Effect of charge-transfer interaction on thermal and rheological properties of silicone–cellulose blends*

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Rheological measurements of silicone polymeric systems with charge-transfer interaction between electron-donor carbazolyl/electron-acceptor dinitrobenzoyl groups have shown a retardation of viscoelastic flow in the final zone. The effect can be explained by 'thermoreversible network' formation and is related to a minimum concentration of interacting groups. In incompatible silicone–cellulose blends, charge-transfer interaction contributes to a stabilization of the two-phase system by a compatibilization effect, thus preventing total demixing into blend components.

(Keywords: polymer blends; charge-transfer interaction; compatibilization; thermal and rheological properties)

INTRODUCTION

In a series of papers it has been shown that charge-transfer (CT) interaction between polymers which contain electron-donor/electron-acceptor groups results in thermoreversible network formation evidenced in the enlargement of the rubber plateau or at least in a retardation of flow of the respective polymer blend when compared with the individual components[1]. The enlargement of the rubber plateau is strictly related to both the content of interacting groups and the overall chain mobility. Intermolecular complexation is effective only above a specific minimum content of interacting groups[2]. Supplementary CT interaction may contribute to a stabilization of heterophase polymeric systems, i.e. may effect a compatibilization of incompatible polymer blends[3].

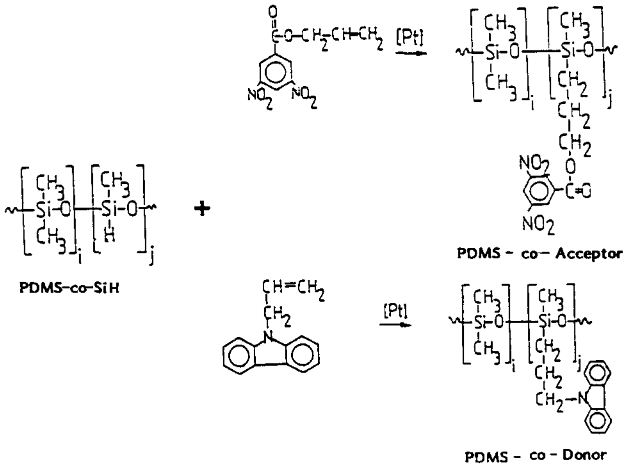
In an extension of studies related mainly to this last effect, we present thermoanalytical and rheological data concerning CT interaction in the polydimethylsiloxane–polydimethylsiloxane or polydimethylsiloxane–cellulose tripropionate electron-donor/electron-acceptor systems.

EXPERIMENTAL

Polymers

Syntheses of silicones which contain electron-donor (*N*- carbazolyl) and electron-acceptor (3,5-dinitrobenzoyl) groups were attempted starting with both poly(dimethylsiloxane-*co*-(2,3-epoxypropoxy)propylmethylsiloxane) (I) and poly(dimethylsiloxane-*co*-hydrogenmethylsiloxane) (II).

Difficulties were encountered in the PDMS4 system (see *Table 1*) during the synthesis of silicones which contained *N*-carbazolyl groups starting with I, because esterification of the intermediate alcohol that resulted after epoxy ring opening was accompanied by chain degradation and network formation. Therefore the syntheses of the silicones which contained electron donors and electron acceptors were carried out by catalytic polymer analogue transformation of II according to the reaction scheme:



The characteristics of the starting silicone copolymers and the resulting donor/acceptor silicone copolymers are shown in *Table 1*. Also listed are the glass transition and melting temperatures, T_g and T_m, measured by d.s.c. and extrapolated to zero heating rate.

The cellulose tripropionate-*co*-acceptor polymer was also prepared by a polymer analogue transformation[4]. A single sample has been employed for blend preparation with the silicone-*co*-donor. The characteristics of the cellulose-*co*-acceptor used were $M_n = 24\,000$ and $M_w/M_n = 2.6$, and the content of 22 mol% acceptor groups (i.e. an average of one acceptor group for three glycosic units—for structure of chain sequence see below).

Polymer blends

Both the blends of the silicone-*co*-donor with either the silicone-*co*-acceptor or the cellulose-*co*-acceptor,

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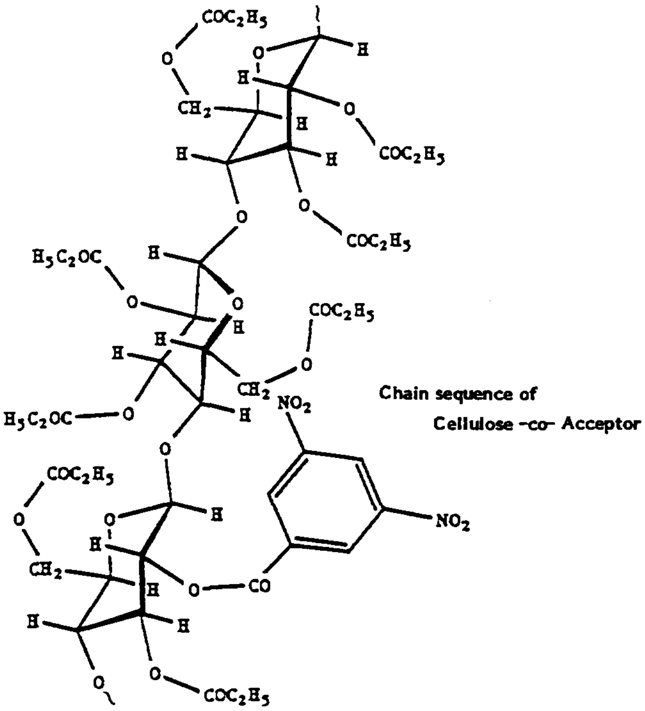

Chain sequence of Cellulose -co- Acceptor

respectively, of equimolecular 1:1 donor/acceptor (D/A) content were prepared by freeze-drying from benzene solution. Subsequently the blends were dried for at least two weeks in vacuum. The vacuum-dried samples were moulded for 40 min in a vacuum-assisted compression mould at 40°C above T_g and a pressure of $1\ \mathrm{kN\,cm^{-2}}$. Only bubble-free discs were used in rheological measurements.

D.s.c. measurements were performed on a Perkin–Elmer DSC 7 at various heating rates after a first controlled heating–cooling cycle. T_g values were determined during heating from the midpoint temperature of the T_g range, whereas T_m values were measured from the onset temperature of the melting peak. Both temperatures were then extrapolated to zero heating rate.

Isothermal dynamic mechanical measurements in the oscillatory mode (frequency range 0.05 to 7.5 Hz) were executed on an Instron 3250 rheometer under flowing nitrogen gas in the cone-and-plate (silicone blends) and plate-and-plate (silicone–cellulose blends) geometry, respectively. A maximum strain amplitude of 0.1% was used to ensure linear viscoelastic behaviour also at the lowest frequency limit of 0.05 Hz. The isotherms in the final zone were superimposed to produce master curves by the usual shift procedure[5].

RESULTS AND DISCUSSION

*Silicone-*co*-donor/silicone-*co*-acceptor blends*

The thermal characteristics of the silicone copolymers shown in *Table 1* indicate the partial crystallinity of the PDMS6 systems and no essential changes in the T_g values, except for the PDMS15-*co*-donor. The rheological data for the PDMS-*co*-acceptors and PDMS-*co*-donors together with those of the corresponding 1:1 D/A blends are shown in *Figure 1*. Also presented are the master curves of the storage moduli shifted to the indicated reference temperatures T_0, related to the appropriate T_g values. The chosen reference temperatures are situated in the middle of the temperature ranges investigated at equal distances from the respective T_g in the supposition of similar temperature dependences of their free volume. Taking account of the fact that CT interaction may retard especially the viscoelastic flow in the final zone, all measurements were limited to the final zone.

In *Figure 2* the master curves of the storage and loss moduli obtained by using the same shift factors for both the PDMS15-*co*-donor (*Figure 2a*) and the PDMS15-D/A blend (*Figure 2b*) are compared.

The rheological data shown support thermoreversible network formation in the D/A silicone blends and the existence of a lower concentration limit of interacting groups in the blend components.

Thus the D/A blend of the PDMS4 system, containing one single interacting group/chain, shows no visible influence of the CT interaction on the rheological properties (*Figure 1a*). Increasing the number of interacting groups/chain in the PDMS6 (*Figure 1b*) and PDMS15-D/A blends (*Figure 1c*), respectively, thermoreversible network formation is evidenced by the enlargement of the rubber plateau and even by the suppression of flow in the investigated temperature range. The effect is stronger the higher the content of interacting groups. Effects due to the partial crystallinity are not observed in the investigated final zone; they can be observed only at lower temperatures, approaching the T_m region.

Table 1 Characteristics of the silicone polymers

Polymer	Content of functional groups[a]	M_n[b]	M_w/M_n[c]	Functional groups per polymer chain	T_g (°C)	T_m (°C)
PDMS4-*co*-epoxy	4 mol%	2000	2.79	1	−126.0	–
PDMS4-*co*-acceptor					−121.0	–
PDMS4-*co*-donor					−125.8	–
Blend D/A 1:1					−122.3	–
PDMS6-*co*-SiH	6 mol%	37000	1.61	29	−127.8	−45.8
PDMS6-*co*-acceptor					−127.6	−38.8
PDMS6-*co*-donor					−121.0	−41.0
Blend D/A 1:1					−122.6	−39.6
PDMS15-*co*-SiH	15 mol%	27000	2.44	51	−125.4	–
PDMS15-*co*-acceptor					−121.4	–
PDMS15-*co*-donor					− 92.4	–
Blend D/A 1:1					−119.3	–

[a] By quantitative i.r. analysis
[b] By vapour pressure osmosis or by membrane osmosis
[c] By g.p.c.

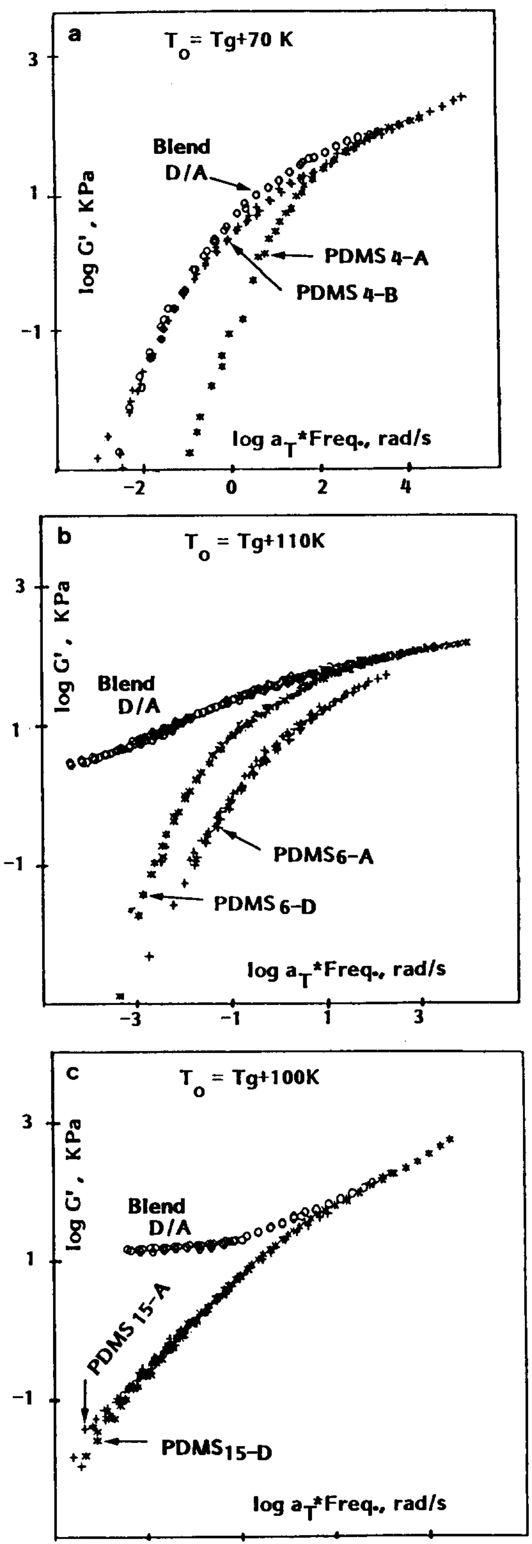

Figure 1 Isotherm master curves of the reduced storage moduli of silicone-*co*-donors, silicone-*co*-acceptors and their 1:1 D/A blends. Reference temperatures T_0 are indicated. (a) The PDMS4 system, (b) the semicrystalline PDMS6 system and (c) the PDMS15 system

Besides the enlargement of the rubber pleateau in D/A blends, CT interaction also influences the temperature dependence of the shift factors, log a_T (see *Figure 3*). A similar change of the temperature dependence of the shift factors was also observed in the compatible poly(vinyl methyl ether)/polystyrene blend[6].

Silicone-co-*donor/cellulose*-co-*acceptor blends*

The thermal properties of these blends are shown in *Table 2*.

The two-phase character of the silicone-*co*-donor/cellulose-*co*-acceptor blends is confirmed by the presence

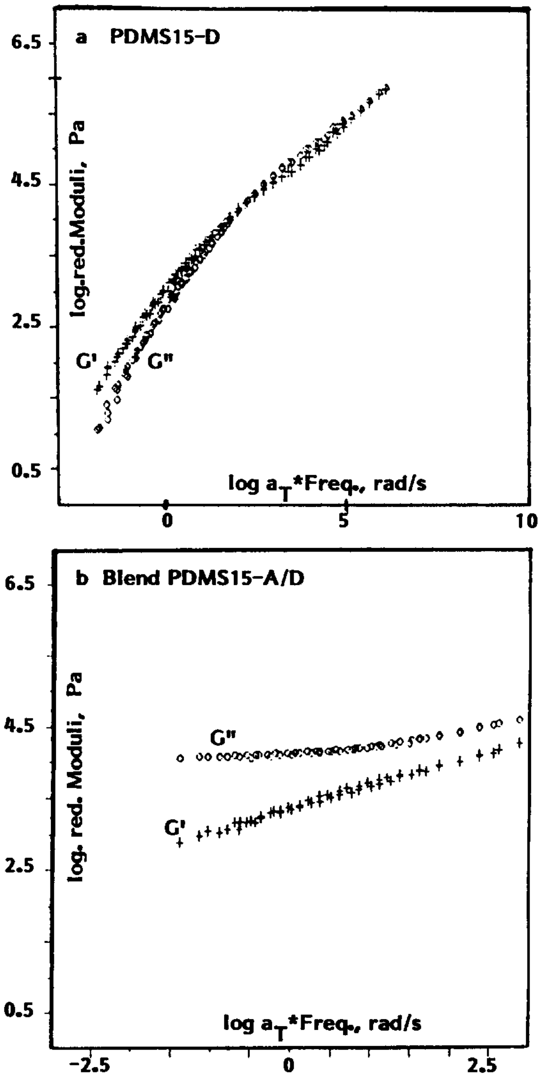

Figure 2 Isotherm master curves of the reduced storage (G') and loss (G'') moduli at the reference temperature $T_0 = T_g + 100$ K. (a) PDMS15-*co*-donor and (b) the PDMS15-*co*-acceptor/PDMS15-*co*-donor 1:1 D/A blend

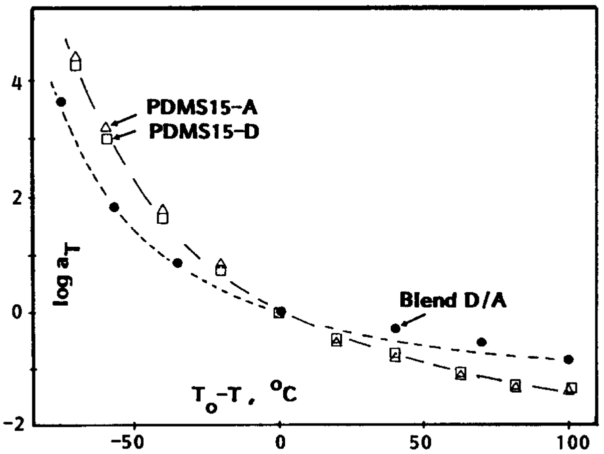

Figure 3 Temperature dependence of the shift factors of the PDMS15 system

Table 2 Thermal properties of the silicone-*co*-donor/cellulose-*co*-acceptor systems

Polymer	T_{g1} (°C)	T_m (°C)	T_{g2} (°C)
Cellulose-*co*-acceptor	–	–	133.6
PDMS6-*co*-donor	−121.0	−41.0	–
Blend D/A 1:1	−133.1	−41.7	127.3[a]
Cellulose-*co*-acceptor	–	–	133.6
PDMS15-*co*-donor	− 92.4	–	–
Blend D/A 1:1	−101.4	–	120.6[a]

[a] The d.s.c. thermograms of the D/A blends were obtained using mould-pressed samples

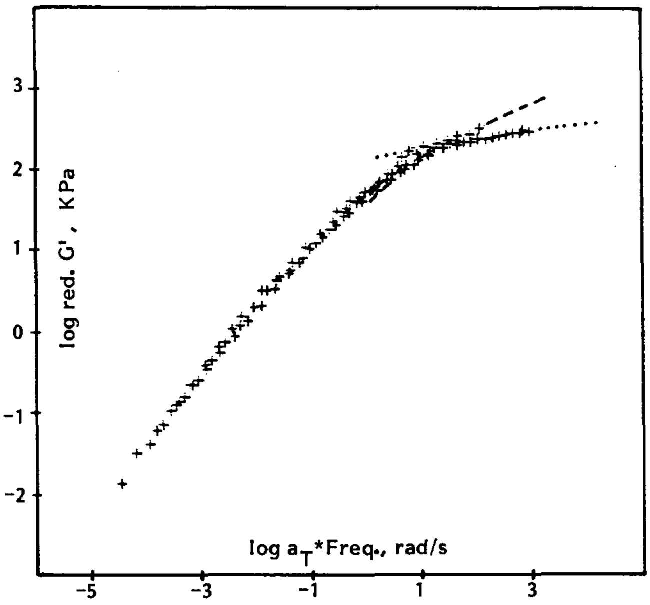

Figure 4 Breakdown of the time–temperature superposition in the cellulose-*co*-acceptor/semicrystalline PDMS6-*co*-donor 1:1 D/A blend at temperatures near T_m

of the two glass transitions. The concomitant shift of the T_g values in the blends, however, suggests interphase interactions. Besides the shift of the T_g values, typical broadening of the T_g range is also observed, characteristic of polymeric systems with increased polydispersity. Comparing the glass transition temperatures of the D/A blend with those of the components, a decrease of about 10°C of both T_g values is observed. Similar results for biphasic systems with CT interaction were reported in a previous paper[3] and by Ohno and Kumanotani[7].

The decrease of both the T_g values in the two-phase D/A blends stabilized by CT interaction points to an increased free-volume fraction as a consequence of the demixing tendency in the incompatible blend.

The compatibilization effect of the CT interaction has already been observed during blend preparation. The freeze-dried mixture of original PDMS-*co*-SiH with cellulose-*co*-acceptor separated instantly into its components during mould compression; the PDMS-*co*-donor (except PDMS4)/cellulose-*co*-acceptor blends resulted in stable yellowish moulded discs.

Concerning the rheological properties in the final zone of the silicone-*co*-donor/cellulose-*co*-acceptor blends, a breakdown of the time–temperature superposition near T_m of the PDMS6 system is observed as illustrated in *Figure 4* for the master curve of G'. The dotted curve refers to the data measured at the nearest temperature above T_m, whereas the broken curve corresponds to the data of the immediately higher temperature.

The master curves of the storage moduli of the PDMS15-*co*-donor/cellulose-*co*-acceptor system are shown in *Figure 5*. This time it was possible to superimpose the rheological data in the final zone by using the same shift factors for both G' and G''. Taking into account the very different T_g values of the blend components, rheological measurements were performed in the following temperature ranges: PDMS15-*co*-donor, −70 to 100°C; cellulose-*co*-acceptor, 170 to 215°C; and the two-phase D/A blend, 150 to 200°C.

The ranges of thermal stability were proved by t.g. measurements in air. At a heating rate of 2°C min^{-1} the weight loss of the cellulose components and of the D/A blend was less than 0.5% at a temperature of 250°C. The silicone component was stable up to 300°C.

The master curves of the storage moduli are compared in *Figure 5a* at the reference temperature of $T_g + 50$ K.

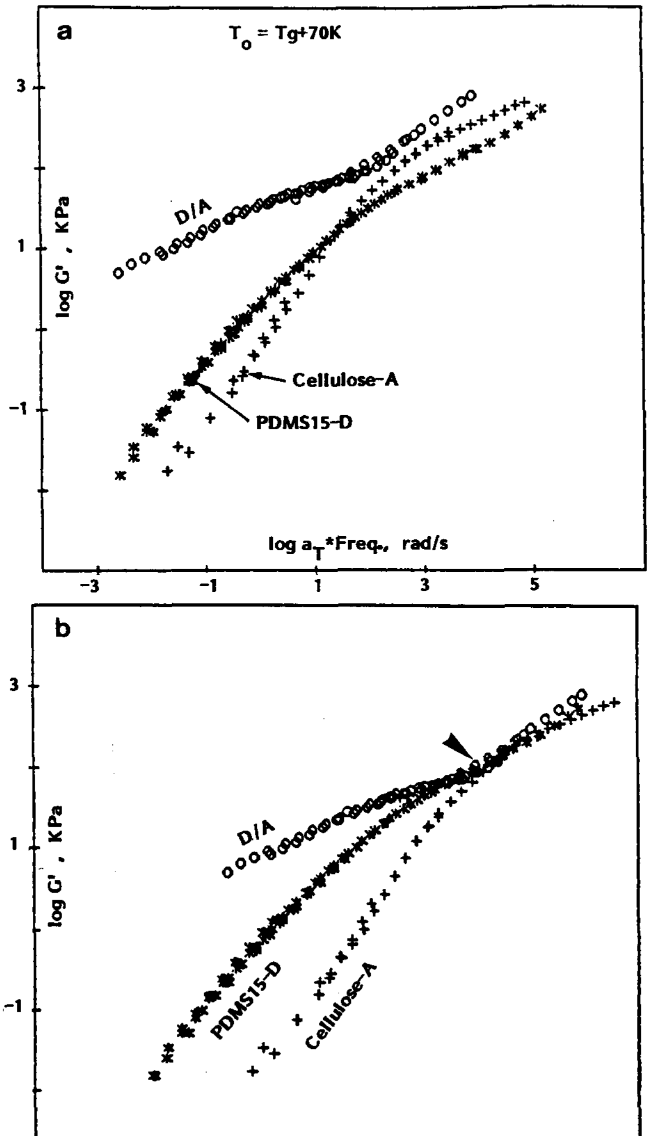

Figure 5 Isotherm master curves of the reduced storage moduli of the cellulose-*co*-acceptor/PDMS15-*co*-donor system. (a) Shifted at the reference temperature $T_0 = T_g + 70$ K. (b) Shifted to superimpose at the inflection point between the rubber plateau and glass transition region (marked by arrow). For PDMS15-*co*-donor the reference temperature was maintained as $T_0 = T_g + 70$ K

Taking into account that only the behaviour in the final zone was of interest, the higher T_g was selected for the two-phase D/A blend for the determination of the rheological reference state.

As the position of the master curves along the frequency axis is quite relative and depends solely on the chosen reference temperature, the master curves of the storage moduli were then shifted again to superimpose at the inflection point (marked by arrow in *Figure 5b*), which delimits the transition between the rubber plateau and the glass transition region. For this additional shift procedure the inflection point of the master curve of PDMS15-*co*-donor at $T_0 = T_g + 70\,\mathrm{K}$ was chosen as the unique reference point. The comparison of the different master curves for this reference state seems more suitable.

But, independent of the chosen reference state, it is evident that CT interaction increases the storage moduli in the terminal zone, i.e. retards the flow in the two-phase blend when compared with the flow of the components. The decrease of the slope of the respective master curve confirms at the same time an increase of polydispersity in the blend due to the CT interaction.

It may thus be supposed that CT interaction between incompatible polymers has a stabilizing effect in two-phase blends, preventing total demixing of the components. This stabilizing effect, however, is related to a minimum of interacting groups. CT interaction contributes at the same time to an improvement of dynamic mechanical properties in compatible polymer blends, as illustrated by the results of the studied silicone-*co*-donor/silicone-*co*-acceptor systems.

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