta C_p(\varphi)$, proved to be very close to the corresponding additive values, $\Delta C_p(O)(1-\varphi)$. Thus, it appears that the claim for the existence of BR (if any) in filled rubbers should be based on experimental evidence other than static heat capacity measurements in the relatively narrow temperature interval around the glass transition [6].

Thermodynamic quantities

Pragmatically, within the limits of experimental uncertainty, the raw values of C_p for all studied samples in the solid (glassy) state below T_g could be fitted to the 6-power polynomials of temperature (Table 2). These polynomials were subsequently used to derive the smoothed values of C_p in the temperature interval from 0 K to T_g; at higher temperatures, the raw data were smoothed graphically on the assumption of a linear temperature dependence of C_p in the rubbery state. The smoothed values of C_p for carbon black below 80 K were calculated from the empirical relationship C_p [J kg^{-1} K^{-1}] $= 0.2195\, T^{1.464}$, which

Table 2 Coefficients of the equation C_p/J kg^{-1} K^{-1} $= A + BT + CT^2 + DT^3 + ET^4 + FT^5 + GT^6$

Sample	A	B	$C\times10^2$	$D\times10^5$	$E\times10^6$	$F\times10^8$	$G\times10^{11}$
M340	–49.32	9.72	–4.18	–8.70	3.87	–2.40	4.84
M342	–43.20	7.58	–2.66	–12.0	3.91	–2.66	5.88
M344	–38.14	7.74	–4.78	21.1	1.03	–1.21	2.91
D200	–54.50	9.08	–3.85	–3.35	2.35	–1.23	2.05
D240	–50.74	8.24	–7.62	77.6	–4.13	1.05	–0.90

quantitatively fitted the raw data in the entire temperature interval 80–300 K (dotted line in Fig. 1).

The absolute enthalpy, $H-H_o=\int C_p\,dT$, the absolute entropy, $S-S_o=\int C_p\,d\ln T$, and the absolute Gibbs free energy, $G=(H-H_o)-T(S-S_o)$ (where H_o and S_o are

Table 3 Thermodynamic functions of M-340

T/K	C_p/J kg^{-1} K^{-1}	$H-H_o$/J kg^{-1}	$S-S_o$/J kg^{-1} K^{-1}	$-G$/J kg^{-1}
2	3.0	3.0	1.5	0
5	8.5	20.25	6.3	11.25
10	43.6	150.5	21.45	64.0
20	128.2	1009	75.3	496.5
30	204.9	2675	141.5	1570
40	274.6	5073	210.0	3327
50	338.6	8139	278.2	5770
60	398.1	11820	345.2	8890
70	454.4	16085	410.8	12675
80	508.2	20900	475.0	17105
90	560.6	26240	538.0	22175
100	611.9	32105	600.0	27865
110	662.4	38475	660.4	34170
120	712.1	45350	720.2	41075
130	761.0	52715	779.1	48570
140	809.0	60565	837.3	56655
150	856.0	68890	894.7	65320
160	902.3	77680	951.4	74550
170	948.8	86935	1007	84350
180	997.1	96665	1063	94700
190	1050	106900	1118	105610
200	1111	117705	1174	117070
210	1500	130760	1237	129090
220	1553	146030	1308	141820
230	1589	161740	1378	155255
240	1625	177815	1447	169380
250	1661	194245	1514	184190
260	1697	211035	1580	199660
270	1733	228180	1644	215780
280	1769	245690	1708	232540
290	1805	263555	1771	249940
300	1840	281780	1832	267955

the zero-temperature enthalpy and entropy of a disordered glass), were calculated from the smoothed values of C_p obtained in this fashion (Tables 3 –8). Finally, the corresponding excess thermodynamic quantities, P_{ex}, where derived from the standard relationship.

Table 4 Thermodynamic functions of M-342

T/K	C_p/J kg^{-1} K^{-1}	H–H_o/J kg^{-1}	S–S_o/J kg^{-1} K^{-1}	$-G$/J kg^{-1}
2	2.8	2.8	1.4	0
5	7.5	18.25	5.75	10.6
10	32.6	118.5	17.65	58.0
20	102.8	795.5	59.65	397.5
30	167.8	2149	113.3	1251
40	228.2	4129	169.8	2664
50	284.9	6694	226.8	4647
60	338.9	9813	283.6	7200
70	390.9	13460	339.7	10320
80	441.5	17625	395.2	13995
90	491.0	22290	450.1	18220
100	539.5	27440	504.4	23000
110	586.8	33070	558.0	28310
120	632.6	39170	611.0	34160
130	676.6	45715	663.4	40530
140	718.9	52690	715.1	47425
150	759.5	60085	766.1	54835
160	799.3	67880	816.4	62750
170	840.2	76075	866.1	71160
180	885.2	84700	915.4	80070
190	939.0	93820	964.7	89470
200	1008	103560	1014	99365
210	1320	115200	1071	109760
220	1378	128690	1134	120790
230	1414	142650	1196	132440
240	1450	156970	1257	144710
250	1486	171650	1317	157580
260	1522	186690	1376	171050
270	1558	202090	1434	185100
280	1595	217860	1491	199730
290	1631	233980	1548	214930
300	1667	250470	1604	230690

$$P=\varphi P_1+(1-\varphi)P_2+P_{ex}$$

where subscripts 1 and 2 refer to filler and rubber, respectively.

The results obtained (Fig. 3) reveal that the thermodynamic stability of the elastomeric phases in all filled samples is invariably lower (i.e. $G_{ex}>0$) than for

Table 5 Thermodynamic functions of M-344

T/K	C_p/J kg^{-1} K^{-1}	$H-H_o$/J kg^{-1}	$S-S_o$/J kg^{-1} K^{-1}	$-G$/J kg^{-1}
2	3.0	3.0	1.5	0
5	7.8	19.2	6.09	11.25
10	34.7	125.5	18.67	61.20
20	99.4	796.2	60.89	421.6
30	157.4	2080	112.0	1279
40	210.1	3918	164.5	2661
50	259.0	6263	216.6	4568
60	305.3	9085	268.0	6994
70	349.9	12360	318.4	9928
80	393.6	16080	368.0	13360
90	437.0	20230	416.9	17290
100	480.2	24820	465.2	21700
110	523.4	29835	513.0	26590
120	566.5	35285	560.4	31960
130	609.2	41165	607.4	37800
140	651.3	47465	654.1	44110
150	692.9	54190	700.4	50880
160	734.2	61320	746.5	58115
170	775.8	68870	792.2	65810
180	819.0	76850	837.8	73960
190	865.7	85270	883.3	82565
200	919.3	94195	929.1	91630
210	1200	104790	980.7	101150
220	1266	117120	1038	111240
230	1302	129960	1095	121910
240	1337	143150	1151	133140
250	1372	156695	1207	144930
260	1407	170590	1261	157270
270	1442	184840	1315	170150
280	1478	199440	1368	183570
290	1513	214390	1420	197510
300	1548	229695	1472	211975

the corresponding unfilled rubbers. The structural implications of this fundamental result are difficult to assess at the present stage; nevertheless, it seems completely consistent with the idea that the macromolecules of both rubbers in filled samples assume somewhat altered (presumably more extended) conformations favoring better intermolecular packing (hence, $H_{ex}<0$) as compared

Table 6 Thermodynamic functions of D-200

T/K	C_p/J kg^{-1} K^{-1}	$H-H_o$/J kg^{-1}	$S-S_o$/J kg^{-1} K^{-1}	$-G$/J kg^{-1}
2	2.8	2.8	1.4	0
5	7.5	18.25	5.75	10.5
10	32.38	118.0	17.60	58.0
20	111.7	838.1	61.70	395.9
30	183.8	2315	120.2	1292
40	249.5	4482	182.1	2801
50	309.9	7279	244.2	4933
60	365.9	10660	305.7	7685
70	418.6	14580	366.1	11050
80	469.0	19020	425.3	15010
90	518.1	23955	483.4	19555
100	566.6	29380	540.5	24680
110	615.0	35285	596.8	30365
120	663.8	41680	652.4	36610
130	713.3	48565	707.5	43415
140	763.5	55950	762.2	50765
150	814.5	63840	816.7	58660
160	866.1	72240	870.9	67100
170	918.4	81165	924.9	76075
180	971.3	90615	978.9	85595
190	1025	100595	1033	95655
200	1080	111120	1087	106255
210	1180	122425	1142	117390
220	1560	136125	1206	129090
230	1577	151810	1275	141500
240	1619	167790	1343	154600
250	1660	184190	1410	168370
260	1702	201000	1476	182800
270	1743	218220	1541	197890
280	1785	235870	1605	213630
290	1826	253920	1669	230000
300	1868	272385	1731	247000

Table 7 Thermodynamic functions of D-240

T/K	C_p/J kg^{-1} K^{-1}	$H-H_o$/J kg^{-1}	$S-S_o$/J kg^{-1} K^{-1}	$-G$/J kg^{-1}
2	2.0	2.0	1.0	0
5	5.9	13.85	4.27	7.5
10	24.8	90.6	13.42	43.6
20	89.2	660.6	48.12	301.8
30	145.8	1836	94.72	1006
40	197.2	3551	143.7	2196
50	245.3	5763	192.9	3879
60	291.5	8447	241.7	6053
70	336.6	11590	290.0	8713
80	381.4	15180	337.9	11850
90	426.2	19215	385.4	15470
100	471.0	23700	432.6	19560
110	516.0	28640	479.6	24125
120	561.0	34020	526.5	29155
130	606.2	39860	573.2	34650
140	651.4	46145	619.7	40620
150	696.8	52890	666.2	47050
160	742.8	60085	712.7	53940
170	789.7	67750	759.1	61300
180	838.2	75890	805.6	69125
190	889.3	84525	852.3	77410
200	944.0	93690	899.3	86170
210	1040	103610	947.7	95400
220	1280	115210	1002	105120
230	1351	128365	1060	115430
240	1385	142050	1118	126320
250	1420	156075	1175	137795
260	1454	170445	1232	149830
270	1489	185155	1287	162430
280	1523	200210	1342	175580
290	1557	215610	1396	189270
300	1592	231360	1450	203500

with their classical random coil shape in unfilled samples; however this new conformational state turns out to be intrinsically less stable ($G_{ex}>0$) due to the concomitant severe loss of intramolecular (conformational) entropy ($S_{ex}<0$).

In this context, the differences observed in the magnitude of the excess quantities for filled samples based on SKI-3 or on SKMS-30 become especially illuminating. In fact, the significantly larger values of $-H_{ex}$ and $-S_{ex}$ implying better lateral packing of extended chain fragments in the filled samples of the former may be regarded as a quite natural consequence of its stereoregular molecular

Table 8 Thermodynamic functions of carbon black

T/K	C_p/J kg^{-1} K^{-1}	$H-H_o$/J kg^{-1}	$S-S_o$/J kg^{-1} K^{-1}	$-G$/J kg^{-1}
2	1.0	1.0	0.5	0
5	2.3	5.95	1.94	3.75
10	6.4	27.7	4.69	19.2
20	17.7	148.2	12.32	98.1
30	32.0	396.7	22.07	265.5
40	48.7	800.2	33.49	539.6
50	67.5	1381	46.33	935.4
60	88.2	2160	60.43	1466
70	110.5	3153	75.67	2144
80	134.4	4378	91.97	2980
90	159.7	5848	109.2	3983
100	186.4	7579	127.4	5164
110	214.3	9582	146.5	6532
120	243.4	11870	166.4	8094
130	273.7	14460	187.0	9860
140	305.0	17350	208.5	11835
150	337.5	20560	230.6	14030
160	370.9	24105	253.4	16450
170	405.4	27990	277.0	19100
180	440.8	32220	301.1	21990
190	477.1	36810	325.9	25120
200	514.3	41765	351.3	28505
210	552.4	47100	377.4	32150
220	591.3	52815	403.9	36050
230	631.1	58930	431.1	40225
240	671.7	65440	458.8	44675
250	714.1	72370	487.1	49400
260	755.2	79720	515.9	54415
270	798.1	87485	545.2	59720
280	841.8	95680	575.0	65320
290	886.2	104320	605.3	71220
300	939.3	113450	636.3	77430

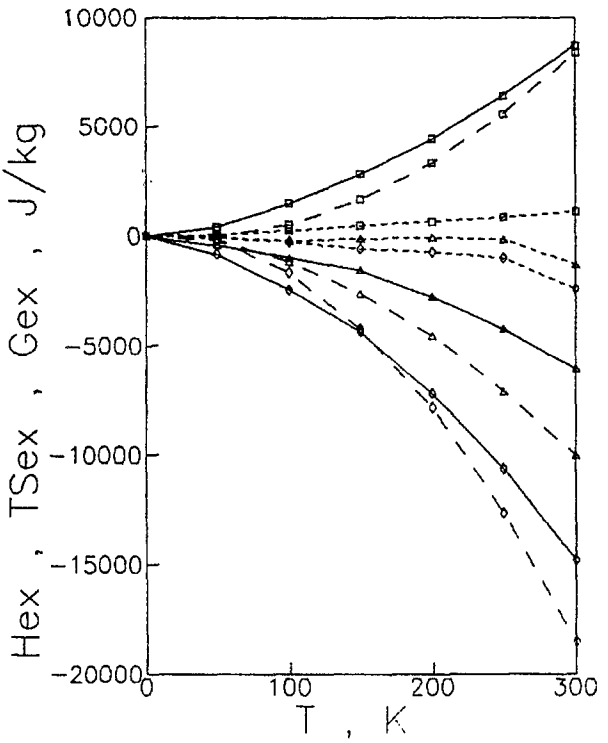

Fig. 3 Temperature dependence of H_{ex} (triangles), TS_{ex} (diamonds) and G_{ex} (squares) for M-342 (solid lines), M-344 (broken lines) and D-244 (dotted lines)

structure as contrasted with the irregular one of SKMS-30 [17]. Moreover, the trend to increases in $-H_{ex}$ and $-S_{ex}$ with filler content for SKI-3 (Fig. 3) is exactly that expected for a structural model of a filled rubber with BR distributed as shells of constant thickness around filler particles. According to a rough estimate, the apparent thickness of an elastomeric interlayer between filler particles in the highest-loaded sample M-344, $\langle L\rangle \cong 2r[(\varphi_M/\varphi)^{1/3}-1] \cong 15$ nm (assuming $2r \cong 30$ nm for the mean filler particle size and $\varphi_M \cong 0.8$ for the maximum packing fraction of polydisperse particles [6]), is comparable to the unperturbed radius of gyration of SKI-3 chains, $\langle R_g\rangle \cong 0.4\langle h_o^2\rangle^{1/2} \cong 11$ nm (assuming $\langle h^2\rangle$ (nm^2) $\cong 10^{-2} M$ [18] for the mean-square end-to-end distance and $M \cong 50\times10^3$ [17] for a typical molar mas of SKI-3 chains). In so far as $\langle R_g\rangle$ may be regarded as the minimum thickness of a polymer layer adsorbed on a solid surface [19, 20], the above estimates suggest that nearly all the elastomeric phase available in M-344 may exist as BR.

It is pertinent to note here that the value of $H_{ex} \cong -10$ J g^{-1} for the latter sample at 300 K (Fig. 3) is very close in magnitude to the enthalpy difference between the equilibrium melt and the ideal crystal (i.e. the melting enthalpy) of *cis*-polyisoprene, $\Delta H_m^o = 12.8$ J g^{-1} [21]. In so far as H_{ex} is a measure of the en-

thalpy difference between the thermodynamic states of SKI-3 in filled and unfilled samples, respectively, it may be concluded that the former state is enthalpically equivalent to the crystalline state of SKI-3; as already emphasized, however, the overwhelming contribution of the unfavorable $S_{ex}<0$ makes this filler-perturbed state intrinsically unstable ($G_{ex}>0$).

Conclusions

1. Unfilled isoprene- and butadiene-methylstyrene-based rubbers behave essentially in a fracton-like way in the temperature interval 6–30 K.

2. Static heat capacity measurements in the glass transition interval are insufficient for a decision as to the existence of bound rubber in carbon black-filled rubbers.

3. The thermodynamic state of the elastomeric phase in carbon black-filled rubbers is intrinsically unstable.

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