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Characterization of the polysiloxane—polytetrafluoroethylene system (SIL—PTFE) by using the DSC method

RAPID COMMUNICATION

Summary - A calorimetric study of the SIL-PTFE system (SIL = polymethylhydrosiloxanol) was carried out over -130-380°C (Perkin-Elmer DSC-7, He or N₂ atmosphere, 20°C/min). The transition temperatures for SIL $(Tg = -121.66^{\circ}C, Tm = -40.1^{\circ}C)$ and PTFE $(Tg = -58.58^{\circ}C, Tm = 327.40^{\circ}C)$ and 341.7°C) were consistent with those reported for silicone rubbers and teflon, respectively. At PTFE \leq 30 wt. %, a distinct *Tg* occurs within the range of *Tg* characteristic for SIL and the values obey the reciprocal law for a single phase blend. At higher PTFE proportions, neither the glass transition nor the melting peak were observed for SIL. Condis crystal melting transitions, characteristic of PTFE, were found to occur at room temperature and a broad melting peak was found to occur over 325—364°C. New transitions (nonexistent in the components) were found, viz., an exothermic peak at ca. 150°C (attributed to ordering phenomena due to crystallization of semi-IPN structures) and an endothermic peak at ca. 250°C (attributed to melting of semi-IPN structures). These suggestions were confirmed in terms of the balance of the thermal effects due to melting, $\Delta H(Tm_{S-F})_x + \Delta H(Tm)_x$, which made it possible to calculate the PTFE contents in the SIL-PTFE system. Key words: polysiloxane-polytetrafluoroethylene system, DSC study of physical transitions, formation of semi-IPN structures, melting heat balance.

A polymethylhydrosiloxanol—polytetrafluoroethylene (SIL—PTFE) system has recently been obtained as a coating material at the Industrial Chemistry Research Institute (ICRI) [1—3]. Solvent-free emulsions containing reactive polysiloxane (SIL) and polytetra-fluoroethylene (PTFE) can form a semi-IPN structure after water has been evaporated and SIL cured with a catalyst. Several properties of the system were investigated, including the characteristic thermal transitions by using differential scanning calorimetry (DSC). Essential DSC results obtained with samples of the SIL—PTFE system of various PTFE contents are described in this communication.

A Perkin Elmer DSC-7 instrument was used and samples were measured within a temperature range of -130 to 380°C at a heating rate of 20 deg/min in an inert atmosphere; helium was used at temperatures lower than 0°C and nitrogen was used above 0°C.

The DSC results for the SIL component coincide with the results obtained for commercially available silicone rubbers (Table 1).

	Material			
Transition temperature	SIL	silicone rubbers		
	temp. values °C	temp. values, °C	refs.	
Glass transition, Tg	-121.5 -121.8	-122.2 -121.7 -119.9	[4] [5] [5]	
Crystallization, Tc	not ob ser ved	-96.8 -97.5	[4] [5]	
Melting, Tm	-40.1	-40.5 -40.8 -39.6	[4] [5] [5]	

T a b l e 1. DSC data for the SIL component

Results for PTFE are shown in Fig. 1 and compared with the published data in Table 2.

The present DSC results for the PTFE component coincide with the literature data reported for Teflon. It



Fig. 1. DSC thermogram for the PTFE component. For transitions see Table 2

	Material			
Transition temperature	PTFE	Teflon, Du Pont		
-	temp. va- lues, °C	temp. values, °C	refs.	
1. Glass transition, Tg	-58.6	from -73 to -20	[4]	
		-74	[6]	
		-73 ±30	[7]	
2. Ordering of macromole- cules (exothermic)	-24.6	not reported	_	
3. Solid-solid transition, un- coiling of macromolecules (endothermic)	23.6 32.6	19 RT 25,5	[4] [6] [8]	
4. Melting, <i>Tm</i> (2nd run, re- melting)	327.4	327 328.4±1.3	[4, 9] [8]	
5. Melting and sintering (1st run, virgin PTFE)	341.7	350 342—343	[6] [9]	

T a b l e 2. DSC data for the PTFE component

should, however, be noted that, for PTFE, a specifically broad glass transition was observed, probably due to local macromolecule chain mobility unhindered by side groups [7] that can be influenced at previous polymer processing stages. The melting point is usually reported as 342—343°C for the virgin polymer and 327°C as the remelting temperature [9].

SIL—PTFE samples of various PTFE contents were investigated within the temperature range of -130 to 380° C. T_g was distinctly observed only for samples con-

taining up to about 30% PTFE. At a higher PTFE content, the content of SIL component is lower and the system is too stiff to allow any glass transition movement of SIL and/or PTFE macromolecule segments. In the range of low contents of PTFE, the experimental data conform to the blending law of reciprocal properties for a single phase blend [10, 11] that can be written as

$$Tg_{S-F}^{-1} = x_F \left(Tg_F^{-1} - Tg_S^{-1}\right) + Tg_S^{-1}$$
(1)



Fig. 2. Tg of the SIL—PTFE system: 1 — the additive rule; 2 — the reciprocal law. Solid circles — experimental data; open circles — values calculated from eq. (1); Tg obtained from a weak inflection are given in parentheses

PTFE, wt. %	Exo peak, Tc _{5-F} , °C (ΔΗ, J/g)	Endo peak, Tm _{S-F} , ⁰C (∆H, J/g)	Endo peak, <i>Tm</i> , ^o C (Δ <i>H</i> , J/g)	PTFE , from ΔH , eq. (2)		PTFE in semi-IPN,
				<i>x_{F,}</i> wt. %	rel. error, %	$\begin{bmatrix} eq. (3), x_{S-F}, wt \% \end{bmatrix}$
0	no transitions observed			0	—	0
13	151.65 (8.44)	258.40 (6.22)	346.52/356.42 (3.13)	15.8	21.5	10.5
	159.73 (47.05)					
21	157.08 (33.58)	253.63 (5.23)	342.95/354.74 (8.15)	22.5	7.1	8.8
35.5	diffuse minimum	256.62 (2.15)	343.71/353.78 (16.89)	32.1	-9.6	3.6
	152.50 (159.26)	253.76 (2.71)	353.98 (17.51)	34.1	-3.9	4.6
75	diffuse minimum	252.43 (1.56)	341.50 (44.36)	77.4	3.2	2.6
100	not observed	not observed	341.66 (59.34)	100	_	0

T a b l e 3. SIL-PTFE transitions within the temperature range of 100 to 380°C

where: x_F is the weight % content of PTFE and the subscripts S-F, S and F denote the SIL—PTFE system and SIL and PTFE components, respectively (cf. Fig. 2).

It should be noted that eq. (1) describes a model of parallelly linked segments to be expected for the semi-IPN structure.

Melting of the SIL component at -40°C was not observed for samples containing PTFE. Certain transition ranges can be ascribed to specific transitions of PTFE, such as the condis crystal transitions at about 20-22°C and 28-32°C, as well as the broad range of melting transition from 325 to 364°C. However, several new transitions were observed that can be considered to be specific for the SIL---PTFE semi-IPN structure (see Table 3).

It is suggested that the exothermic peak at about 150° C can be ascribed to the ordering effects of the semi-IPN structure, denoted as Tc_{S-F} (*i.e.*, the crystallization temperature of semi-IPN SIL—PTFE), while the endothermic peak at about 250°C, denoted as Tm_{S-F} , corresponds to the melting range of the semi-IPN structure. The melting process is continued at about 325—364°C. This suggestion is confirmed by the effects of the melting heat Δ H. It has been observed that any PTFE structures are molten at both Tm_{S-F} and Tm transition ranges and the PTFE content can be calculated from the sum of heat effects. Thus

$$x_F = 100[\Delta H(Tm_{S-F})_x + \Delta H(Tm)_x] / \Delta H(Tm)_F$$
(2)

where: x_F is the weight % content of PTFE and $\Delta H(Tm)_F = 59.34$ J/g (cf. Table 3). The calculated values of x_F are given in Table 3. The agreement of assumed with calculated values of x_F is quite good and can even be improved by adjusting the onset and the end points on the thermograms. The relative error of calculations was in the range of $\pm 10\%$ at medium SIL/PTFE compositions.

Moreover, the amount of PTFE involved in the semi-IPN structure, x_{S-F} , can also be calculated from the

heat effects by assuming that $\Delta H(Tm_{S-F})_x$ is the melting heat of the semi-IPN structure:

$$x_{S-F} = 100 \ \Delta H(Tm_{S-F})_{\rm x} / \Delta H(Tm)_{\rm F} \tag{3}$$

The results of calculations are shown in Table 3.

It should be noted that the accuracy of our measurements of heat effects can be assessed by comparing the heat of PTFE remelting, $\Delta H(Tm) = 22.76 \text{ J/g}$, obtained in this work, with the value of $\Delta H(Tm) = 20.83 \pm 1.96 \text{ J/g}$ reported for the standard Teflon sample [8]. Thus, our result is accurate to within $\pm 9\%$, *i.e.*, within the precision of the measurement of the standard Teflon sample.

Thus, it was concluded that the specific transitions observed in the SIL—PTFE system, *i.e.* exothermic at about 150°C and endothermic at about 250°C, can be ascribed to crystallization and melting of the semi-IPN SIL/PTFE structure, respectively. Therefore, not only the temperatures of the transitions can be determined by the DSC method, but also the content of PTFE and the fraction of PTFE in the semi-IPN structure can be calculated from the heats of melting.

ACKNOWLEDGMENT

This work has been financially supported by the State Committee for Scientific Research (KBN), Research Project No. 7 T08E 05215.

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Received 1 X 1998.



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