Journal of Thermal Analysis and Calorimetry, Vol. 68 (2002) 147–158

THERMAL ANALYSIS OF THE POLY(SILOXANE)–POLY(TETRAFLUOROETHYLENE) COATING SYSTEM[*]

Z. Dobkowski and M. Zielecka

Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warszawa, Poland

Abstract

Thermal properties of poly(siloxane)–poly(tetrafluoroethylene) (SIL–PTFE) system were investigated, using Perkin Elmer DSC-7 differential scanning calorimeter and TGA-7 thermogravimetric analyzer. For SIL–PTFE compositions, one glass transition temperature T_g has been found, in accordance with the reciprocal rule up to about 40 mass% of PTFE. However, for higher PTFE contents, T_g values about –118 to –112°C were observed that can be ascribed to motions of cross-linked SIL structures. Endo- and exothermic transitions, found in the range from 70 to 290°C, not observed for pure SIL and PTFE components, are considered as specific ones for the SIL–PTFE semi-IPN structures.

The SIL–PTFE system, as well as its components, is thermally stable, if degradation reactions are considered; the temperatures of decomposition at the maximum decomposition rate were above 530°C. It has been found that the thermal stability of the SIL–PTFE system is increasing with the increase of the PTFE content.

Keywords: DSC, poly(siloxane)-poly(tetrafluoroethylene) system, semi-IPN, TG, thermal stability, thermal transitions

Introduction

Fluorinated poly(siloxanes) have become of great interest, mainly as coating materials, since they combine excellent hydrophobic and thermal stability properties of poly(siloxanes) and those of fluoropolymers [1,2]. Moreover, special poly(dimethylsiloxane) (PDMS)–poly(tetrafluoroethylene) (PTFE) systems, such as semiinterpenetrating polymer networks (semi-IPNs), where PTFE is trapped into a PDMS network, have found useful applications, e.g. as waterproof membranes [3].

The poly(siloxane)–poly(tetrafluoroethylene) (SIL–PTFE) system of excellent hydrophobic properties has recently been developed in the Industrial Chemistry Research Institute (ICRI) as a coating material [4–6]. It is composed of poly(tetrafluoroethylene) (PTFE) and cross-linked poly(dimethylsiloxanol) (SIL) components. The method of preparation suggests that the investigated SIL–PTFE system forms a semi- IPN system. Surface properties of the system, such as wetting properties, surface elemental composi-

---

[*] Paper was presented at CCTA 8, Zakopane (Poland), September, 2000

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

tion, and surface morphology and roughness, were investigated [6, 7]. It is supposed that the regular pattern of fluorine atoms and methyl groups of cross-linked SIL component is immobilized at the surface by the semi-IPN [8].

Simultaneously, thermal analysis techniques have been applied to find additional information on ordering of components in the semi-IPN system and on the stability of the system. Preliminary results using differential scanning calorimetry (DSC) have been published elsewhere [9, 10]. Further investigations have been carried out and the results are presented in this paper.

Experimental

Materials

Laboratory samples of pure components (SIL and PTFE) and of the SIL–PTFE system of various compositions were investigated. SIL component was prepared from poly(methylhydrogensiloxanol) (PMHS) in emulsion which was cured, after evaporation of water, in the presence of a catalyst without PTFE component. PHMS of Mn about 1 kD was used, and the concentration of emulsion was about 40 mass% with typically about 1.5% of non-ionic emulsifier. The droplet size in emulsions was of the order of 200 nm. SIL emulsion did not contain any catalyst, however, a catalyst have to be added before application of emulsion.

Similarly, the SIL–PTFE samples were prepared if PMHS was cured in the presence of a specified amount of PTFE. Thus, PTFE macromolecules can be trapped into poly(siloxane) cages formed due to cross-linking reactions. A model presenting an idea, how a stiff PTFE macromolecule can be placed inside a cell of the cross-linked SIL network, is shown in Fig. 1. Recently, similar siloxane cages were also described in literature, e.g. [11] and relevant references quoted there.

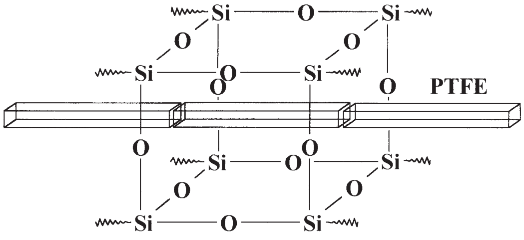

Fig. 1 Model of cross-linked SIL cage with trapped PTFE macromolecule

PTFE component itself was in the form of aqueous dispersion, delivered by the Tarnów S.A. Chemical Works, Poland, as a special grade of environmental-friendly, solvent-free system under the trade name of Dyspersja tarflenowa® (Tarflen dispersion grade).

Commercial samples of Antigraf®, i.e. of SIL–PTFE system used as antigraffiti coatings, produced by the Silicone Pilot Plant, Nowa Sarzyna, Poland, were also investigated.

Moreover, PDMS reference material, CF 386, Rheometrics, of molecular mass M_w=400 kD [12], as a pure linear polymer, was used for comparison with the cross-linked SIL component.

Measurements

A Perkin Elmer DSC-7 instrument was used to find characteristic transitions in the system, and samples were measured in the temperature range from –130 to 380°C, mainly at the heating rate of 20 deg min^{-1} in an inert atmosphere; helium and nitrogen were used at temperatures below and above 0°C, respectively. Temperature was calibrated using the pure indium metal CRM. Cooling and second heating were carried out in cases discussed below.

The thermal stability was tested in air at various heating rates in the range from 1.3 to 20 deg min^{-1}, using a Perkin Elmer TGA-7 thermogravimetric analyser. Samples of about 15 mg were used. Temperatures of initial mass loss T_{di} and temperatures at maximum decomposition rate $T_{d,max}$ were determined.

Results and discussion

DSC measurements

Components

The results obtained for SIL and PTFE components are in agreement with literature data for silicone rubbers and Teflon, respectively (Tables 1 and 2). Thus, the reliability of the procedure has been confirmed.

Table 1 DSC transitions for the SIL component

Transitions	Temperature values/°C			
	SIL component	PDMS ref. mater.	Silicone rubbers	
Glass transition, T_g	–121.5 –123.8	–118.9	–122.2 –121.7 –119.9	[13] [14] [14]
Crystallization, T_c	Not observed	–81.2	–96.8 –97.5	[13] [14]
Melting, T_m	–40.1	–36.4	–40.5 –40.8 –39.6	[13] [14] [14]

SIL–PTFE compositions

Glass transitions

One glass transition temperature T_g was found for all samples. However, distinct T_g transitions were observed for samples containing up to about 40% PTFE. In this

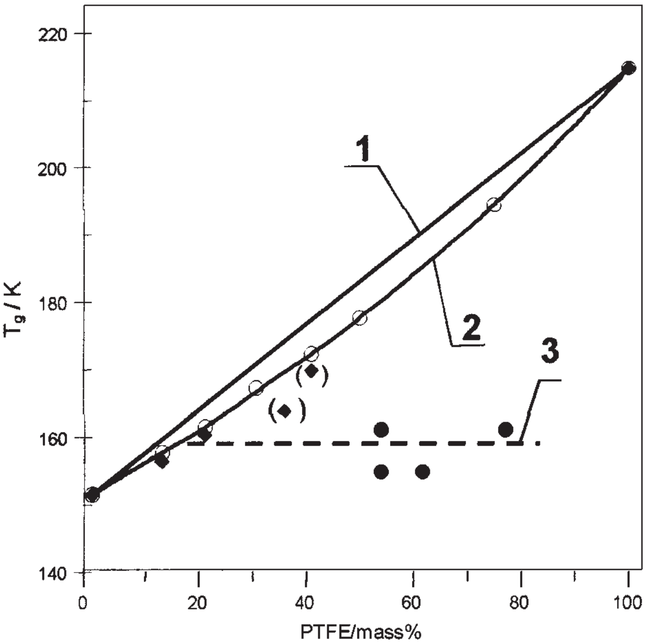

Fig. 2 Glass transitions for the SIL–PTFE system. Notes: ◆ – obtained values; (◆) – T_g values from weak inflections of DSC curves; 1 – the additive rule; 2 – the reciprocal law; 3 – supposed motions in cross-linked SIL structures

range of low content of PTFE, the experimental data conform to the blending law of reciprocal properties for a single phase blend, [21, 22], that can be written as

$$T^{-1}_{\mathrm{gS-F}}=x_{\mathrm{F}}\,(T^{-1}_{\mathrm{gF}}-T^{-1}_{\mathrm{gS}})+T^{-1}_{\mathrm{gS}} \tag{1}$$

where x_F is the mass% content of PTFE, and subscripts S–F, S, and F denote SIL–PTFE system, SIL, and PTFE components respectively, (Fig. 2). It suggests that the components are well mixed.

At higher PTFE percentage the T_g transitions were less distinct or were not observed. However, T_g values, characteristic of SIL component, were observed for some samples of high PTFE content. Thus, it can be supposed that a portion of SIL component is out of the semi-IPN entities in such cases, or that the semi-IPN has not been formed. It might be suggested that in the temperature range from –118 to –112°C (from 155 to 161 K) some movements in amorphous domains of SIL cross-linked structures can proceed irrespectively of the existence of a semi-IPN structure.

Any T_g transitions which might be ascribed to the PTFE component was not found for SIL–PTFE samples. Maybe, this T_g transition is covered by the endothermic (melting) peak at –51°C (222 K), cf. Table 3. PTFE T_g transition at temperature –58.6°C (214.6 K) was observed for the pure component only, cf. Tables 2 and 3.

Table 2 DSC transitions for the PTFE component

Transitions	Temperature values/°C		
	PTFE component	Teflon, DuPont	
Glass transition, T_g	–58.6	from –73 to – 20 –74 –73±30	[13] [15] [16]
Ordering of macromolecules (exothermic)	–24.6	not reported	
Solid–solid (condis crystal) transition (endothermic)	23.6 32.6	19 RT 25.5 30	[13, 18, 19] [15] [17] [18–20]
Crystallization, T_c (on cooling)	307.6	observed, values not reported	[19]
Melting, T_m reversible (2^{nd} run)	327.4	327 328.4±1.3	[13, 18–20] [17]
Melting, T_m irreversible (virgin PTFE, 1^{st} run)	341.7	335–345 342 342–343 350	[18] [19] [20] [15]

PTFE melting transitions

There are two endothermic transition ranges that are specific for PTFE, i.e. the *condis* crystal transition at room temperature in the range about 20–24 and about 28–33°C, as well as the range of melting transition above 300 up to about 360°C [18, 19]. The *condis* crystal transitions were observed for all samples containing PTFE, cf. Table 3. It means that the presence of SIL component does not influence any conformational disordering of PTFE macromolecules in crystal domains.

In the melting range of PTFE, irreversible melting at 340–355°C has been observed during the 1st heating, where the extended chain structure melts. The crystallization proceeds on subsequent cooling, where a folded chain structure is formed, and then the reversible T_m has been determined during the 2nd heating (Table 3). This melting behaviour is typical for PTFE and it is analogous to that of linear PE [19].

Specific transitions of the SIL–PTFE system

New transitions (not found for the pure components) were observed in the temperature range from about 70 to 290°C that can be considered as a specific feature of SIL–PTFE semi-IPN structures, Table 3, Fig. 3a. It has been suggested that the exothermic peak at about 150°C (denoted as T_{cS-F}) can be ascribed to the ordering effects of the semi-IPN structure, while the endothermic peak at about 250°C (denoted as

Table 3 DSC transitions for the SIL–PTFE system

PTFE content/ mass%	Temperature values/°C								
				Specific for SIL-PTFE			PTFE melting range		
	SIL T_g range	PTFE T_g range	PTFE condis, endo	~80 endo	~150 exo	~260 endo	T_c cooling	T_m 2nd heating	T_m 1st heating
0 PDMS	–118.9	–81.2 (c) –36.4 (msil)	–	–	–	–	–	–	–
0 SIL	–121.5 –121.7 –123.8	–40.1 (msil)	–	–	–	–	–	–	–
13	–116.7 –117.1	–	20.6 28.5	85.0 118.4	151.4 159.7	258.4	nm	318.9 327.1	346.0
20	–112.9	–	21.0 29.1	81.0	157.1	258.1 253.5	298.2 307.4	329.3	349.8 354.0
36	–109.3	–95.0 (c) –51.3 (m)	– –	– –	152.5	253.8 256.6	307.8	324.7	354.0 353.1
50	–112.6	–	20.9 31.0	–	–	266.7	307.9	327.2	344.3
50	–118.5	–83.6 (c) –51.0 (m)	23.5 33.6	126.6	156.0	294.8	303.6	326.2	339.3
75	–112.9	–	21.6 30.8	–	–	252.4	306.9	325.3	341.5
100 PTFE	–	–58.6	23.6 32.6	–	–	–	307.6	327.4	341.7

Note: (msil) – melting of SIL or PDMS; (c) – crystallisation peak of SIL; (m) – melting peak of SIL; nm – not measured. Heating rate 20 deg min^{-1}. In the case of 50 mass% of PTFE, two samples, prepared in different conditions, were measured

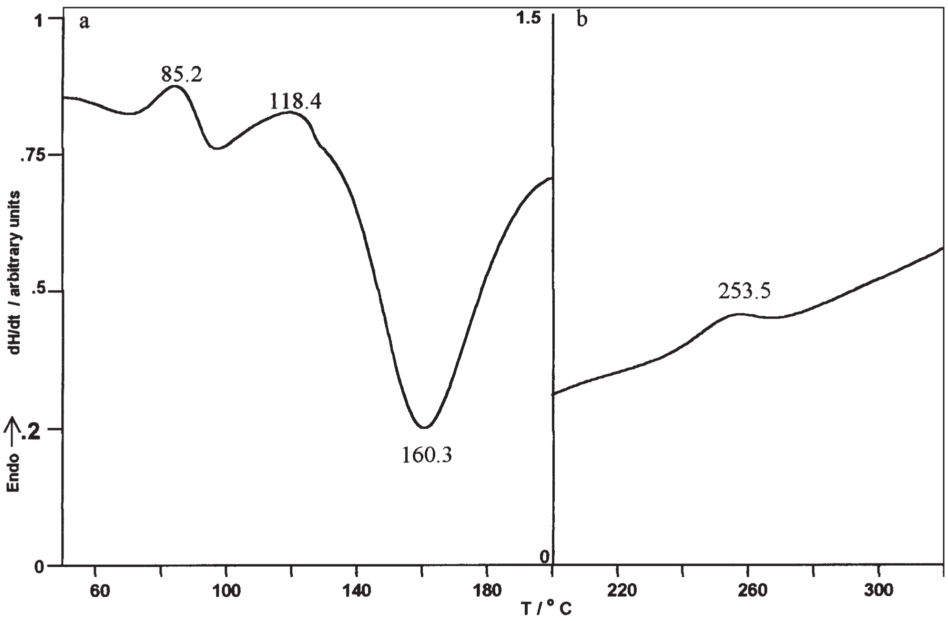

Fig. 3 Specific transitions for the SIL–PTFE system; a – 60–200°C; b – 200–320°C

$T_{\mathrm{mS-F}}$), Fig. 3b, corresponds to the disordering of such structures. It has also been suggested that any PTFE structures melt at both $T_{\mathrm{mS-F}}$ and T_{m} transition ranges, and the PTFE content can be calculated from the sum of heat effects [10]. Thus

$$x_{\mathrm{F}}=100[\Delta H(T_{\mathrm{mS-F}})_{\mathrm{x}}+\Delta H(T_{\mathrm{m}})_{\mathrm{x}}]/\Delta H(T_{\mathrm{m}})_{\mathrm{F}} \tag{2}$$

where x_{F} is the mass% content of PTFE, and $\Delta H(T_{\mathrm{m}})_{\mathrm{F}}=59.34\ \mathrm{J\ g^{-1}}$.

Moreover, the amount of PTFE involved in the semi-IPN structure, $x_{\mathrm{S-F}}$, can also be calculated from the heat effects assuming that $\Delta H(T_{\mathrm{mS-F}})_{\mathrm{x}}$ is the melting heat of the semi-IPN structure:

$$x_{\mathrm{S-F}}=100\Delta H(T_{\mathrm{mS-F}})_{\mathrm{x}}/\Delta H(T_{\mathrm{m}})_{\mathrm{F}} \tag{3}$$

The fraction of PTFE in semi-IPN, $x_{\mathrm{sIPN,F}}$, can also be calculated as

$$x_{\mathrm{sIPN,F}}=x_{\mathrm{S-F}}/x_{\mathrm{F}} \tag{4}$$

where x_{F} is the PTFE content in the SIL–PTFE system.

The results of calculations are given in Table 4. An excessive value of the relative error for x_{F}, found for some samples, may be resulted from a rather high uncertainty in determination of heat effects in these cases. The fraction of PTFE present in semi-IPN structures is shown in Fig. 4. The data for $x_{\mathrm{sIPN,F}}$ in Fig. 4 seem to be in accordance with T_{g} results (Fig. 2): for high PTFE contents, where small amounts (below 5%) of PTFE could be trapped by the cross-linked SIL structures, the observed T_{g} values were similar to those for such cross-linked SIL structures.

Table 4 Heat effects for the SIL–PTFE system

	Peak T_{mS-F}		Peak T_{mx}		PTFE content, calcd		PTFE in semi-IPN		
								PTFE fraction $x_{sIPN,F}$, Eq. (4)	
PTFE content/ mass%	T_{mS-F}/ °C	ΔH/ T_{mS-F}, J g^{-1}	T_{mx}/ °C	ΔH/ T_{mx}, J g^{-1}	x_F/mass% Eq. (2)	Rel. error/ %	x_{S-F}/mass% in the system, Eq. (3)	if x_F nominal (column 1)	if x_F calcd. from Eq.(2) (column 6)
0	Not obs.	–	Not obs.	–	0.0	–	0.0	0.000	0.000
13	258.40	6.22	346.52 356.42	3.13	15.8	21.5	10.5	0.810	0.660
21	253.63	5.23	342.95 354.74	8.15	22.5	7.1	8.8	0.420	0.390
36	253.76	2.71	353.98	17.51	34.1	–3.9	4.6	0.130	0.130
50	266.70	1.30	339.90	33.80	59.2	18.4	2.2	0.044	0.037
75	252.43	1.56	341.50	44.36	77.4	3.2	2.6	0.035	0.034
100	Not obs.	–	341.60	59.34	100.0	–	0.0	0.000	0.000

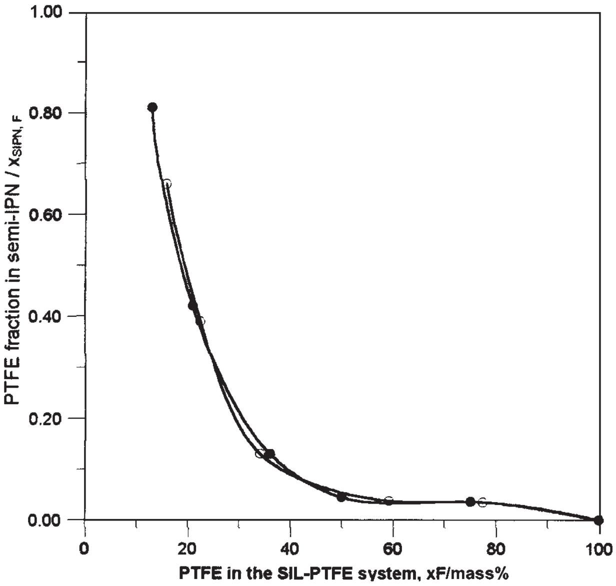

Fig. 4 PTFE fraction in semi-IPN, $x_{\mathrm{sIPN,F}}$, Eq. (4)
Note: solid circles – if x_F is nominal, according to composition (PTFE content); open circles – if x_F is the calculated PTFE content, according to Eq. (2)

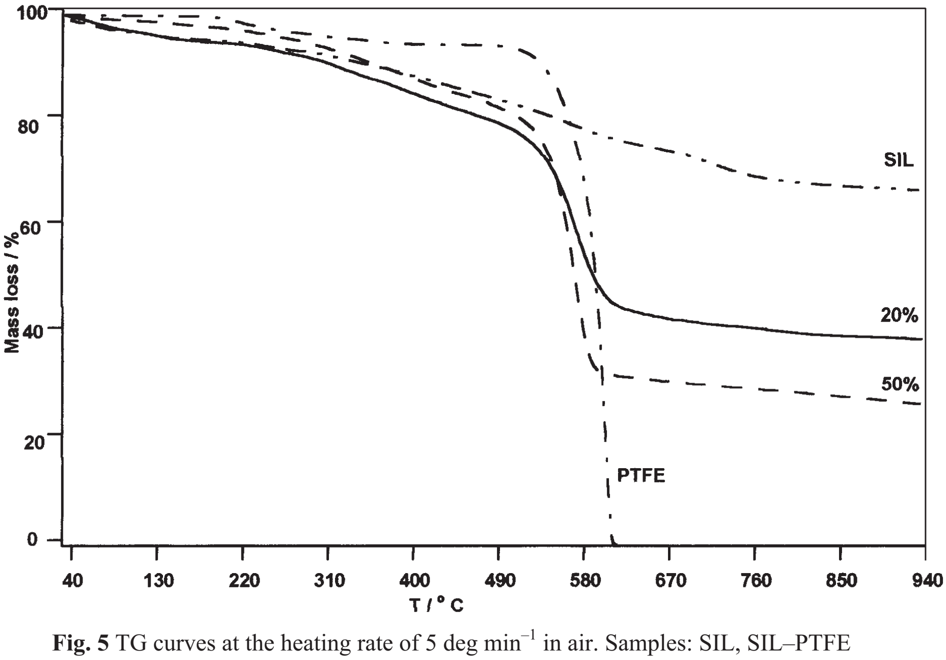

Fig. 5 TG curves at the heating rate of 5 deg min^{-1} in air. Samples: SIL, SIL–PTFE 20%, SIL–PTFE 50%, and PTFE

TG measurements

The samples were heated from room temperature up to 900°C and plots of mass loss *vs.* temperature (TG curves) at various heating rates in air, i.e. in the usual performance atmosphere, were obtained. An example, for selected samples of the SIL–PTFE system at the heating rate of 5 deg min^{-1}, is shown in Fig. 5.

Hence, specific degradation temperatures of the system, such as the temperature of initial mass loss T_{di} and the temperature at maximum decomposition rate $T_{d,max}$, as well as the residues, were determined from the TG and DTG curves at various heating rates in air. The results obtained at the heating rate of 5 deg min^{-1} are shown in Table 5.

Table 5 Degradation parameters from the mass loss curves at the heating rate 5 deg min^{-1} in air

Sample	PTFE/mass%	T_{di}/°C	$T_{d,max}$/°C	Residue/mass%
PDMS	0	160	534	0
SIL	0	53	558	66
SIL-PTFE 20	20	60	566	38
SIL-PTFE 50	50	102	565	26
PTFE	100	208	598	0

Thus, it has been found that the SIL–PTFE system, as well as its components, are thermally stable, if degradation reactions at the maximum decomposition rate are considered; the values of $T_{d,max}$ are above 530°C. However, the mass loss was also observed at lower temperatures, even below 100°C (values of T_{di} in Table 5), since volatile substances contained in the SIL component can be evolved. Moreover, the complex degradation pattern for the SIL sample results not only from the loss of volatile components of the emulsion, but also from the formation of various cross-linked fragments, eventually giving char-like residues. Such residues are not formed in the case of linear PDMS (Table 5). Therefore, it is evident that the degradation of the SIL–PTFE system is governed by various mechanisms, and more detailed investigations of this system are needed.

For preliminary comparative estimations of the thermal stability of the SIL–PTFE samples, the plots of $1/T_{di}$ *vs.* $\log\beta$, where β is the heating rate in deg min^{-1}, were used, as it has earlier been suggested for other polymer materials [23], Fig. 6. Thus, the thermal stability is increased in the following sequence:

$$\text{SIL} < \text{SIL–PTFE } 20\% < \text{SIL–PTFE } 50\% \ll \text{PTFE}$$

i.e. it is increasing with the increase of PTFE content in the system.

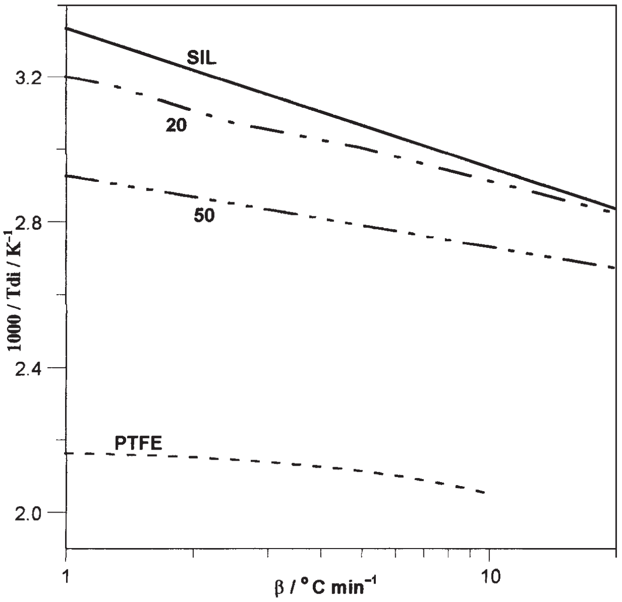

Fig. 6 The plots of $1/T_{\mathrm{di}}$ *vs.* log (heating rate) for the SIL–PTFE system. Samples: SIL, SIL–PTFE 20%, SIL–PTFE 50%, and PTFE

Conclusions

Specific transitions, not found for the pure components, were observed in the temperature range from about 70 to 290°C that can be considered as a feature of SIL–PTFE semi-IPN structures. It has been suggested that the exothermic peak at about 150°C and the endothermic peak at about 250°C can be ascribed to the ordering and disordering effects of the semi-IPN structures, respectively. Therefore, the content of PTFE and the fraction of PTFE ordered in the semi-IPN structure can be calculated from the heats of melting.

The SIL–PTFE system, as well as its components, are thermally stable, if degradation reactions are considered; the temperature of decomposition at the maximum decomposition rate is above 530°C. However, the mass loss was also observed at lower temperatures, even below 100°C, since volatile substances can be evolved, in particular from the SIL component.

Preliminary comparative estimations indicate that the thermal stability of SIL–PTFE samples is increasing with the increase of PTFE content in the system.

* * *

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

References

1 P. Boutevin and Y. Pietrasanta, Progr. Organization Coatings, 13 (1985) 297.

2 B. Ameduri, P. Boutevin and F. Guida-Pietrasanta, Fluoropolymers containing silicon, in: 'Properties of Structured Poly(siloxane)-Poly(tetrafluoroethylene) Coating System', Z. Dobkowski and M. Zielecka, Eds, ICRI, Warszawa 2001.

3 M. E. Dillon and D. K. Lange, Polym. Mater. Sci. Engng., 62 (1990) 814; id. ibid. 65 (1991) 64.

4 M. Zielecka, D. Sobkowiak, A. Winiarska and K. Cyruchin, ICRI Annual Report '94, ICRI, Warsaw 1995, p. 65.

5 M. Zielecka, The Effect of Emulsifiers on Application of Emulsions, in: Congress Proceedings, 2nd World Congress on Emulsion, Bordeaux, 23-26 September 1997.

6 M. Zielecka, Surface Properties of Coatings Obtained from Silicone-Hybrid Systems, in: Conference Papers, Silicones in Coatings II, Florida, 24-26 March 1998.

7 M. Zielecka and Z. Dobkowski, Surf. Coat. Int., in print.

8 M. Zielecka, Studies on preparation and physicochemical surface properties of the poly(siloxane)–poly(tetrafluoroethylene) system (in Polish), PhD Thesis, ICRI, Warsaw 1998.

9 Z. Dobkowski and M. Zielecka, ICRI Annual Report '98, ICRI, Warsaw 1999, p.104.

10 Z. Dobkowski and M. Zielecka, Polimery, 44 (1999) 222.

11 K. Dusek and M. Duskova-Smrckova, Progr. Polym. Sci., 25 (2000) 1215.

12 Z. Dobkowski and M. Zielonka, Polimery, 42 (1997) 321.

13 E. Kaiserberger and H. Mohler, DSC on Polymeric Materials, Vol. 1, Netzsch Ann. Sci. Ind., Selb–Wurzburg 1991.

14 E. Kaiserberger, S. Knappe and H. Mohler, TA for Polymer Engineering, Vol. 2, Netzsch Ann. Sci. Ind., Selb–Wurzburg 1993.

15 E. Kaiserberger, S. Knappe, H. Mohler and S. Rahner, TA for Polymer Engineering, Vol. 3, Netzsch Ann. Sci. Ind., Selb–Wurzburg 1994.

16 S.-F. Lau, J. P. Wesson and B. Wunderlich, Macromolecules, 17 (1984) 1102.

17 M. F. Fleszar, J. Thermal Anal., 49 (1997) 219.

18 C. A. Sperati, Physical Constants of Fluoropolymers, in: 'Polymer Handbook', 3rd Ed., J. Brandrup and E. H. Immergut, Eds, Wiley, New York 1989, p. V/35.

19 D. I. McCane, Tetrafluoroethylene Polymers, in: 'Encyclopedia of Polymer Science and Technology', H. F. Mark and N. G. Gaylord, Eds, Interscience Publishers, New York 1970.

20 D. L. Kerbow, Poly(tetrafluoroethylene), in: 'Polymeric Materials Encyclopedia', J. C. Salamone, Ed., CRC Press, Boca Raton 1996, p. 6884.

21 T. G. Fox, Bull. Am. Phys. Soc., 1 (1956) 123.

22 Z. Dobkowski, Polimery, 23 (1978) 402.

23 Z. Dobkowski and E. Rudnik, J. Thermal Anal., 48 (1997) 1393.