Semi-interpenetrating polymer networks of maleimide end-capped oligoesters

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The crosslinking and thermal properties of networks obtained from a series of maleimide-terminated terephthalates have been studied by differential scanning calorimetry and thermomechanical analysis. The semi-interpenetrating polymer networks obtained from these bismaleimides and linear terephthalate oligomers of the same chemical structure, have also been studied and compared with those obtained from bis(4-maleimidophenyl) methane and the same linear oligomers. All blends showed compatibility before crosslinking. However, the behaviour of the crosslinked materials was affected by the fraction of crosslinked component, the curing schedule, the bismaleimide structure and the degree of cure.

(Keywords: networks; crosslinking; thermal properties; imides)

INTRODUCTION

In previous papers[1,2] we reported the synthesis and characterization of a series of maleimide-terminated oligoterephthalates capable of being cured by an addition reaction to give crosslinked systems. These oligoterephthalates show relatively low transition temperatures, do not crystallize from the melt and are soluble in common solvents, which qualify them as models to be used in the investigation of the mechanisms involved in the cure of reactive oligomers. Moreover, they can be used in the preparation and study of semi-interpenetrating polymer networks (SIPNs).

Multicomponent polymer systems usually present stability problems due to their well known thermodynamic incompatibility. However, if mixing and crosslinking are carried out simultaneously, as in SIPNs, the phase separation may be kinetically controlled by permanent interlocking of entangled chains[3,4].

In this work we evaluate blends of these bismaleimides with linear oligoesters of the same chemical structure to obtain SIPNs.

The major factors controlling the morphology of SIPNs include the chemical compatibility of both components, the crosslinking density of the network and the composition of the system[4,5]. Consequently, linear polymers and reactive oligomers of identical and different chemical structures have been mixed in various ratios and polymerized to SIPNs by crosslinking the curable components, and the results related to the nature of the initial blend compositions.

As the glass transition is a simple and reliable method for determining whether a system is miscible, particular attention has been paid to the study of the influence of the above factors on the glass transitions, determined either by differential scanning calorimetry (d.s.c.) or thermomechanical analysis (t.m.a.), and hence, on the compatibility of the systems.

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EXPERIMENTAL

Materials

Hydroxy- and bismaleimide-terminated oligomers with degree of polymerization, X_n, ranging from 1 to 22 were synthesized and characterized as described previously[1].

Bis(4-maleimidophenyl)methane (BMI) was synthesized from bis(4-aminophenyl)methane and maleic anhydride according to reference 6. The product was recrystallized from acetone/water giving yellow crystals (m.p. 160°C, yield 80%).

Sample preparation

One-component networks (bismaleimide oligomers) were obtained in the form of films. In the case of two components (blends of maleimide and hydroxy-terminated oligomers), both films and compact cylinders were used.

Several small-scale experiments were performed in advance to determine the optimum curing conditions (initiator amount, time and temperature of reaction, mixing procedure, etc.) by preparing samples in aluminium calorimetry pans.

Films were cast in a Teflon mould ($5 \times 3 \times 0.2$ cm) from chloroform solutions of mixtures of the oligomer(s) (0.8 g dissolved in 2 ml) and dicumyl peroxide (0.06 mol per mol of double bond) and dried under vacuum at 60°C. This yielded films $\sim$0.2 mm thick that were cured by heating at 130°C for 20 h.

In the case of cylindrical samples, homogeneous blends of oligomers and initiator were obtained by dissolving the latter in n-hexane and allowing it to precipitate on to the highly pulverized mixture of oligomers (non-soluble) as the n-hexane evaporated under vacuum[7]. These pulverized samples were used to fill glass tubes in order to obtain cylinders 4 mm in diameter and $\sim$15 mm in height. These were cured by thermal treatment at 140°C for 1 h, 160°C for 1 h, 200°C for 1 h and 225°C for 30 min to obtain completely crosslinked networks. After this treatment, the cylindrical samples were machined to obtain discs with parallel sides (2–4 mm in height).

Differential scanning calorimetry

Differential scanning calorimetry data were obtained on a Perkin-Elmer DSC-4 attached to a 3600 data station, at a heating rate of 20°C min^{-1} under nitrogen atmosphere, using powdered samples weighing 15 ± 1 mg. Low temperature experiments were performed using a liquid nitrogen cooling accessory.

The glass transition temperature (T_g) values were taken as the midpoints in the curves as measured from the extension of the pre- and post-transition baselines. At least two assays were performed in each case to determine T_gs, crosslinking temperatures (T_{peak}) and enthalpies (ΔH_c). The reproducibility of T_g measurements by d.s.c. and t.m.a. depended on the intensity and broadness of the transition; there was an error of ± 2°C for sharp transitions and ± 5°C for broad transitions. In the same way, the experimental scattering for T_{peak} was ± 1°C, while for ΔH_c was ± 5 J g^{-1}.

Thermomechanical analysis

Thermomechanical analyses were carried out at 10°C min^{-1}, under a nitrogen flow, by means of a Perkin-Elmer TMA-7 device connected to a data station PE-7700. Expansion and penetration modes were used. Different forces were applied ranging between 500 mN for the films and 1500 mN for the cylindrical samples. The temperature corresponding to the onset of the penetration or expansion curves was taken as the transition temperature.

Thermogravimetric analysis

Thermogravimetric analyses (t.g.a.) were obtained on a Perkin-Elmer TGS-2 device under a nitrogen flow at a heating rate of 20°C min^{-1} up to 500°C. The temperature at which the first onset in the t.g.a. curve took place was taken as the degradation temperature.

RESULTS AND DISCUSSION

One-component networks

The crosslinking kinetics of the bismaleimide oligomers have been studied by d.s.c. and the results have been reported in a previous publication[8]. The crosslinking causes an increase in T_g which is inversely proportional to the molecular weight of the oligomer. This effect can be clearly observed in *Table 1*. *Table 1* shows the T_g after a dynamic run at 20°C min^{-1} up to 250°C.

However, although this treatment can be considered sufficient if we do not consider a remaining crosslinking enthalpy, T_g increases if a larger amount of initiator is used or if the sample is postcured. Therefore, several experiments were carried out to obtain fully cured networks by varying the conditions according to the kinetic results previously obtained[8].

Table 1 Glass transition temperatures of the bismaleimide oligomer series after curing and postcuring treatment

Sample	X_n	M_n	T_g cured (°C)	ΔT_g (°C)	T_g post-cured (°C)	ΔT_g[a] (°C)
1M	1.3	800	128	85	160[b]	127
2M	3.2	1250	70	46	84	60
3M	8.5	2500	38	12	44	18
4M	12	3300	34	7	39	12
5M	16	4200	28	4	34	10
6M	21	5300	26	2	30	6

[a] $\Delta T_g = T_g$ crosslinked $- T_g$ linear
[b] Undetected by d.s.c. measured by t.m.a.

Table 2 Glass transition temperature dependence of oligomer 3M with the amount of initiator and cure temperature

Initiator (%, w/w)	T_g (°C) after treatment at 140°C for 1 h	 150°C for 1 h	 160°C for 1 h	 170°C for 1 h
0.75	36	38	39	40
1.50	37	42	44	44
3.00	37	42	44	44

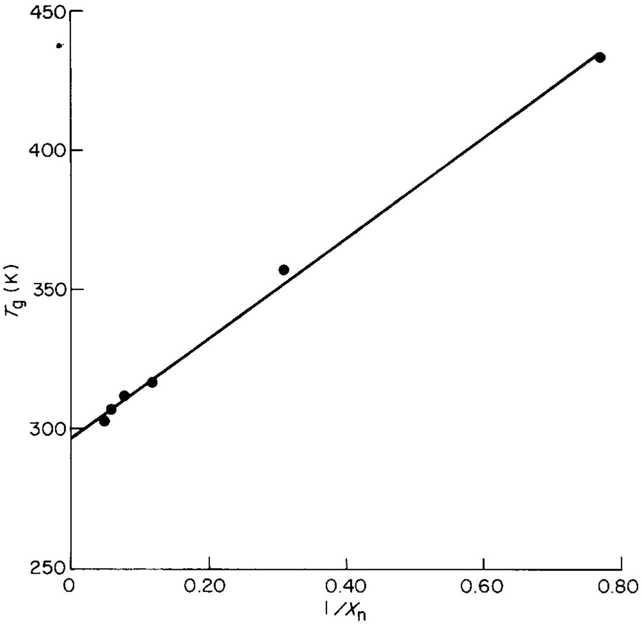


Figure 1 Dependence of T_g on degree of polymerization (X_n) between crosslinking sites for the crosslinked oligomer series

As an example, *Table 2* shows this influence on the T_g of oligomer 3M. As can be seen, T_g increases with curing temperature, T_c, reaching a maximum value when $T_c \simeq 160$°C. The influence of initiator concentration is significant only up to 0.06 mol of initiator per mol of double bond (1.5% w/w).

Since the T_g of the final networks is clearly below T_c, except in the case of oligomer 1M, a lower curing temperature (130°C) was applied for a longer time (20 h), calculated from the activation energy of the crosslinking reaction[8]. This treatment gave better films than the high temperature crosslinking. In the case of 1M, higher temperatures were necessary to avoid vitrification.

The influence of this postcuring treatment on the T_g is significant only in the lower molecular weight (higher crosslinking density) oligomers (*Table 1*).

The dependence of T_g on the length between crosslinking sites could be seen by plotting T_g *versus* $1/X_n$ (*Figure 1*). Extrapolation to $1/X_n = 0$ ($X_n = \infty$) yielded a value of $T_{g\infty} = 25°C$ corresponding to an hypothetical uncrosslinked polymer with an infinite molecular weight. This value is in very good agreement with the T_g (22°C) reported for linear poly(diethyleneglycol terephthalate) by Guzmán *et al.*[9].

Thermomechanical analyses (penetration mode) gave values of T_g very similar to those obtained by d.s.c. In addition, the penetration percentages were directly related to the crosslinking density, ranging from 0.1% for oligomer 1M to 25% for oligomer 6M.

A second onset of penetration was observed at ~350°C corresponding to polymer degradation with loss of mechanical properties. The degradation could also be checked by t.g.a., a value of ~380°C being observed for the first onset of weight loss. No significant difference with the behaviour of uncrosslinked oligomers was found by t.g.a.

Semi-interpenetrating polymer networks

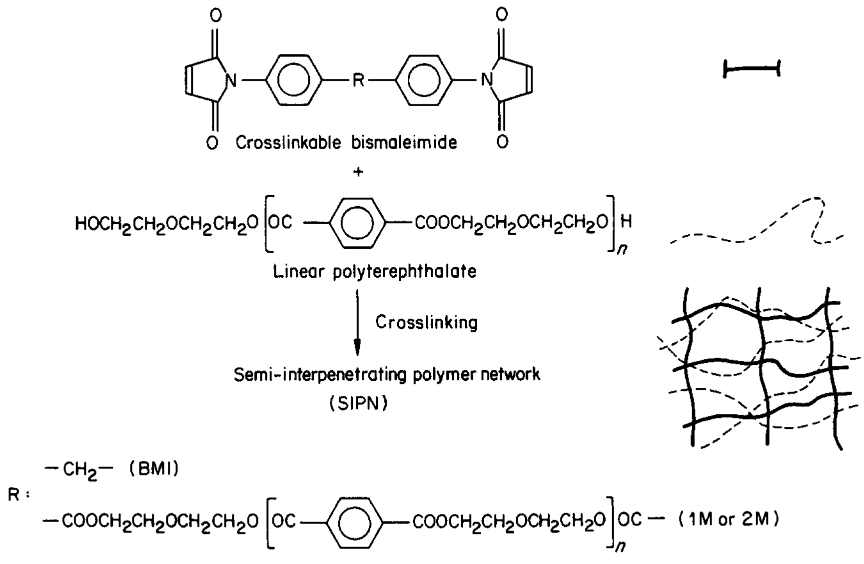
Two series of SIPNs (*Scheme 1*) were obtained in order to evaluate the influence of the different factors, i.e. chemical structure, fraction of crosslinkable component (f) and molecular weight, governing the compatibility of this type of system.

The compositions tested are summarized in *Table 3*. The use of two different types of bismaleimides (1M, with the same chain structure as the linear polymer, or BMI, with a different structure) allows the study of the influence of chemical structure[10]. Moreover, the variation of the molecular weight of the linear (3 or 6) and the crosslinkable oligomer (1M or 2M) and the use of different weight fractions, f, of crosslinkable component ($f = 0.33$, 0.5 and 0.67) permits evaluation of other factors affecting compatibility.

Blend compatibility

The SIPNs were made in a two-step process. In the first step the thermoplastic and crosslinkable oligomers were blended. In the second step, the system was heated to obtain a crosslinked system.

The resin mixtures were characterized using the T_g as a criterion of compatibility[11,12]. As could be expected from the low molecular weight and from the existence of polar structures in both components, the blends showed



Scheme 1

Table 3 Composition, T_g, crosslinking enthalpies (ΔH_c) and T_{peak} of the different blends used to obtain SIPNs

Bismaleimide		Linear polymer		Weight fraction (f) of crosslinkable component	T_g (°C)	T_{peak} (°C)	ΔH_c (J g^{-1})
Sample	M_n	Sample	M_n				
1M	800	3	2000	1	33	165	215
				0.67	20	164	158
				0.50	17	166	109
				0.33	13	168	79
				0	8	–	–
BMI	358	3	2000	1	53	160	345
				0.67	34	152	240
				0.50	27	154	185
				0.33	20	155	163
2M	1250	3	2000	1	24	–	–
				0.67	12	–	–
BMI	358	6	4500	0.50	32	–	–
				0	20	–	–

compatibility before crosslinking. However, to obtain compatible blends it was necessary to previously melt the mixture in order to obtain an amorphous material that did not crystallize upon cooling. After this treatment only a single T_g was observed by d.s.c. ranging between the T_gs of both components as a function of composition. These values are summarized in *Table 3*. It should be noted that the blends with a weight fraction of BMI of 0.5 or more, always showed a very small endotherm of melting before crosslinking.

Differential scanning calorimetry was also used to investigate the cure reactions of the resin mixtures. As is well known, the chemical environment affects the kinetics of the cure reactions, and the extent of the reaction in turn affects the tendency to separate both components.

All samples showed a broad exotherm with a maximum at ~160°C, due to the crosslinking reaction initiated by dicumyl peroxide. *Table 3* shows the values of crosslinking enthalpy (ΔH_c) and temperature (T_{peak}) of both bismaleimides and their corresponding blends with linear oligomer 3 in different proportions.

It should be noted that T_{peak} was practically constant, irrespective of the crosslinkable to linear ratio, whereas the reaction enthalpy was directly related to the number of double bonds in the blend, as could be observed from the cure enthalpies of the net oligomers. In the case of pure BMI, the crosslinking enthalpy could not be accurately determined because of the overlapping with the melting process and had to be measured from the non-initiated reaction.

This behaviour indicated that the blends were truly SIPNs, as the crosslinking reaction was independent of the linear component.

Cured samples

The influence of the thermal treatment on the behaviour of the cured systems was evaluated by t.m.a. and d.s.c. With this aim the samples were tested after a constant temperature schedule (140°C for 1 h, 160°C for 1 h, 200°C for 1 h and 225°C for 30 min).

The compatibility of the SIPNs once cured was strongly dependent on the crosslinked fraction as can be observed from the data listed in *Table 4*. For the lower proportion of the crosslinkable oligomer ($f = 0.33$), compatibility of the SIPNs is very difficult for the two systems 1M/3 and BMI/3. Two transitions were observed in both cases, shifted inwards with respect to that of pure linear and pure crosslinked components. The shifting of the T_g of the linear polymer was greater for the system 1M/3 (from 10 to 45°C) than for the system BMI/3 (from 10 to 35°C), indicating a greater degree of compatibility in the first case, due to greater similarity in chemical structure of the linear component 3 and the reactive oligomer 1M.

Table 4 Thermal transitions of the final SIPNs determined by t.m.a.

Sample	f	Cylindrical (C) or film (F)	Penetration T_g (°C)	Expansion T_g (°C)
1M/3	0.33	C	45, 110	50, 110
		F	42[a]	
	0.50	C	82	79
	0.67	C	95	90
		F	100	
BMI/3	0.33	C		35, 120
		F	34, 110	
	0.50	C		120
	0.67	C		130
2M/3	0.50	F	45	
BMI/6	0.50	C		126

[a] Complete penetration

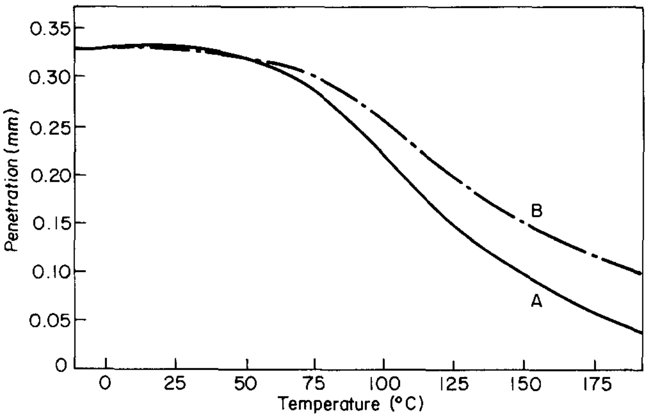


Figure 2 Thermomechanical analysis penetration curves (1500 mN) of 1M/3 ($f = 0.50$) treated at 140°C for 1 h and 160°C for 1 h (A) and 140°C for 1 h and 160°C for 1 h and 200°C for 1 h (B)

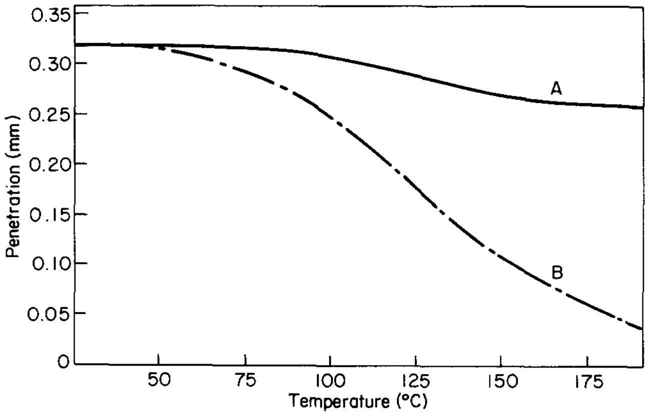


Figure 3 Thermomechanical analysis penetration curves (1500 mN) of 1M/3 with $f = 0.67$ (A) and 0.5 (B)

For higher values of f, full compatibility was achieved in every case, regardless of the chemical nature of the crosslinkable species. Thus, only one T_g was observed for the systems 1M/3 and BMI/3 with crosslinkable fractions of 0.5 and 0.67. The value of T_g increased when the thermal treatment proceeded as can be seen in *Figure 2*. The higher T_g of the pure crosslinked BMI with respect to the pure crosslinked 1M gave rise to higher values for the T_gs of the compatible systems containing BMI, contrary to the observation when $f = 0.33$.

Thus, the fraction of crosslinkable component seems to play an important role in the control of the compatibility[13,14]. As a rule, the richer the system in crosslinked component, the better the compatibility. So, although both cured mixtures with $f = 0.67$ and 0.5 showed only one transition, this transition is broader in the second case (*Figure 3*), which agrees with a lower compatibility[11].

The change in the molecular weight of the crosslinkable or the linear component did not seem to play a significant

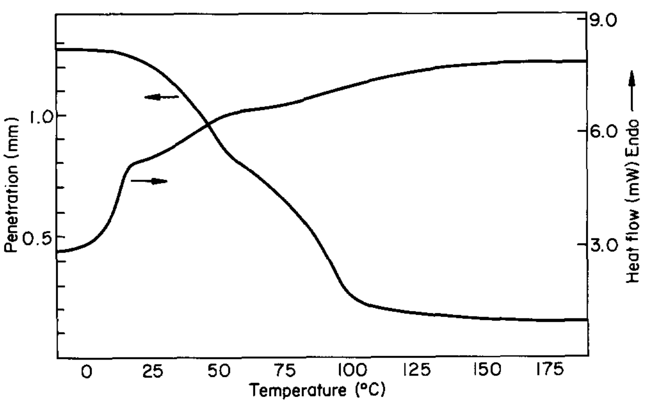


Figure 4 Thermomechanical analysis penetration (1500 mN) and d.s.c. curves of 1M/3 ($f = 0.33$) treated at 140°C for 1 h

role in the compatibility (*Table 4*: 2M/3 and BMI/6), within the limits of our samples.

It is worth noting that, although the final materials are compatible in most cases, the process is far from being simple. Curves with two or three transitions, more or less visible using d.s.c. and t.m.a., were obtained at intermediate stages in the curing. This is illustrated in *Figure 4*, where the d.s.c. and t.m.a. curves for sample 1M/3 ($f = 0.33$) are reproduced at an intermediate stage in the curing process.

It appears as if the initially compatible blend passes through stages of incompatibility or phase segregation as curing proceeds, to achieve a fully compatible state at the end of the process again when network density is high enough to immobilize the linear and crosslinked components.

The influence of crosslinking density on the penetration percentage is also illustrated in *Figure 3*. In the case of the BMI systems, no penetration was detected except in the case of composition 1/2, even by applying the strongest possible force (2500 mN). Consequently, the transitions were determined by expansion in these cases.

The expansion coefficients were one order of magnitude larger for 1M systems $\simeq 10^{-5}\,K^{-1}$ than for BMI systems ($10^{-6}\,K^{-1}$), also reflecting the influence of crosslinking density.

The thermal stability (t.g.a.) seemed to be determined by the low thermal resistance of the terephthalate structures, so that T_{onset} was practically constant in all cases ($\simeq$380°C). However, the percentage of weight loss decreased when the amount of crosslinkable component increased, as expected.

CONCLUSIONS

The maleimide-terminated oligoesters studied can be easily crosslinked to give polymeric networks. The T_gs of these networks are inversely proportional to the molecular weight of the oligomer and can be used to extrapolate to the T_g of a hypothetical linear polymer of $M_n = \infty$.

All the blends studied are compatible before curing due to the similar chemical structure of both components and the amorphous character of the linear oligoesters.

The presence of the linear oligomers does not affect the curing process. Thus, crosslinking temperature remains constant while crosslinking enthalpy is proportional to the fraction of double bonds in the system.

The compatibility of the SIPNs is directly related to the amount of crosslinkable component and increases with this amount. The chemical structure seems to play a significant role only when the crosslinking density is low ($f = 0.33$). For higher values of f, the network density overcomes the tendency to separate of both components, even when the chemical structures of the linear and crosslinkable components are different.

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