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Crystallization of polydimethylsiloxane: effect of silica filler and curing

Mirta I. Aranguren*
Institute of Research in Materials Science and Technology (INTEMA), Universidad Nacional de Mar del Plata, Juan B. Justo 4302, 7600 Mar del Plata, Argentina
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Previous publications on the low temperature behavior of polydimethylsiloxane (PDMS) described semiquantitatively or in an incomplete way the different features appearing during the heating cycle of previously cooled PDMS. The main deficiency of these descriptions is in the quantitative measurement of the heat of fusion. This value was reported per mole of chain atom, which has been misunderstood by other researchers as being per mole of structural units. The object of the present work is to give a systematic view of the low temperature behavior of PDMS with special attention to the melting behavior of the polymer. The effects of the previous cooling rate, molecular weight of the polymer, filler addition and crosslinking on the characteristics of d.s.c. thermograms of PDMS are reported and discussed. A simplified view of the different effects is presented, which allows the calculation of the heat of fusion of the different samples from the corresponding value of a completely crystalline polydimethylsiloxane. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polydimethylsiloxane; PDMS; crystallization)

INTRODUCTION

Previous publications on the low temperature behavior of polydimethylsiloxane (PDMS) described semiquantitatively or incompletely the low temperature behavior of PDMS[1–3]. In general, they are focused on the temperatures at which different features appeared (glass transition or temperatures of the maximum heat flux of endo- or exothermic peaks)[4]. The main deficiency appeared in the quantitative measurement of the heat of fusion. One problem is that old papers deal with the results of dynamic thermal analysis (DTA), instead of dynamic scanning calorimetry (d.s.c.), or they only report the ratios of peak areas without informing the absolute values[2]. In this respect, the only value of the heat of fusion of a 100% crystalline PDMS (ΔH_{th}) is that reported by Lee *et al.*, who measured it from the melting point depression of the polymer in toluene[3]. Unfortunately, this value was reported per mole of chain atom, which has been misunderstood by other researchers as being per mole of structural units[5,6]. This problem is further discussed in the present paper.

The effects of the addition of silica, the usual reinforcement of silicone rubbers, was addressed by Yim and St. Pierre, but the study focused only on the temperature at which crystallization takes place during the heating cycle (cold crystallization)[7].

More recent papers analyze more complex features, such as the kinetics of PDMS crystallization[5], partial crystallization of adsorbed chains[6], the effect of the morphology of copolymers on the crystallization of PDMS blocks[8] or the effect of the molecular weight of the copolymer on the glass transition temperature of the blocks[9]. However, in none of these cases the value of the heat of fusion is reviewed, and in some cases is misused[5,6].

The object of the present work is to give a systematic view of the low temperature behavior of PDMS. The effects of the previous cooling rate, molecular weight of the polymer, filler addition and crosslinking on the characteristics of d.s.c. thermograms of PDMS are reported and discussed. A simplified view of the different effects is presented, which allows the calculation of the heat of fusion of the different samples from the corresponding value of a completely crystalline polydimethylsiloxane.

EXPERIMENTAL

Two vinyl-terminated linear polydimethylsiloxanes of different molecular weight (Dow Corning, Midland, MI, USA) and a mixture of these two were used in this study, the results of their characterization are shown in *Table 1*. It was previously shown, that vinyl groups are only important to the crosslinking of the materials, but do not affect the behavior of silica suspensions[10].

A fumed silica (Aerosil R972, Degussa Corp., Teterboro, NJ) with a surface area of 108 $m^2 g^{-1}$ and partially methylated was mechanically mixed with bulk PDMS to obtain the suspensions and cured elastomers.

The crosslinking reaction consisted in the hydrosilation of the terminal double bonds of the PDMS chains. The crosslinker was a hydrosilane functionalized siloxane oligomer (Dow Corning) of average functionality of 5. The ratio SiH to C=C was kept equal to 1.8 to compensate for SiH groups consumed in secondary reactions. The reaction catalyst and the inhibitor, used to avoid reaction during mixing, were also provided by Dow Corning. Curing was performed at 150°C with nitrogen flow through the oven[11].

The low temperature thermal characterization of the materials were carried out in a Mettler TA 3000 DSC and all the heating runs were done at 10°C min^{-1}. Sample weights were in the range between 7 to 14 mg.

The glass transition temperatures were read as the temperature at which the regression line, constructed through the trace below the starting point of the transition, intersects the tangent drawn from the inflection point of the glass transition step. The construction is shown in *Figure 1*. The temperatures of the peaks reported in *Tables 2–5*,

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* To whom correspondence should be addressed

take into account the maximum in heat flux after a baseline correction.

RESULTS AND DISCUSSION

Different cooling rates

Figure 1 shows the thermograms obtained for the 118K PDMS, which was previously cooled at −140°C using different cooling rates: fast cooling (*ca.* 50°C min^{-1}), 8°C min^{-1} and 3°C min^{-1}. The curves show a glass transition, an exothermic peak and two endothermic peaks, in total agreement with results already published[2–4]. Some of these features are affected by the rate at which the sample was cooled and will be discussed below.

The location of the glass transition temperature did not change with the cooling rate appearing at −122 to −124°C in good agreement with the accepted reported values, which are in the range of −120 to −125°C[1–4,8,9]. On the other hand, the variation in heat capacity at the transition is smaller for slower cooling rates (*Table 2*). As the cooling rate increases the chains have less time to form ordered crystals and the sample has a larger amorphous phase. For this reason, the transition is more noticeable in less crystalline samples, what is observed in the Δcp values reported in *Table 2*. If the change is referred to the amorphous fraction of material present at T_g, the Δcp averages 0.45 J/g°C, slightly lower than a previously reported value (0.50 J/g°C)[12]. In the calculation of the fraction of amorphous material a theoretical value of ΔH_{th} = 37.4 J/g (to be further discussed) was used. Clarson *et al.* had reported that linear PDMS polymers are highly crystalline and do not show a glass transition, when they are cooled at rates of less than about 1°C min^{-1}, in agreement with the trend presented here[4].

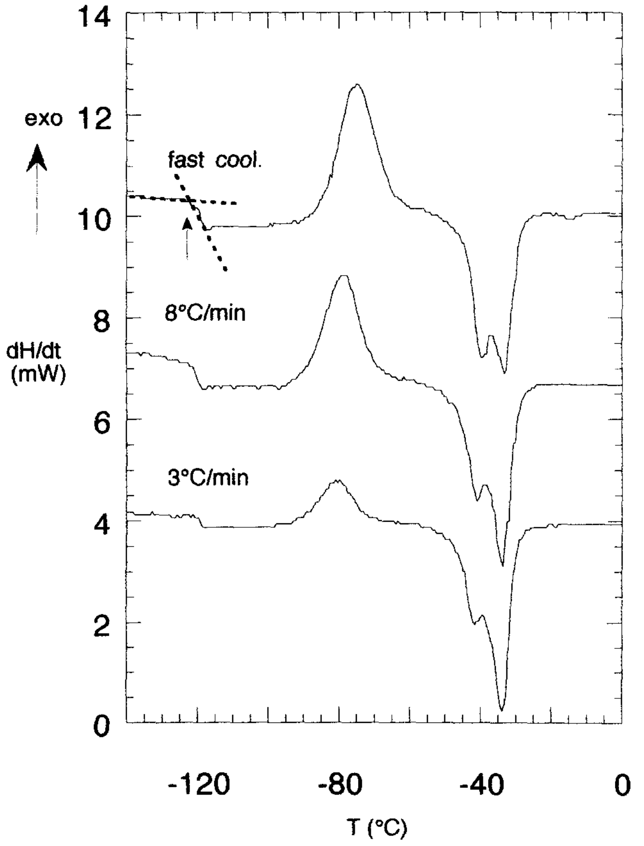

Figure 1 D.s.c. thermograms of PDMS 118K obtained at a heating rate of 10°C min^{-1}. Previous cooling rates are indicated in the figure. Weight sample = 7.33 mg. Dotted lines indicate how the glass transition temperature was determined.

Table 1 Molecular weights and polydispersity of the used polydimethylsiloxanes

	118K[a]	88K[b]	17K[a]
M_n	66 400	22 600	8 900
M_w	118 000	87 600	16 500
M_w/M_n	1.8	3.9	1.9

[a] Measured in Dow Corning Laboratories (Midland, MI), PDMS calibration was used

[b] A mixture of 118K and 17K, 70:30 wt.%, respectively; M_n and M_w are calculated values

The second feature is an exothermic peak. During the heating run, the chains recover enough mobility to reaccommodate and crystallize. The position and size of this peak (cold crystallization) also depends on the rate of the previous cooling, as can be seen in *Table 2*. The faster the sample is cooled, the higher the temperature of cold crystallization and the larger the area under the peak. Other authors have noticed also the presence of crystallization during heating. Clarson *et al.*[4] reported an exotherm at −91.5°C, Yim and St. Pierre[7] found it at −90°C and Ke[1] noticed the peak at − 100°C. The most complete work in this respect is that by Helmer and Polmanteer who reported the cold crystallization peak at −94 to −100°C and studied the effect of the cooling rate on it[2]. They found that as the cooling rate increases the polymer can be supercooled and the area of the cold crystallization peak increases accordingly. At their maximum controlled cooling rate 52°C s^{-1}, 85% of the crystallization took place during the heating cycle and the cold crystallization was completely suppressed if the cooling rate was lower than 1.6°C s^{-1}. In this respect, Lee *et al.* reported that the cold crystallization peak becomes smaller as the cooling rate decreases and eventually disappears if the cooling rate is less than 4.2°C min^{-1}[13]. Data obtained for this work show the same trend; however, cold crystallization was present even after cooling at 0.05°C s^{-1} (3°C min^{-1}). Differences may be due to the use of different molecular weight PDMS in the different works, since no characterization data were reported in those publications.

The melting zone shows two peaks, whose positions did not change appreciably with the previous cooling rate (T_{m1} = −42°C and T_{m2} = −35.9°C, *Table 2*). Fast cooling favors the crystallization that occurs during the heating cycle, and in this case the two endothermic peaks that follow

Table 2 Effect of the cooling rate on the 118K PDMS thermograms (M_n = 66 400; heating rate, 10°C min^{-1})

	Cooling rate		
	Fast cooling[a]	8°C min^{-1}	3°C min^{-1}
T_g (°C)	−123.95	−123.97	−123.14
Δcp (J/g°C)	0.442	0.368	0.175
Δcp^c (J/g°C)	0.456	0.466	0.424
$T_{cold\ cryst.}$ (°C)	−77	−80	−84
$\Delta H_{cold\ cryst.}$ (J/g)	27.64	20.80	7.05
% cryst.[b]	95.87	72.52	24.29
T_{melt1} (°C)	−42	−42.6	−42.6
T_{melt2} (°C)	−35.9	−35.8	−36.0
ΔH_p (J/g)	28.83	28.68	29.02

[a] The maximum cooling rate corresponds to the uncontrolled cooling mode of the apparatus and is approximately 50°C min^{-1}

[b] Ratio of the exothermic peak, cold crystallization, to that of the endothermic melting peaks ($\Delta H_{cold\ cryst.}/\Delta H_p$)

[c] Corrected taking into account only the fraction of amorphous material present at T_g

are of similar areas. Slow cooling favors the ordering of the chains to form crystals that melt at −35.9°C during heating.

Helmer and Polmanteer realized that the relative area of the two peaks depends also of the rate of the previous quenching, and proposed that the two melting peaks correspond to two different type of crystals[2]. Lee *et al.* considered that the cold crystallization corresponds to a recrystallization of metastable crystals, which finally melt at the higher melting temperature (T_{m2}), while the peak at T_{m1} corresponded to the melt of the less perfect crystals formed during cooling[3]. As the cooling rate was decreased T_{m1} increased since the crystals formed are more perfect, and they observed an intermediate very small peak between T_{m1} and T_{m2}, which moved towards higher temperatures (T_{m2}) as the cooling rate was decreased.

Our results are in agreement with the latter work. When the sample is cooled at high rates it can be supercooled, then, the crystals are formed at lower temperatures resulting in less perfect crystals, which consequently lower the melting point of the crystals produced. The large cold crystallization peak is the result of further crystallization and recrystallization of the imperfect crystals formed during cooling. At low cooling rates, more perfect crystals are formed, the cold crystallization peak is smaller and melting occurs at the higher temperature. Thus, the relative height of the low temperature melting peak decreases as the cooling rate decreases.

Effect of the molecular weight

The effect of different molecular weight of the chains was investigated in samples that were previously fast cooled.

The glass transition appears at −122 to −123°C, thus it is rather independent of the molecular weight or the PDMS chains in the range studied (*Table 3*). It has been shown that T_g reaches the value corresponding to an infinite molecular weight PDMS, when M_n is about 4000 g/mol[4]. The values measured for Δcp per gram of polymer are also comparable, but again somehow lower than previously reported values.

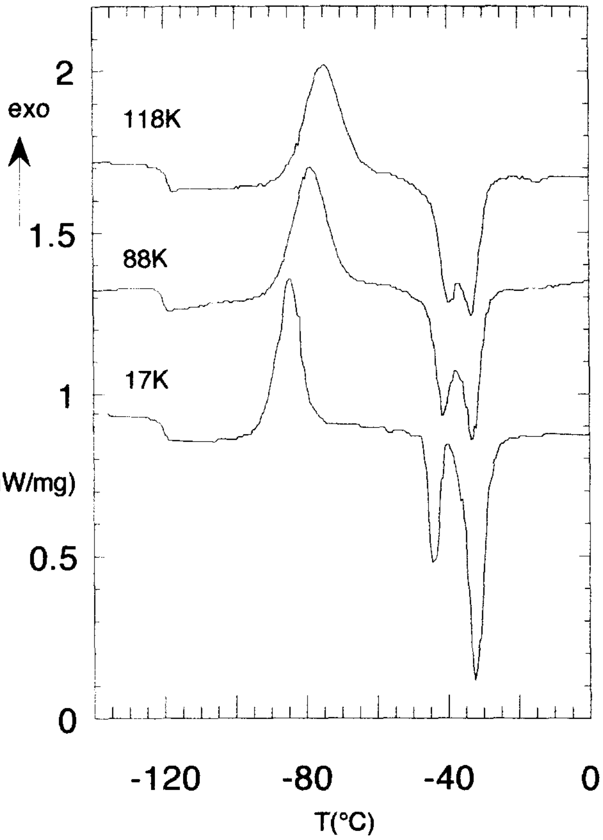

Figure 2 Thermograms obtained from previously 'quenched' (fast cooled) PDMS samples of different molecular weights. Heating rate 10°C min^{-1}.

The location of the cold crystallization peak depends on the molecular weight and appears at lower temperatures for shorter chains (*Table 3*). The ratio of the cold crystallization peak to that of melting ($\Delta H_{\text{cold cryst.}}/\Delta H_p$) decreases with decreasing molecular weight. This is understandable, since shorter chains have larger mobility during the previous fast cooling and, thus, they can form more perfect crystals and in a larger proportion than higher molecular weight PDMS.

The analysis of the melting region from *Figure 2* or from data in *Table 3* indicates that as the molecular weight increases the temperature T_{m1} (lower temperature melting) increases about 3.4°C, while T_{m2} decreases 2°C. Thus, the two peaks tend to overlap as the molecular weight increases. Moreover, the relative area of the lower temperature-melting increases with respect to the high temperature-melting, indicating that a larger percentage of imperfect crystals have been formed.

Clarson *et al.* reported that the higher the molecular weight, the larger the area of low-temperature melting peak and the smaller the area of the high-temperature melting peak, for the case of essentially monodisperse samples[4]. The difference between their results and those presented here is probably due to the polydispersity of the samples, since in this work commercial samples were utilized without fractionation.

Heat of fusion

The endothermic heat of melting requires a special discussion. The value commonly cited in the literature, which incidentally is the only one reported in the *Polymer Handbook*[13] is the one measured by Lee *et al.*[3] These authors give a value of ΔH_{th} of 325 cal mol^{-1} of chain atom, which has been misunderstood as per mole of structural unit[5,6], leading to erroneous results. However, the PDMS structural unit posses two chain atoms (Si, O), which leads to a ΔH_{th} of 650 cal mol^{-1} of structural units or 36.7 J/g. To check if this was the correct interpretation of the reported value, the ΔH_{th} of polystyrene, also reported by Lee *et al.*, was reviewed. The value reported for PS was ΔH_{th} = 1000 cal mol^{-1} of chain atom, while the value found in the *Polymer Handbook* is 8.37 ± 0.08 kJ mol^{-1} monomer unit, that is 2000 cal mol^{-1} monomer unit. Since the PS monomer unit has two carbon atoms in the main chain, the interpretation presented here is validated.

The measurement of the heat of fusion of the 17K PDMS (37.43 J/g) is in close agreement with the value discussed

Table 3 Thermal characterization of polydimethylsiloxanes of different molecular weights (fast cooling; heat scanning at 10°C min^{-1})

	Sample		
	118K	88K	17K
T_g (°C)	−122	−122.5	−123
Δcp (J/g°C)	0.456	0.420	0.432
$T_{\text{cold cryst.}}$ (°C)	−76.7	−80.1	−86.4
$\Delta H_{\text{cold cryst.}}$ (J/g)	27.64	28.37	24.75
% cryst.	95.87	87.97	66.12
T_{melt1} (°C)	−42.0	−43.0	−45.4
T_{melt2} (°C)	−35.9	−35.0	−33.9
ΔH_p (J/g)	28.83	32.25	37.43

Superscripts have the same meaning as in *Table 2* above. Thus, the higher molecular weight samples, showing lower heats of melting do not crystallize completely. Actually, Lee *et al.* reported a degree of crystallinity of the order of 79% for one commercial PDMS sample. This result is comparable to the degree of crystallinity that can be calculated for 118K PDMS (i.e., 28.8/37.4 × 100 = 77%).

Effect of the filler: fumed silica

Fumed silica was mechanically mixed into 88K PDMS to obtain suspensions and cured elastomers as described above. It should be added here that it was impossible to obtain silica–PDMS suspensions by this method at concentrations higher than those reported here.

Uncured material. The thermograms of the suspensions (*Figure 3*) do not show any appreciable change in the location of T_g with the increasing silica concentration (*Table 4*), as found by other researchers (Smit, 1966)[14]. The values of Δcp at the glass transition vary with the amount of silica added when they are expressed per total mass of the sample. However, if they are reported per mass of polymer, values in the range of 0.421–0.480 J/g°C are obtained, close to the experimental value for the pure polymer (0.420 J/g°C, *Table 2*). This would indicate that the presence of the filler does not produce important changes in the segmental mobility of the polymer chains in the case of the suspensions (uncured state).

Cold crystallization also occurred during the heating cycle for the uncured suspensions. Except for the 40 pph sample, the ratio of $\Delta H_{\text{cold cryst.}}$ to ΔH_{fs} was about 76%, irrespective of the filler load. As can be seen in *Figure 3*, the general trend is that $T_{\text{cold cryst.}}$ is lower at higher silica concentrations. This is contrary to the results found by Yim and St. Pierre and the difference may be due to a different interfacial energy, since they also found that $T_{\text{cold cryst.}}$ was lower if a treated silica was used instead of an untreated one[7].

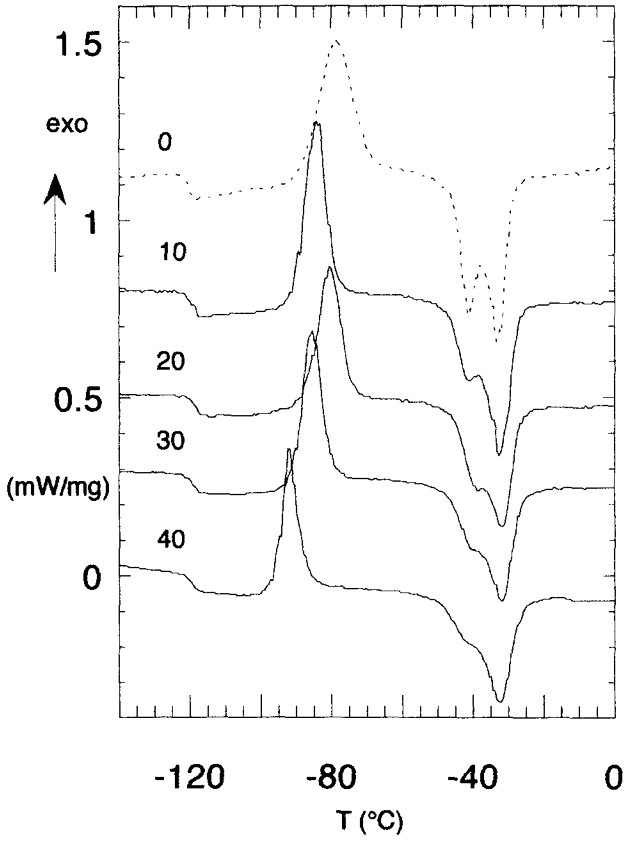

Figure 3 Thermograms corresponding to suspensions made from 88K PDMS and fumed silica. Silica concentrations, shown in the plot, are expressed as parts of silica per 100 parts of polymer (pph). Heating rate 10°C min^{-1}.

The presence of a filler at the low temperature of the tests may introduce internal stresses enhanced by the presence of the crystals formed during the cooling cycle and, thus, it may promote the crystallization of the bulk polymer. As a result, cold crystallization should appear at lower temperatures for higher internal stresses, that is for higher filler loads.

The lower melting temperature increased with respect to the pure polymer, but almost no change was observed for the high melting temperature.

It is also noticed that the larger the silica concentration, the lower the measured heat of fusion per gram of sample mass (ΔH_{fs}). If the effect of the silica were only to act as a 'heat sink', one would expect the measured values to follow an expression, such as:

$$\Delta H_{\text{fs}} = \Delta H_{\text{p}} w_{\text{p}} \qquad (1)$$

where ΔH_{p} is the measured heat of fusion of the pure polymer and w_{p} is the weight fraction of polymer.

Figure 4 shows that there exists a linear relationship between ΔH_{fs} and w_{p}, at least in the range of concentrations used. The value read at $w_{\text{p}} = 1$ is 32.37 J/g, in excellent agreement with the heat of fusion of the pure polymer (32.25 J/g). However, the straight line has a small, but non-zero intercept and the slope is slightly higher than the measured ΔH_{p} (−3.23 and 35.61 J/g, respectively). These differences will be discussed in more detail together with the results obtained for the cured samples.

Cured material. The location of the T_g is unchanged by the network formation. However, its measurement is more difficult because the change in specific heat at the transition is smaller in these samples (*Figure 5*), due to the restricted mobility imposed by the crosslinking points (highly constrained amorphous phase). The values are reported in *Table 5* per unit of sample mass or per unit of polymer mass. In the last case, the Δcp is about 0.140J/g°C, which is about one-third of the value measured for the uncured polymer.

The exothermic peak is very small or negligible, that is, there is essentially no supercooling. Actually, it is present only in the thermogram of the 10 pph sample and at a lower

Table 4 Fumed silica and PDMS 88K: uncured samples

	Silica conc.[a]			
	10	20	30	40
T_g (°C)	−124	−123	−124	−124
Δcp_s (J/g sample°C)	0.410	0.351	0.369	0.304
Δcp_p (J/g polym.°C)	0.451	0.421	0.480	0.426
$T_{\text{cold cryst.}}$ (°C)	−85	−83	−87	−93
$\Delta H_{\text{cold cryst.}}$ (J/g)[b]	22.46	20.08	18.37	13.93
% cryst.[c]	77.13	75.92	76.12	62.75
T_{melt1} (°C)	−43	−40	−40	−40
T_{melt2} (°C)	−35	−34	−34	−35
ΔH_{fs} (J/g)[b]	29.12	26.45	24.13	22.20
$\Delta H_{\text{fs,calc.}}$ (J/g)[d]	28.97	26.29	24.02	22.07

[a] Expressed as parts of silica per 100 parts of the polymer

[b] The values reported are expressed per total mass of the sample

[c] Ratio of the exothermic peak, cold crystallization, to that of the endothermic melting peaks ($\Delta H_{\text{cold cryst.}}/\Delta H_{\text{fs}}$)

[d] Calculated using equation (2), the corresponding calculated value at $w_{\text{p}} = 1$ is 32.20 J/g

temperature than $T_{\mathrm{cold\ cryst.}}$ reported for the pure polymer or for the corresponding suspension. The last observation indicates that the restrictions imposed by crosslinking contribute to the enhancement of internal stresses in the sample, which low the cold crystallization temperature.

A single endothermic melting peak appears at −40°C. It has been reported that, for polymers showing two endotherms, with the higher melting peak due to the ultimate melting of materials that have been reorganized during the experiment, irradiation was used to crosslink the polymer and suppress the formation of the higher melting species[15]. The values of T_m reported in *Table 5* are in accord with the previous observation, since the temperature coincides with the lower melting temperature measured before crosslinking.

The measured heat of fusion decreases with increasing silica concentration and it is lower than that of the corresponding uncured suspension. This is due to crosslinking, which reduces both the extent and the stability of the crystal phase. The network junctions not only cannot crystallize, but also restrict the network chains topologically from incorporation into the crystal phase.

Figure 4 shows the linear relationship that exists between ΔH_{fs} and w_p. The value read at $w_p = 1$ is 28.35 J/g, as expected, lower than that of the pure uncured PDMS, but the slope is much higher, 46.38 J/g, and there is a clear nonzero intercept (− 18.03 J/g). An extrapolation of the line shows that it intercepts the x-axis at $w_p = 0.389$ ($\Delta H_{fs} = 0$). These results and those corresponding to the uncured suspensions are discussed below.

Calculation of Δh_{fs}. From the results presented above, it is obvious that silica not only acts as a diluent of the measured heat, but it also interferes with the crystallization process, and thus it affects the ΔH_{fs} values.

Bordeaux and Cohen-Addad studied the crystallization of PDMS adsorbed onto fumed silica (bound rubber) after extraction of the free chains from suspensions originally prepared by mechanical mixing[6]. Even though some of their results (absolute values) were affected by the value of ΔH_{th} used, the observations realized and the conclusions are still valid. They showed that the filler introduces topological constraints to the movement of the polymer chains, the segments attached to the solid surface cannot crystallize while loops and chain ends may participate in the crystal formation depending on their length. As a result, the bound rubber reaches a lower degree of crystallization than the 'free' polymer. The same study shows that there is a critical ratio, adsorbed polymer/silica weight, below which crystallization cannot take place.

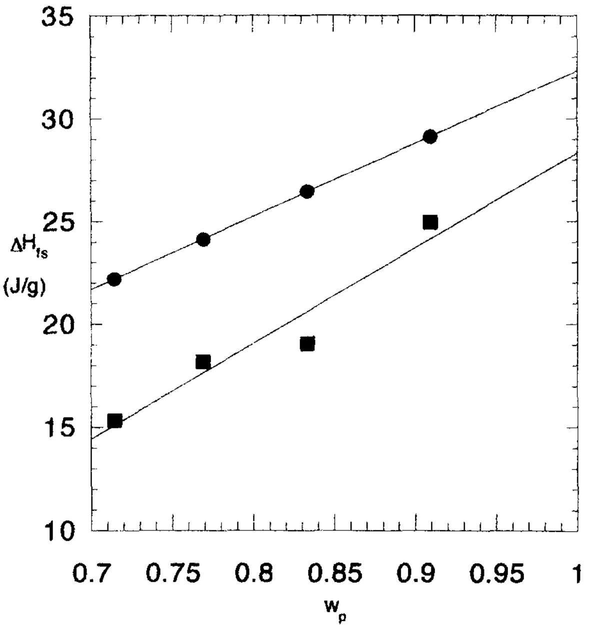

Figure 4 Heat of fusion as a function of the polymer fraction. Filled circles correspond to uncured suspensions (linear fitting, $\Delta H_{fs} = -3.23 + 35.595w_p$). Filled squares correspond to filled cured PDMS rubbers (linear fitting, $\Delta H_{fs} = -18.03 + 46.376w_p$).

The effects of the different variables on the measured value of the heat of fusion of PDMS may be summarized in a simplified way as follows:

(1) The dilution effect of the filler: since crystallization occurs in the polymer phase, the values should be compared in a polymer base.

(2) The 'bound rubber' effect: there is a portion of the polymer that will not crystallize due to the presence of the filler (adsorption). This portion should be less important in the uncured state (results from Bordeaux and Cohen-Addad indicate partial crystallinity of the adsorbed layer) and more important in the cured rubber. In this last case, the movement of the adsorbed layer is further restricted by crosslinking (ex: chain ends no longer exist, since the reaction proceeds by chain end hydrosilation).

(3) The 'free' polymer does not completely crystallize, as can be seen from the results obtained for the pure high molecular weight polymer. The percentage of crystallinity that can be reached after curing should be even lower because of the reduced mobility of the chains after crosslinking, which restricts the ordering of the chains to form a crystal.

It is proposed that the measured heat of fusion of the samples, ΔH_{fs}, can be calculated as follows:

$$\Delta H_{fs} = \Delta H_{th} w_c \qquad (2)$$

where ΔH_{th} is the theoretical value of the enthalpy of fusion per gram of PDMS, a true characteristic constant, independent of the amount of crystalline state. It will be taken as 37.43 J/g, the value measured for the low-molecular weight PDMS, which also coincides with the previously reported value[3], as was discussed above. w_c is the fraction of crystallizable polymer.

The calculation of w_c requires the description of the silica–PDMS samples. Let us consider the case of the PDMS–silica suspensions. Extrapolation of the straight line (A) in *Figure 4* shows that crystallization is absent if the PDMS suspension is prepared at a ratio polymer/silica = 0.1 g/g ($w_p = 0.0909$). On the other hand, *Table 2* indicates

Table 5 Fumed silica and PDMS 88K: cured samples

	Silica conc.[a]			
	10	20	30	40
T_g (°C)	−122	−121	−121	−122
Δcp_s (J/g sample°C)	0.142	0.085	0.112	0.106
Δcp_p (J/g polymer°C)	0.156	0.102	0.146	0.148
$T_{\mathrm{cold\ cryst.}}$ (°C)	−92	—	—	—
$\Delta H_{\mathrm{cold\ cryst.}}$ (J/g)[b]	3.39	—	—	—
% cryst.[c]	14	0	0	0
T_{melt} (°C)	−41	−39	−41	−41
ΔH_{fs} (J/g)[b]	24.94	19.05	18.17	15.33
$\Delta H_{fs,\mathrm{calc.}}$ (J/g)[d]	24.21	20.69	17.70	15.14

Superscripts *a*, *b* and *c* have the same meaning as in *Table 4*

[d] Calculated using equation (2), the corresponding calculated value at $w_p = 1$ is 28.45 J/g

that the 88K PDMS crystallizes only partially, $\Delta H_p/\Delta H_{th} = 32.25/37.43 = 0.86$.

For example, for the uncured suspension with 40 pph of silica, there are 40 g of silica per 100 g of PDMS. Part of the polymer bound to the silica will not crystallize: 0.1 g/g silica, that is 4 g of polymer. The 'free' polymer is then 96 g, but only 86% of it will crystallize, that is 82.56 g. Now, the fraction of crystallizable polymer can be calculated as 82.56 g/140 g of total sample, $w_c = 0.5897$. The resulting value of ΔH_{fs} is 22.07 J/g, while the measured value was 22.20 J/g.

The calculated data of ΔH_{fs} for different silica concentrations are also shown in *Table 4*, and as can be seen the calculations are in excellent agreement with the measured values.

A relation between ΔH_{fs} and w_p can be obtained from equation (2), by rewriting w_c as a function of w_p, the noncrystallizable bound rubber (ncBR = 0.1 g/g silica) and the percentage of crystallinity of the pure PDMS (%cryst. = 86%) the following equation of a straight line is obtained:

$$\Delta H_{fs} = \Delta H_{th} \cdot (\%\text{cryst.}/100) \cdot [(1 + \text{ncBR}) \cdot w_p - \text{ncBR}]$$

that is: $\Delta H_{fs} = 35.38 \cdot w_p - 3.22$ (J/g), for the uncured suspensions.

The analogous calculation for the cured filled rubbers uses the same value of the true constant ΔH_{th}, noncrystallizable bound rubber in a proportion of 0.637 g/g silica (obtained from *Figure 4*) and a percentage of crystallizable free PDMS of 76%. A higher value of ncBR and lower percentage of crystallinity of the free PDMS is in accord with the previous discussion of the effect of filler and curing. The predicted values of ΔH_{fs} are tabulated in *Table 5*, the agreement with the experimental results is quite good, despite the complexity of the real system.

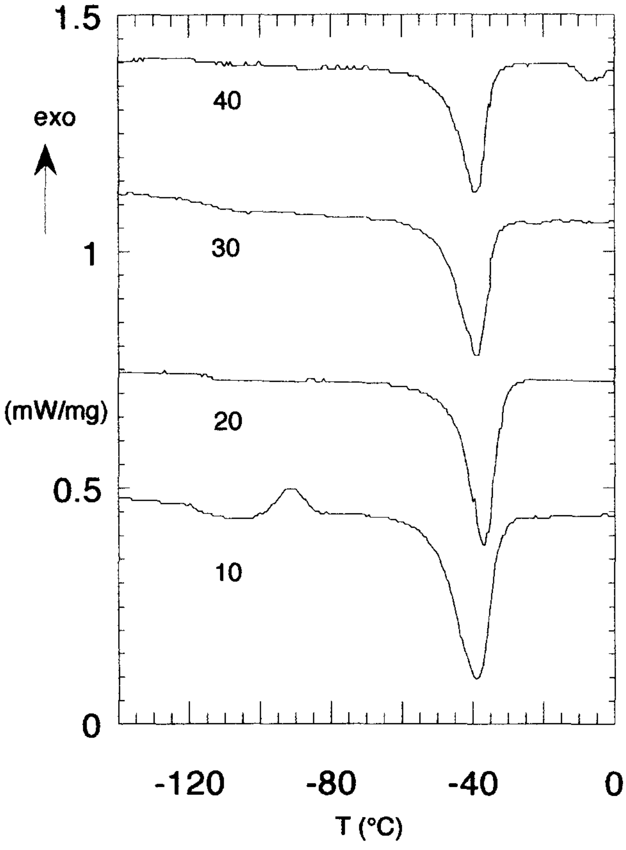

Figure 5 D.s.c. thermograms corresponding to filled cured PDMS rubbers. Silica concentrations, shown in the plot, are expressed as parts of silica per 100 parts of polymer (pph). Heating rate 10°C min^{-1}

The calculations require an extrapolation far from the region of the experimental data, thus it cannot be assured that the predicted behavior is valid down to low w_p values. However, the physical picture gives a good explanation of the behavior of suspensions and rubbers in the concentration range of commercial interest, where it also shows predictive capacity.

CONCLUSIONS

The low temperature behavior of polydimethylsiloxane was revisited and presented in a systematic way.

The glass transition temperature was unchanged in the range of molecular weights used and was essentially unaffected by previous cooling rate, filler addition or crosslinking, a common fact in elastomers. The change in heat capacity at the transition was similar for all the uncured samples, if it was expressed per mass of polymer. After curing the Δcp_p was reduced to about one-third, due to the restricted mobility of the chains in the filled network.

The cold crystallization temperature, as well as the area of the peak was affected by all the variables studied, depending on the facility of the chains to crystallize during cooling.

The value of the inherent enthalpy of fusion, ΔH_{th}, of the completely crystalline polymer is given and a previous misunderstanding of the literature clarified.

The double melting endotherms of the samples is explained by recrystallization of imperfect crystals formed at low temperatures followed by melting of perfect and imperfect crystals.

A simplified description of the silica PDMS suspensions and the corresponding networks was used to calculate the d.s.c.-measured heat of fusion, ΔH_{fs}, as a function of silica concentration, with very good results. The calculation requires to know the amount of noncrystallizable bound rubber and the degree of crystallinity that the pure polymer reaches under identical conditions of cooling and heating.

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