Polydimethylsiloxane/poly(methyl methacrylate) interpenetrating polymer networks: 2. Synthesis and properties

X. W. He*, J. M. Widmaier*‡, J. E. Herz† and G. C. Meyer*
** Institut Charles Sadron, EAHP, 4 rue Boussingault, F-67000 Strasbourg, France*
† Institut Charles Sadron, CRM, 6 rue Boussingault, F-67000 Strasbourg, France
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The synthesis of full and graft interpenetrating polymer networks (IPNs) based on polydimethylsiloxane and poly(methyl methacrylate) is described. IPNs were obtained by an *in-situ* sequential synthesis. Most samples were opaque; however, in a few cases, transparency was noted. Other properties like stress–strain behaviour, hardness and glass transition temperature were examined. Owing to the particular behaviour of silicone-containing polymers, the surface properties and the permeability to oxygen of these IPNs were also studied.

(Keywords; interpenetrating polymer networks; polydimethylsiloxane; poly(methyl methacrylate); optical properties; mechanical properties; surface properties; permeability)

INTRODUCTION

In recent years, much research has been carried out on polymer blends, mainly because of the enhanced mechanical properties that these materials possess[1]. Interpenetrating polymer networks (IPNs) are combinations of crosslinked polymers held together by permanent entanglements[2]. Like other multicomponent systems, IPNs exhibit restricted phase separation. Owing to their interlocking configuration, the state of phase separation obtained at the end of their synthesis is frozen in, so that the properties are not influenced by ageing. IPNs are therefore well suited for the combination of highly incompatible polymer pairs.

Polydimethylsiloxane (PDMS) shows several interesting properties[3] such as low surface energy[4], high permeability to many gases[5] and biocompatibility[6], but its mechanical properties are rather poor, even after crosslinking. Hence, reinforcing becomes necessary for many applications. Usually, inorganic fillers like silica are used[7], but an alternative approach consists of introducing glassy polymers into the silicone[8].

Little work has taken advantage of the IPN structure. Only a few examples of IPNs containing organosilicon polymers have been reported in the literature[9–14]. Typically, they are prepared in two steps by swelling crosslinked PDMS with the precursors of the second network and polymerizing. Recently, attempts were made to prepare PDMS-based IPNs via a one-shot, two-stage process following the basic procedure developed in our laboratory for polyurethane/poly(methyl methacrylate) (PUR/PMMA) IPNs[15,16]. In the first paper of this series[17], we investigated PDMS network formation in the presence of methacrylic monomers and examined the efficiency of stannous octoate as a catalyst. In this paper, we describe the synthesis of full and graft PDMS/PMMA IPNs, obtained by the *in-situ* sequential synthesis process. Some properties of the resulting materials are detailed, such as transparency, glass transition temperatures, stress–strain behaviour, hardness, surface tension and gas permeability. In addition, preliminary results on morphology are reported.

EXPERIMENTAL

The following materials were used after drying. α,ω-Dihydroxy-polydimethylsiloxane (Wacker) was heated at 80°C under vacuum for 24 h to eliminate the low-molar-mass cyclic compounds. Two prepolymers having a number-average molar mass of 4200 and 860 $\mathrm{g\,mol^{-1}}$, respectively, were used in this study. Tetraethyl orthosilicate (TEOS; Merck) or trimethoxysilylpropyl methacrylate (TMSPM; Fluka) were used as the crosslinker. Stannous octoate (Goldschmidt) was the catalyst for the polycondensation reaction. Methyl methacrylate (MMA; Fluka) and 1,1,1-trimethylolpropane trimethacrylate (TRIM; Degussa) were stored over 0.4 nm molecular sieves, but not otherwise freed from inhibitor. Radical copolymerization was initiated by thermal decomposition of azobisisobutyronitrile (AIBN; Merck).

The *in-situ* sequential synthesis consists of the following steps. A mixture of α,ω-dihydroxy-PDMS, crosslinker, stannous octoate, MMA, TRIM and AIBN was poured into a mould formed by two glass plates separated by a 3 mm thick gasket and clamped together. The ratio $K = [\mathrm{SiOR}]/[\mathrm{SiOH}]$, where $\mathrm{R} = \mathrm{CH_3}$ or $\mathrm{C_2H_5}$, which represents the number of alkoxy functions per hydroxyl function, was varied from 1 to 4. For all syntheses, stannous octoate was present in an amount corresponding to 2.5% by weight of the polymer; the

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‡ To whom correspondence should be addressed

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concentrations of AIBN and TRIM were 0.5% and 5% by weight, respectively. The PDMS network was formed first at room temperature. After gelation of the medium, the temperature was raised to 60°C to initiate the copolymerization of the methacrylic monomers. The resulting IPN was cured overnight at 75°C and post-cured under vacuum at 120°C for 3 h. In order to remove uncrosslinked species, these IPNs were extracted with ethyl acetate for 7 days in a Soxhlet apparatus. No characterization of the sol fraction was carried out. Before examining their properties, the samples were again dried under vacuum to constant weight.

The light transmittance was determined with a Varian DMS 80 spectrophotometer. Hardness measurements were made with a Zwick durometer, according to DIN 53 456. At least five measurements at different positions were made to determine the mean value. Tensile measurements were performed using an Instron 8031 tester at room temperature with a crosshead speed of 5 mm min^{-1}. Young's modulus E, ultimate tensile strength σ_u and ultimate elongation ε_u were determined. Results reported are the average of five specimens. The surface energy γ was determined through the classical evaluation of the contact angle. Measurements were made on IPNs as obtained, and also on samples whose surface had been abraded ($\sim$1 mm) prior to the measurement, in order to obtain a surface representing the core of the sample. The permeability towards oxygen was determined with a YSI model 58 dissolved-oxygen tester on standard discs. Differential scanning calorimetry (d.s.c.) was conducted in a Perkin-Elmer DSC-4 apparatus operating at a heating rate of 20°C min^{-1}. Several quenching-heating cycles were performed on each sample to ensure a uniform thermal history. The third and subsequent scans were reproducible. The glass transition temperature T_g, was taken at the half-height of the corresponding heat capacity jump. The melting temperature T_m was recorded at the maximum of the endothermic peak. Dynamic mechanical measurements were performed with a Rheometrics model RMS 7200 mechanical spectrometer at a fixed frequency of 1 rad s^{-1} through a temperature range from -160 to $+150$°C under dry nitrogen. Electron micrographs were taken on a Zeiss EM 902 transmission electron microscope equipped with an integrated electron energy-loss spectrometer, which allows element-specific image analysis[18]. Experiments were carried out at the Institut für Makromolekulare Chemie, University of Freiburg, FRG.

RESULTS AND DISCUSSION

For the present study, two series of IPNs were synthesized: a series in which both networks are physically entangled, i.e. no covalent bonds exist between them (full IPN), and a series in which TEOS has been replaced by TMSPM (the presence of the methacrylic double bond on the PDMS crosslinker induces grafts between the networks).

Optical properties

Owing to its very low surface energy, PDMS is among the most incompatible polymers, so that transparency is not expected for IPNs based on PDMS. *Table 1* shows, however, that by selecting adequate synthesis parameters, highly transparent material may be obtained in some cases: the combination of a low-molar-mass PDMS network precursor with internetwork grafts leads to PMMA-like transparency. For the 30/70 composition (*Table 2*), it is easy to follow the increase of transparency by introducing grafts and/or additional crosslink sites into the elastomeric network (increase of the K ratio). Similar results have already been obtained with polyether-based polyurethane/polystyrene IPNs[19] and are therefore confirmed even in the case of a quite incompatible polymer pair.

Table 1 Light transmission (%) of full and graft IPNs[a]

	$\bar{M}_{n,PDMS}$ = 4200 g mol^{-1}		860 g mol^{-1}	
PDMS/PMMA	Full	Graft	Full	Graft
5/95	0	0.1	0.5	88.1
10/90	0	23.7	0.6	85.1
20/80	0.4	56.0	41.7	85.7
30/70	0.9	45.0	49.5	84.6
40/60	0.4	35.0	41.0	79.5
50/50	0.4	25.0	39.0	81.0
60/40	0.4	41.0	28.0	83.0
70/30	0.4	46.0	18.0	91.5

[a] Wavelength = 700 nm; sample thickness = 3.5 ± 0.2 mm

Table 2 Influence of PDMS crosslink density on transparency of IPNs[a]

K	1	2	3	4
Full	0.9	9.0	17.0	21.0
Graft	20.0	45.0	55.0	62.5

[a] PDMS/PMMA = 30/70; $\bar{M}_{n,PDMS}$ = 4200 g mol^{-1}; wavelength = 700 nm; sample thickness = 3.5 ± 0.2 mm

Mechanical properties

Hardness. Figure 1 shows the hardness of various IPN samples, as a function of PDMS content. The different curves are all located below the straight line representing the arithmetic mean based on the values of the individual networks. This suggests that the surface is enriched in PDMS. As a matter of fact, IPNs containing 80% of rigid phase lose nearly half of their hardness value. It is obvious that the actual hardness of the bulk material cannot be evaluated by this method. As for transparency, factors that increase the crosslink density have a positive effect on hardness, as well as grafting.

Stress–strain behaviour. The main stress–strain values of full and graft IPNs of various compositions are listed in *Table 3*. Even at a high PMMA content, i.e. at 70%, the tensile modulus E decreases by a factor of 6 compared to bulk PMMA, whereas the strain remains unchanged. Grafting and crosslinking improve E with a subsequent drop in the ultimate elongation ε_u. A noticeable result is that the poor mechanical properties of the PDMS network may be reinforced significantly by adding barely 30% of rigid PMMA: E increases from 2 to 47 MPa, with $\varepsilon_u \simeq 15\%$. Thus, at first sight, materials with a high silicone content seem more interesting, from an improvement point of view, than IPNs in which the rigid component predominates.

Surface properties

Table 4 and *Figure 2* show the dependence of surface energy γ of full and graft IPNs on composition. Clearly, for full IPNs, the values of γ remain constant and equal to that of pure PDMS up to 80% PMMA. This result confirms that for IPNs, as for classical blends, the silicone component, owing to its low surface energy, tends to phase-separate strongly and to migrate towards the surface. For the graft series, the surface energy of neat PDMS is somewhat higher, as the polarity of TMSPM (the trifunctional crosslinker used in this case) intervenes, but again this value holds up to 80% PMMA.

However, contrary to polymer blends, IPNs are materials in which the two systems are interlocked by crosslinks, so that the migration of the PDMS towards the surface is impeded. In order to measure γ of the core of the sample, the surface was abraded to a depth of 0.1 mm: it was found that the values of the surface energy correspond to the arithmetic mean value computed from the respective PDMS content (see *Figure 2*, broken line). Thus, on the surface, the silicone chains can migrate so as just to cover up the rigid chains and give a low surface energy; whereas in the core, both components contribute to γ, indicating an intimate mixing of the two phases.

Also, it was interesting to know whether newly created surfaces would undergo the same phenomenon, i.e. tend to a low surface energy around 25 mJ m^{-2}. *Figure 3* confirms this hypothesis. At room temperature, the recovery takes time, and is not completed after two months. But, by operating above the glass transition temperature T_g of the rigid phase, owing to the increased mobility of the chains, the various samples recover the value of the surface energy corresponding to pure PDMS within a few hours, whatever the PDMS content.

Table 4 Surface energy of PDMS/PMMA IPNs

PDMS/PMMA	γ (mJ m^{-2}) Full IPN	Graft IPN
0/100	52.9	52.9
5/95		37.8
10/90		35.2
20/80	25.6	33.3
30/70	24.9	31.7
40/60	24.7	30.9
50/50	24.5	30.9
60/40	24.3	30.3
70/30	24.3	30.2
85/15	24.3	29.3
100/0	24.1	28.9

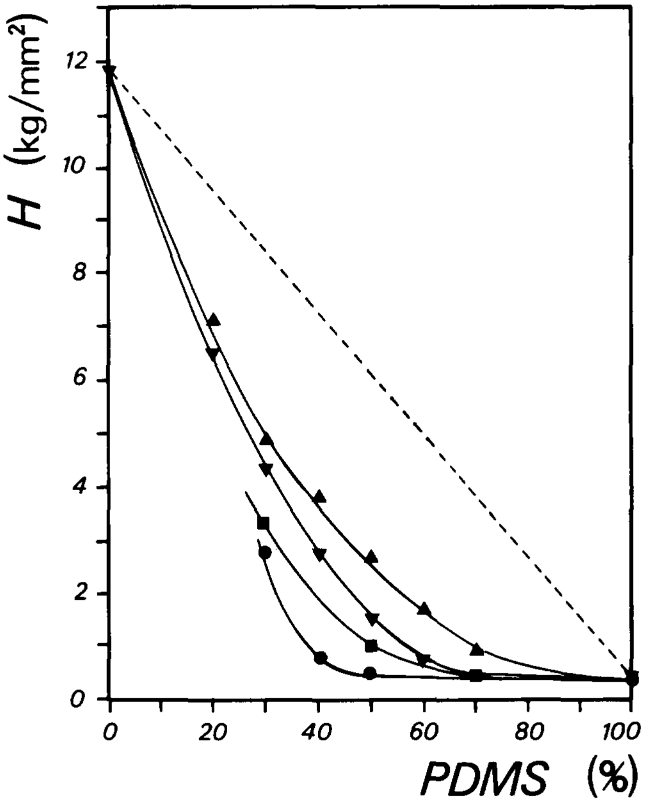

Figure 1 Hardness H of PDMS/PMMA IPNs *versus* PDMS content: (●) full IPN, $\bar{M}_{n,PDMS} = 4200$ g mol^{-1}; (■) graft IPN, $\bar{M}_{n,PDMS} = 4200$ g mol^{-1}; (▼) full IPN, $\bar{M}_{n,PDMS} = 860$ g mol^{-1}; (▲) graft IPN, $\bar{M}_{n,PDMS} = 860$ g mol^{-1}

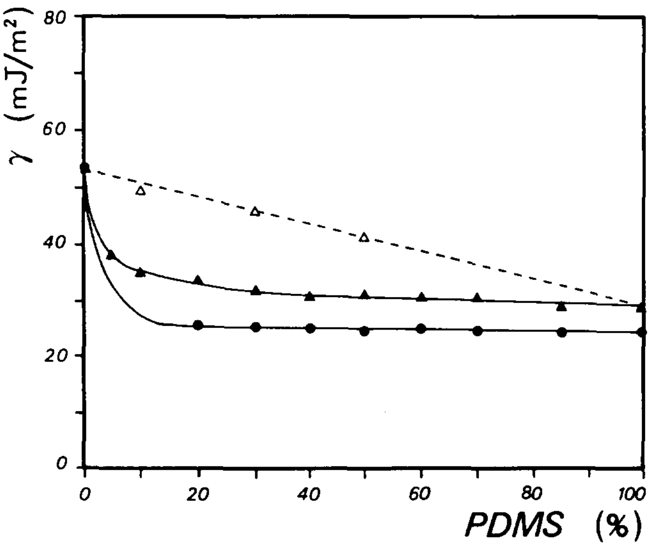

Figure 2 Surface energy γ of PDMS/PMMA IPNs *versus* PDMS content: (●) full IPN; (▲) graft IPN; (△) graft IPN after abrasion

Table 3 Mechanical properties of PDMS/PMMA IPNs[a]

PDMS/PMMA	Full IPN E (MPa)	Full IPN σ_u (MPa)	Full IPN ε_u (%)	Graft IPN E (MPa)	Graft IPN σ_u (MPa)	Graft IPN ε_u (%)
0/100	2800	76.6	2.9	2800	76.6	2.9
30/70	420	9.96	2.4	840	29.8	9.4
40/60	69	3.01	7.9			
50/50	18	2.05	49.6	210	11.3	14.7
60/40	2.5	0.64	320			
70/30	1.4	0.64	200	47	3.23	15.5
100/0	3.0	0.25	26	2.1	0.15	15.9

[a] E = Young's modulus; σ_u = tensile strength at break; ε_u = elongation at break; $\bar{M}_{n,PDMS} = 4200$ g mol^{-1}

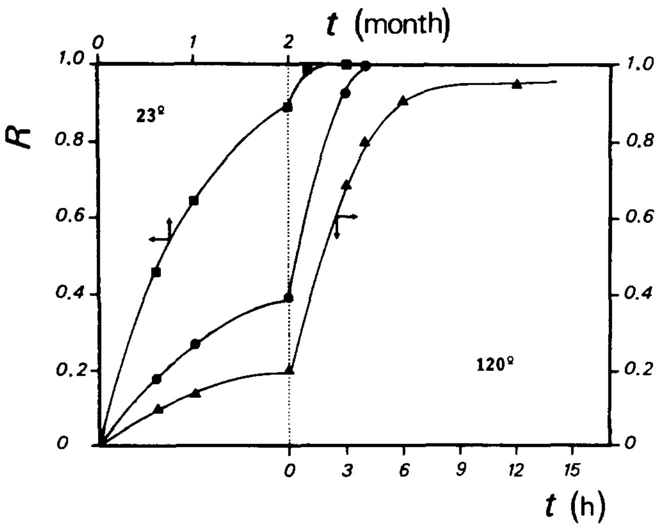

Figure 3 Energy recovery R at room temperature and at 120°C of abraded graft IPNs of various PDMS content: (▲) 10%; (●) 30%; (■) 50%

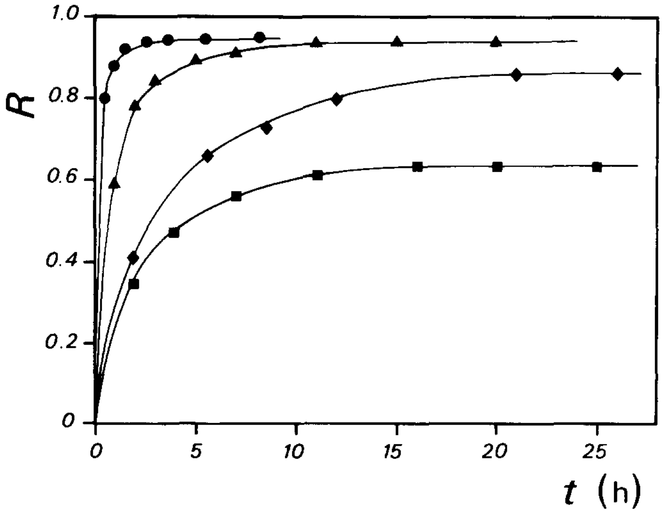

Figure 4 Energy recovery R of an abraded graft IPN under various conditions: (◆) at room temperature in saturated methyl ethyl ketone atmosphere; (■) at 90°C; (▲) at 120°C; (●) at 140°C

For a given composition, recovery is faster as the temperature (above T_g) is raised (*Figure 4*). A fast recovery is also possible at room temperature when the sample is kept in a saturated atmosphere of methyl ethyl ketone (MEK), a good solvent for PMMA, which increases chain mobility, like temperature. *Figure 5* illustrates recovery, at 120°C, for samples having the same composition: the IPN made from PDMS with a molar mass of 4200 g mol^{-1} reaches its primary surface energy first, owing to its longer chain length. For the samples with a more densely crosslinked elastomeric phase, the ungrafted one recovers faster than the grafted one; here, also, chain mobility plays an important role.

Oxygen permeability

As PDMS is the polymer that is the most permeable to gases, but has otherwise poor mechanical properties, a combination with a reinforcing polymer like PMMA could yield gas-permeable materials with both high permeability and good mechanical resistance. *Figure 6* shows oxygen permeability of IPNs with various PDMS contents: the permeability is proportional to the amount of silicone, and again a linear composition law establishes the intimate mixing of both phases. Furthermore, as oxygen diffusion proceeds along the elastomeric chains, the PDMS network is continuous through the IPN. Note that the amount of oxygen diffusing in a 50/50 IPN, for example, is still rather higher than for other polymers[20].

Transition behaviour

The transition behaviour of several IPNs has been examined by differential scanning calorimetry (d.s.c.) and dynamic mechanical spectrometry (d.m.s.), and the results of both methods reported in *Table 5* are found to be consistent. The PDMS with the molar mass of 4200 g mol^{-1} and the corresponding IPN exhibit a fusion peak around −65°C, which disappears at higher degrees of crosslinking or by introducing internetwork grafts (*Table 6*). This observation shows that even the presence of rigid domains in the IPN does not impede the formation of organized domains in the PDMS phase, at least when

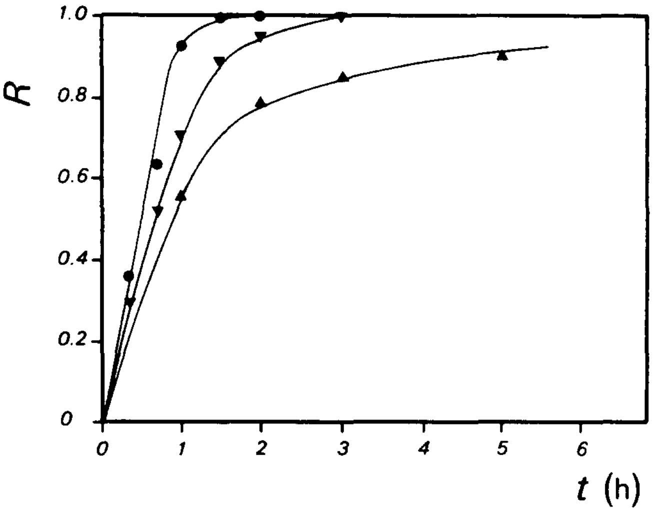

Figure 5 Energy recovery R at 120°C of abraded PDMS/PMMA IPNs: (●) full IPN, $\bar{M}_{n,PDMS} = 4200$ g mol^{-1}; (▼) full IPN, $\bar{M}_{n,PDMS} = 860$ g mol^{-1}; (▲) graft IPN, $\bar{M}_{n,PDMS} = 860$ g mol^{-1}

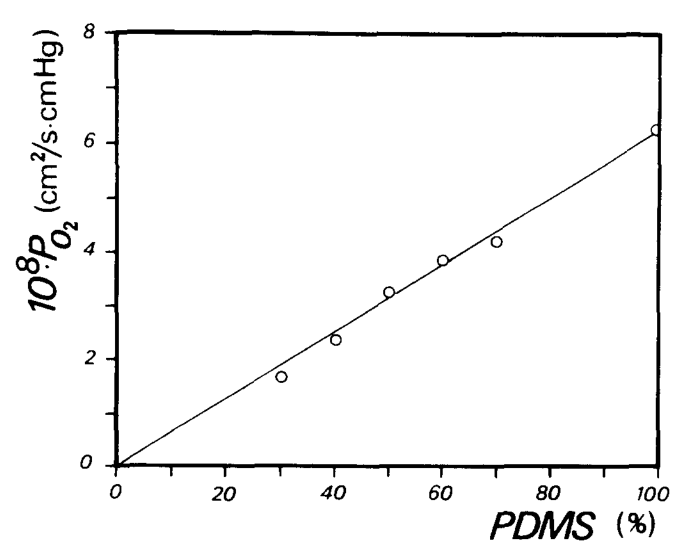

Figure 6 Oxygen permeability constant P_{O_2} of full IPN *versus* PDMS content

Table 5 Glass transition and melting temperatures from d.s.c. and d.m.s. data

	$\bar{M}_{n,PDMS}$ =	4200 g mol^{-1}		860 g mol^{-1}	
PDMS/PMMA		Full	Graft	Full	Graft
0/100	T_g (d.m.s.)	121	121	121	121
	T_g (d.s.c.)	116	116	116	116
30/70	T_g (d.m.s.)	−121	−137	−137	−126
		134	130	130	120
	T_g (d.s.c.)	−126.6	−134	−133.6	–
		126	119		
	T_m (d.m.s.)	−67	–		–
	T_m (d.s.c.)	−64.9	–	–	–
100/0	T_g (d.m.s.)	−120			−110
	T_g (d.s.c.)	−125.4	−122.6		−112.5
	T_m (d.m.s.)	−65.3			–
	T_m (d.s.c.)	−60	–		–

Table 6 Influence of PDMS crosslink density on thermal behaviour of PDMS/PMMA graft IPNs[a]

K	1	2	3	4
T_g (d.m.s.)	−122	−137		
	134	130		
T_g (d.s.c.)	−131	−134		−136
	120	119	120	122
T_m (d.m.s.)	−70	–		
T_m (d.s.c.)	−67	–		–

[a] PDMS/PMMA = 30/70; $\bar{M}_{n,PDMS}$ = 4200 g mol^{-1}

crosslinking and/or grafting have no adverse effect. Apart from the melting peak, all the IPNs exhibit a low-temperature and a high-temperature transition, corresponding to the elastomeric silicone phase and to the rigid PMMA phase, respectively. Considering the low-temperature transition (*Figure 7*), the IPN made with $K = 1$ has the same T_g as pure PDMS, though usually a shift towards higher temperatures is observed for IPNs[2]. This could be explained by the pronounced incompatibility of silicone towards PMMA. But for $K = 2$, i.e. a more densely crosslinked PDMS phase, the T_g is displaced to an even lower temperature, so that one suspects a plasticizing effect due to an incompletely formed PDMS network.

The elastomeric network based on the low-molar-mass prepolymer ($\bar{M}_{n,PDMS} = 860$ g mol^{-1}) shows T_g values superior to the preceding ones, consistent with their higher crosslink density. Again, the related IPNs undergo glass transition at a temperature lower than that of the pure PDMS network.

The T_g of the crosslinked PMMA is 116°C by d.s.c. and 120°C by d.m.s.. One observes that the T_g values of all the IPNs are above these values, an observation that corroborates a recent result on *in situ* simultaneous polyurethane/poly(methyl methacrylate) IPNs[21]: owing to specific synthesis conditions, and presumably syneresis effects, a part of the rigid phase is dispersed in the elastomeric component, but another part exists as rather pure PMMA domains, with higher crosslink density, and hence modulus and T_g, as in the dispersed phase.

This investigation on transition behaviour of *in situ* sequential PDMS/PMMA IPNs shows as a main result that, contrary to other IPNs, the lower and upper T_g values are shifted left- and rightwards, respectively, on the temperature scale as compared to the T_g of the corresponding pure networks. Though the incompatibility factor has to be kept in mind, incomplete formation of the elastomeric network and the higher crosslink density of the rigid network may also contribute to such behaviour.

Morphology

In *Figure 8*, transmission electron micrographs are shown for two 30/70 PDMS/PMMA IPNs. The samples differ in the molar mass of the PDMS precursors. To enhance contrast and sharpness, the micrographs were taken with monoenergetic electrons of $\Delta E = 165$ eV, just after the silicon ionization edge. Therefore, the white areas represent the PDMS phase. As expected[2], the elastomeric network, which was the first-formed network, constitutes the continuous phase. Increasing the level of crosslinking by decreasing the molar mass of the PDMS precursor leads to more dispersion and reduction of the size of the methacrylic domains. A more detailed study of the morphology including graft IPNs will be given in a future paper.

CONCLUSIONS

Through the formation of polydimethylsiloxane/poly(methyl methacrylate) interpenetrating polymer networks, the poor mechanical properties of the silicone network are improved. The crosslinked nature of PDMS impedes its usually observed migration, so that the bulk properties are not expected to vary. The surface properties are PDMS-like, but by abrasion a less hydrophobic surface can be created, which is suited for adhesive purposes. The gas permeability of these materials remains high, and, as it is associated with an improved mechanical behaviour, important industrial applications can be expected for PDMS/PMMA IPNs.

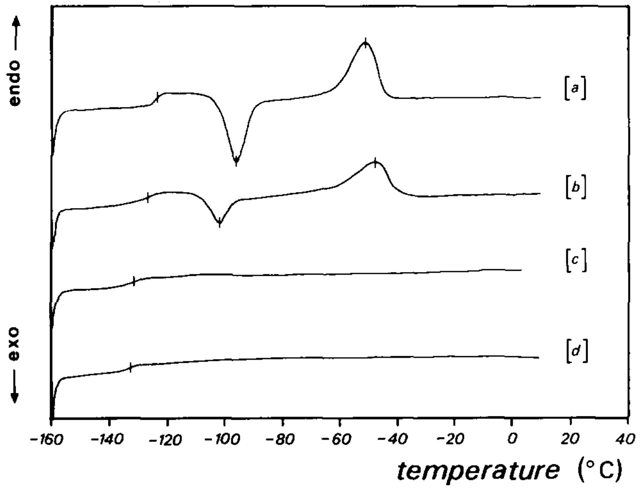

Figure 7 D.s.c. curves of 30/70 PDMS/PMMA IPNs, $\bar{M}_{n,PDMS}$ = 4200 g mol^{-1}: (a) full IPN; (b) graft IPN, $K = 1$; (c) graft IPN, $K = 2$; (d) graft IPN, $K = 4$

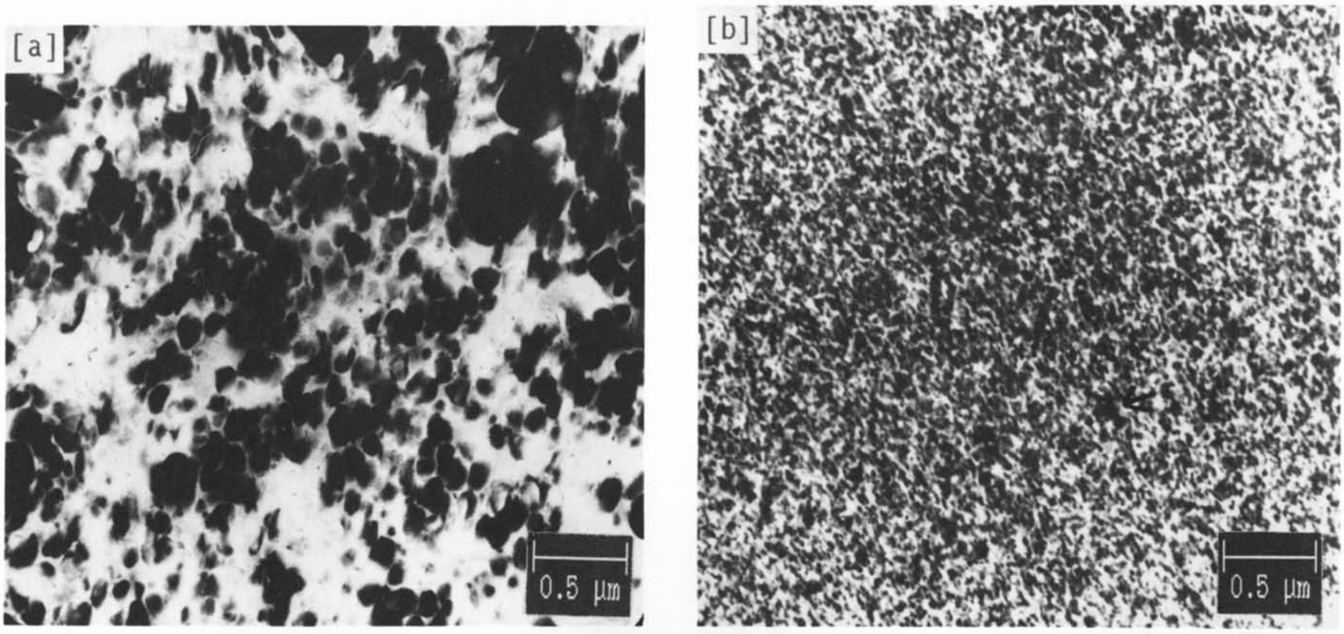

Figure 8 Transmission electron micrographs ($\Delta E = 165$ eV) of 30/70 PDMS/PMMA IPNs: (a) $\bar{M}_{n,PDMS} = 4200$ g mol^{-1}; (b) $\bar{M}_{n,PDMS} = 860$ g mol^{-1}

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