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Miscibility and properties of polyglutarimide poly(styrene-co-maleic anhydride) blends

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Abstract

In the present study, blends of polyglutarimide (PGI) with styrene/maleic anhydride (SMA) copolymers showed complete miscibility with SMA containing 25, 33 and 50 mol.% maleic anhydride (MA), whereas blends with SMA containing 8 mol.% MA were found to be immiscible. These blends were studied using a variety of methods including thermal microscopy, FTIR and DSC. Positive T_g deviations from the ideal (linear) behaviour and changes in FTIR spectra of the blends indicate the presence of significant specific interactions between the two polymers. These interactions were found to be of a polar nature, involving the carbonyls of anhydride and imide rings, respectively. The intramolecular repulsion effect is possibly another factor contributing to enhanced miscibility. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer blends; Polyglutarimide; Polymer miscibility

1. Introduction

During the last 20 years the area of polymer blends has been the focus of intense interest from both the academic and the industrial point of view. There are obvious advantages of the physical blending of polymers over the chemical synthesis of new polymers and, owing to their flexibility, much effort is focused on the exploitation of the price–performance–composition profiles of new polymer blends [1]. Many facets of their study have now reached a significant level of maturity.

Polymer–polymer miscibility is not a sine-qua-non-condition for a blend to be a useful product. Thus the so-called compatible blends are two phased materials which nevertheless show satisfactory mechanical properties. Yet, the knowledge of the degree of miscibility between the component polymers is always important for a rational design of useful new polymeric materials. From the thermodynamic point of view, polymer–polymer miscibility is expected in mixtures with a non-positive free energy of mixing ($\Delta G_{\mathrm{mix}} = \Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}}$), as long as the ΔG versus composition diagram does not exhibit any maxima.

This free energy of mixing in the frame of the well-known Flory–Huggins theory of polymer solutions is given by:

$$\frac{\Delta G_{\mathrm{mix}}}{\mathrm{R}T} = \frac{\varphi_1 \ln \varphi_1}{r_1} + \frac{\varphi_2 \ln \varphi_2}{r_2} + \chi_{12}\varphi_1\varphi_2, \qquad (1)$$

where ϑ_1 and r_1 are the volume fractions and the number of segments (degrees of polymerisation in terms of a reference volume) of the two polymers, respectively, and χ_{12} is the so-called Flory–Huggins interaction parameter. In the case of high polymers r_1, $r_2 \gg 1$ and, as a result, the first two entropy terms become vanishingly small, leaving the third enthalpic term the main factor determining miscibility. Therefore, in order for two polymers to be miscible they must have a negative heat of mixing or else $\chi_{12} < 0$.

Unfortunately, in the presence of only dispersive interactions, χ_{12} is also positive (proportional to the square of the solubility parameter difference, in the frame of the classical regular solutions theory) and, as a result, most polymer pairs in the presence of only non-polar interactions are immiscible, unless their solubility parameters are very similar [1,2]. Eq. (1) does not explicitly show a third contribution to the free energy of mixing, namely, the free-volume contribution. This latter contribution, which is lumped into the χ_{12} term, is always positive and, hence, unfavourable for mixing. Thus stronger intermolecular interactions are needed for polymer–polymer miscibility. One possible way to induce miscibility is the introduction into the polymers of complementary units capable of developing specific

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Table 1
Information on SMA copolymers used in this study

Abbreviation	Wt.% MA anhydride	Molecular weight	Source
SMA8	8	$M_n = 100{,}000$ $M_w = 200{,}000$	Acro Chemical Co. (Dylark 232)
SMA25	25	$\eta = 4.73^a$	Monsanto Co.
SMA33	33	$M_n = 1700$	Scientific Polymer Products
SMA50	48.5	$M_n = 50{,}000$	Scientific Polymer Products

[a] Viscosity of a 10 wt.% solution in methyl ethyl ketone at 25°C.

interactions [2]. Such interactions can be of the dipole–dipole, ion–dipole, ion–ion and most importantly, hydrogen bonding type. These interactions can lead to a negative enthalpy of mixing and can render the system miscible.

There is, however, an additional possibility of miscibility in mixtures involving random copolymers. Many studies have shown that several copolymer–homopolymer and copolymer–copolymer blends are miscible at least over a certain composition range (the so-called ‘‘miscibility window’’) even though the pure homopolymers are pairwise immiscible and no specific interactions develop between them. In this case intramolecular rather than intermolecular interactions play a significant role. When a copolymer is comprised of very dissimilar monomer units, a highly repulsive interaction exists between them. Dilution of these unfavourable interactions by less unfavourable ones by mixing with another polymer can produce negative heats of mixing [3–8]. This is the well-known ‘‘intramolecular repulsion effect’’ and was reviewed and examined in an equation-of-state framework for random copolymer mistures [9]. The overall net interaction energy in these blends can be expressed, using simple ‘‘binary interaction’’ models, in terms of interactions between binary polymer pairs of the various monomers present [3,6,9,10].

Polyglutarimides (PGIs) are thermoplastic methacrylate-based copolymers which can be produced by reaction of poly(methyl methacrylate) (PMMA) with amines or ammonia [11]. A series of PGIs derived from the reaction of methylamine with PMMA have become commercially available by Rhom and Haas. These products are essentially methyl glutarimide–methyl methacrylate copolymers. The introduction of the polar imide groups offers the possibility for strong intermolecular interactions with other polymers, thus increasing the potential for miscibility. Thus, PGI polymers have shown miscibility at least within a certain copolymer composition range styrene–acrylonitrile (SAN) copolymers and poly(vinyl chloride) (PVC) [12] as well as bisphenol-A polycarbonate (PC) [13].

In a recent study [14] we have found that a styrene–maleic anhydride (SMA) copolymer containing 14 mol.% of maleic anhydride (MA) is miscible with poly(*N*-methyl glutarimide) (PGI) over the entire composition range. Pure polystyrene (PS), however, is immiscible with PGI. This fact indicates that the introduction of a relatively small amount of a polar monomer (MA) in the polymer (PS backbone can enhance its miscibility with PGI. The miscibility of this blend was explained solely in terms of interactions developing between the MA and glutarimide units but a possible interaction between the phenyl ring and glutarimide was also considered. In the present study we decided to study the aforementioned SMA–PGI system in conjunction with the previously mentioned intramolecular repulsion effect and over a wider composition range of SMA copolymers. This enables us to understand better how the content of interaction groups affects miscibility and how this content can be optimised in order to get an acceptable thermomechanical performance.

2. Experimental

2.1. Materials

A series of SMA copolymers containing 8, 25, 33 and 48.5 wt.% MA was used in this study. Table 1 gives information about composition, molecular weight (where available), source and abbreviation used in this study for SMA copolymers.

Poly(*N*-methyl glutarimide) ($M_n = 31\,000$, $M_w = 81\,000$), with a trade name HT 510, was supplied from Rohm and Haas. This is a random copolymer containing methyl methacrylate and glutarimide units (71 mol % imide) and is free from acid or anhydride units and will be referred to as PGI thereafter. Tetrahydrofuran used as solvent for the preparation of blends was of analytical grade (Riedel de Haen).

2.2. Blend preparation

Blends of various compositions were prepared by solution casting. Tetrahydrofuran solutions with 10 wt.% polymer content were prepared and cast on aluminium dishes. Seven different blends were prepared for each SMA copolymer containing 20%, 30%, 40%, 50%, 60%, 70% and 80% by weight SMA, respectively. The solvent was initially evaporated under ambient conditions. The final traces of solvent were removed by heating the blends under vacuum at 100°C for several days until weight constancy was achieved. The prepared polymer films had a thickness of approximately 150 μm.

Melt blending of PGI/SMA8 copolymers, was conducted

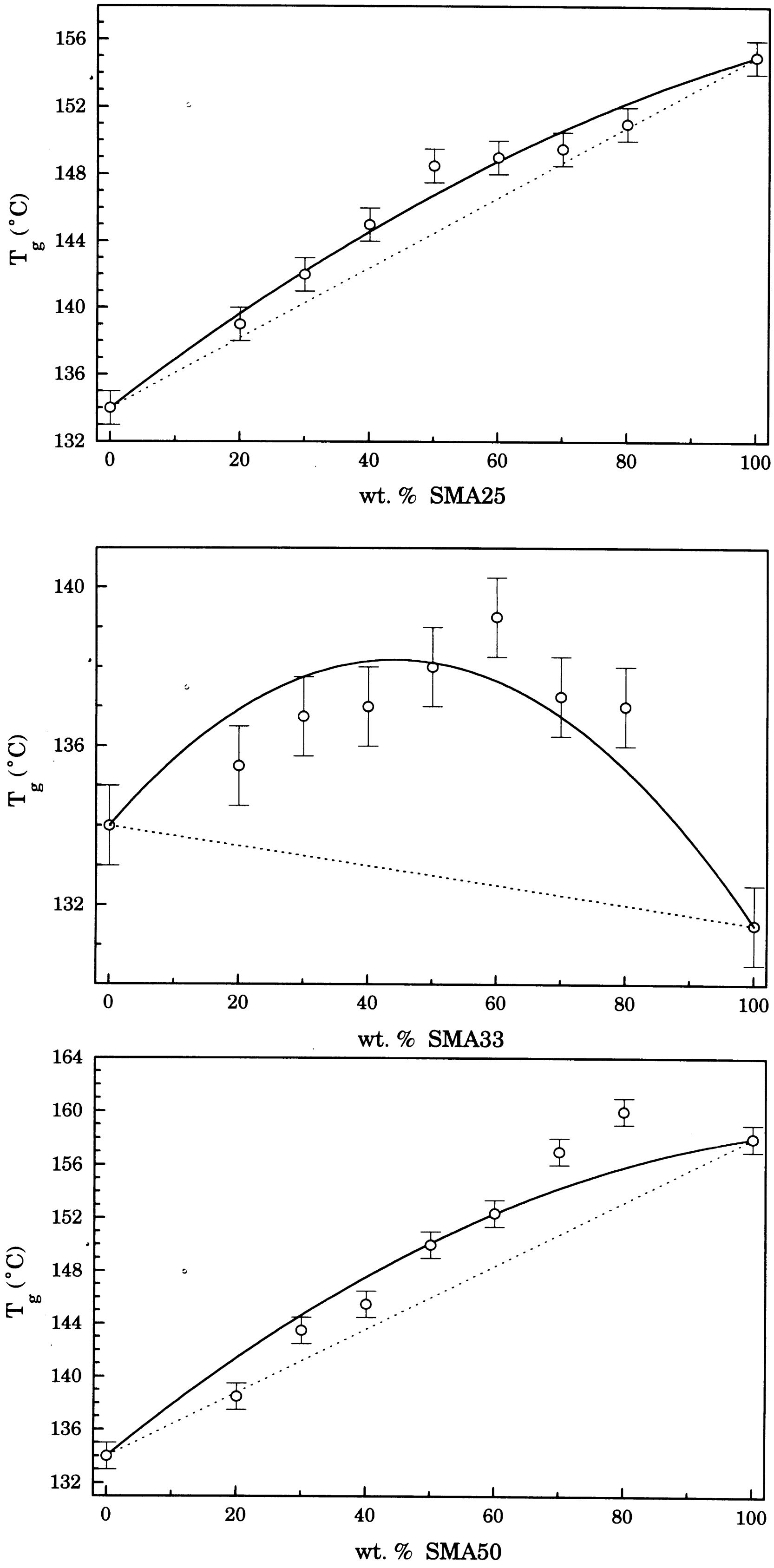


Fig. 1. T_g-composition diagram for the PGI/SMA blends.

in a Hakke Buchler Reomixer model 600, equipment with roller blades and a mixing head with a volumetric capacity of 69 cm^3. The temperature used was 200°C.

2.3. Characterization

Thermal studies were conducted on a Mettler FP82HT Hot Stage, controlled by a FP90 Central Processor unit according to an isothermal heating method described in our previous paper [3].

DSC thermograms were recorded using a fast-quenching. Shimadzu differential scanning calorimeter (model DSC-50Q) with indium as a calibration standard. About 8 mg from each sample were placed in sealed aluminium pans. The samples were initially heated under a nitrogen atmosphere up to 200°C in order to erase all previous thermal history and to remove final traces of solvent and subsequently they were immediately quenched. Each sample was rescanned at a heating rate of 10°C/min and from this second recording the glass transition temperatures were determined. The quenching scan cycle was repeated when necessary until repeatability of the DSC scan was achieved.

Samples for FTIR measurements were prepared by solution casting of polymer solutions in tetrahydrofuran directly onto KBr plates. After initial evaporation of solvent under ambient conditions, the samples were dried overnight at 90°C under vacuum in order to remove all traces of solvent. FTIR spectra were acquired in a Biorad FTS-45A FTIR Spectrometer. For each spectrum 64 consecutive scans with 2 cm^{-1} resolution were coadded. All spectral manipulations were done using the Win-IR$^{\text{TM}}$ software accompanying the instrument.

The morphology of the blends was studied using the technique of scanning electron microscopy (SEM). Samples were fractured at liquid nitrogen temperatures and the surfaces were sputtered with gold. Measurements were performed on a Jeol, model JSM-840A, scanning electron microscope.

2.4. Molecular modelling

Sketching and energy minimisation of the studied structures was performed using the Cerius$^{2\ \text{TM}}$ software package by Molecular Simulations Inc. The initially sketched structures were first roughly energy minimised and then subjected repeatedly to NVT molecular dynamics between 300 and 1000 K, in order to escape from any local energy minimum. The structures were finally minimised using the Minimister module. Quantum mechanical calculations upon the energy minimised structures were performed using the MOPAC 6.0 program. For the quantum mechanical calculations the PM3 Hamiltonian was used.

3. Results and discussion

The blends of PGI with SMA copolymers containing 25, 33 and 48.5 wt.% anhydride groups gave transparent films over the entire composition range. Transparency was also observed in previously studied PGI/SMA14 blends [14] which were found to be miscible. However, transparency is only an indication and not a definite proof of miscibility. Immiscible polymer can also give transparent films when the refractive indices of the two polymers are very similar. On the contrary, blends of SMA8 appeared cloudy with large droplets of varying size being dispersed within the main matrix. The large size of the droplets suggests a grossly immiscible system. This was also supported by the DSC study in which two glass transitions were recorded in all the composition range.

However, one must take into consideration that the solvent can sometimes interfere with the mixing process giving a two-phase system even when the two polymers are miscible, especially in the case of weakly interacting polymer pairs. This is the well-known $\Delta\chi$ effect [15] which occurs when the solvent is much more selective for one of the two polymers. In fact, we switched from acetone used in our previous study of the PGI/SMA14 system [14] to tetrahydrofuran in order to ensure a good solvent selectivity for SMA8. As PS is insoluble in acetone, the latter might be a poor solvent for SMA copolymers with a low MA content. In contrast, tetrahydrofuran is a good solvent for PS and this applies for SMA copolymers as well. This practice, however, does not ensure that the solvent does not interfere with the mixing process, as it is still possible that a wide difference in solvent selectivity for the two polymers exists. In order to avoid any solvent interference, we also performed melt mixing of SMA8 and PGI. The melt mixed blends also appeared two-phased, indicating that the immiscibility was not the result of a solvent effect.

DSC measurements confirmed the miscibility of PGI with SMA25, SMA33 and SMA50. All the aforementioned blends showed a single glass transition temperature (T_g) which was composition dependent and was situated between those of the pure components. This behaviour is typical of miscible polymer blends [16]. The T_g-composition diagrams for the miscible PGI/SMA blends are given in Fig. 1.

It is worth observing that the T_g of SMA33 is smaller than that of SMA25. According to Hall et al. increasing the MA content by 1 wt.% causes a 2°C increase in the observed T_g of SMA copolymers [17]. Thus SMA33 was expected to have a T_g higher than that of SMA25, being close to 160°C instead of 131°C which is the experimentally observed glass transition temperature. This abnormally low value of T_g for the SMA33 must be attributed to the very low molecular weight of the particular SMA33 copolymer used which was only 1700.

For the correlation of the T_g-composition data we used the well-known Kwei formula [18].

$$T_g^{\text{blend}} = \frac{w_1 T_g^1 + k w_2 T_g^2}{w_1 + k w_2} + q w_1 w_2, \qquad (2)$$

where w_i and T_g^i are the weight fractions and glass transition

Table 2
Values of the q parameter (Eq. (2)) for PGI/SMA miscible blends

Blend	q
PGI/SNA25	9.1
PGI/SMA33	21.3
PGI/SMA50	16.5

temperatures of the two polymers, respectively, and k, q are adjustable empirical parameters. In the fitting process, we set $k = 1$ and kept it constant, letting only q to vary as suggested by Kwei. In this case, the parameter q is regarded as a measure of the strength of the intermolecular interactions. The resulting q values for the blends are given in Table 2.

Fitting curves are given as solid lines in the diagrams, whereas dotted lines represent the ‘‘ideal’’ (arithmetic mean) behaviour. The fit is generally satisfactory, considering the simplicity and the semiempirical character of the method. A recently developed method based on Lattice–Fluid theory has a more firm thermodynamic basis and is expected to give better results [19]. Unfortunately, the scaling constants (T^*, P^*, ρ^*) necessary for the application of this method are not available for PGI and the SMA copolymers.

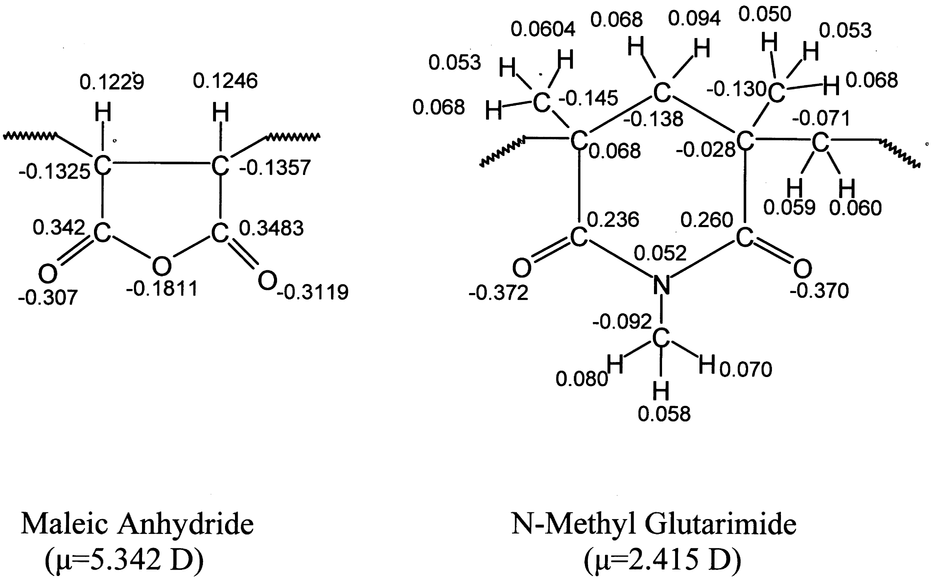
All the blends show positive deviations from the ideal (linear) behaviour as is reflected in the relatively high values of q. The deviations from linearity (and thus the interaction strength) generally increase with increasing content of MA in the SMA copolymer, as reflected in the q values. A minor upset in the trend is the rather high value of q for the SMA33 blends. However, we must take into account that this particular polymer has a very low molecular weight and as a result shows a relatively low glass transition temperature, as already mentioned, closer to that of PGI.

Positive deviations from linearity are typical for systems where strong specific interactions, usually hydrogen bonds develop between the components [20,21]. These interactions are orientation dependent and act as virtual crosslinks, increasing chain stiffness and causing an increase in T_g [18,22]. In the already mentioned blends of PGIs with SAN, PVC and PC negative deviations from linearity appear, which, in part, is an indication that in these systems no strong interactions develop between the components. Miscibility in these systems was explained solely on grounds of the already mentioned ‘‘repulsion effect’’.

Hydrogen bonding can have a profound effect upon polymer miscibility. This effect, however, is not always positive (favourable). In previously studied blends of PGIs with SAN and PVC, imidized acrylics containing acid functionality showed immiscibility or much reduced miscibility compared to those which did not contain acidic groups [12]. The detrimental effect of acid moieties upon miscibility was attributed to the large energy needed to break up hydrogen bonding interactions between the carboxyl groups. In our case the two polymers theoretically lack any hydrogen donors and thus, the formation of hydrogen bonds is not possible. Of course it is possible that accidental hydrolysis of MA groups by air moisture may produce carboxylic groups capable of hydrogen bonding. However, an FTIR study of the SMA copolymers did not show any signs of hydrolysis as –COOH characteristic frequencies were absent both in the hydroxyl and in the carbonyl regions.

Besides hydrogen bonds, polar interactions between strong dipoles are also considered to be specific and orientation dependent. The attractive component of the potential energy in this case is given by

$$E(d) = -\frac{\mu_1^2\mu_2^2}{d^3} f(\theta, \phi) \tag{3}$$



Maleic Anhydride
(μ=5.342 D)

N-Methyl Glutarimide
(μ=2.415 D)

Fig. 2. Computed charge distribution and dipole moments for the MA and *N*-methyl glutarimide units.

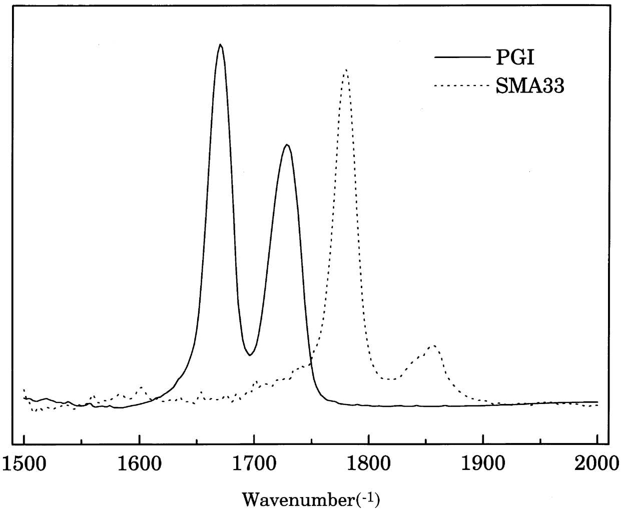


Fig. 3. Carbonyl region spectra of PGI and SMA33.

where $f(\theta,\phi)$ is a geometric function depending on the relative orientation of the two molecules (is equal to 1 for parallely aligned dipoles), μ_1 and μ_2 are the dipole moments of the two molecules and d is the distance between the dipoles. It is noteworthy to observe that this energy has a d^3 dependence, whereas dispersion (London) and weak polar forces show a d^6 dependence.

In our case the imide group of PGI and the anhydride group of MA units in SMA are highly polar and thus PGI and MA units are expected to be strong dipoles. In order to have a view of the charge distribution within the polymer units we resorted to quantum mechanical calculations upon low molecular weight analogues. For the simulation of the MA unit a styrene–MA–styrene trimer was used. This compound is thought to adequately represent the environment of the MA segment, as in SMA copolymers, because of the strong alternating character of SMA copolymerization, almost all of the MA segments are placed between styrene units even in the case of SMA50. For the simulation of the *N*-methyl glutarimide unit, a PGI trimer was used. Although HT 510 is actually a copolymer containing also methyl methacrylate units, the high imidization degree (71%) means that the aforementioned trimer is the most abundant within the HT 510 macromolecules. The point charges of the central MA and *N*-methyl glutarimide, as calculated by MOPAC 6.0 are shown in Fig. 2, along with the respective dipole moments (based on these charges only). As can be seen, both molecules are polarised mainly because of the presence of electron withdrawing oxygen atoms. Especially in the MA unit, all negative charges are located in the anhydride unit at the lower part of the ring. This highly asymmetric placement of positive and negative charges gives rise to a high dipole moment (5.342 d). In the glutarimide unit, the placement is less asymmetric and thus, the respective dipole moment is lower (2.415 d). At this point it must be emphasised that the calculated charges are only approximate as in the real polymer they depend also upon the conformation of the molecule and on the presence of segments beyond the adjacent ones. However, they can still give a reasonable (at least qualitative) view about the true state of the units in the polymers.

Another fact confirming the presence of strong interactions in our blends is that all miscible blends studied do not show phase separation up to 300°C. Blends at this high temperature developed a deep brown colour which is a sign of extensive degradation. TGA studies have shown that the thermal stability limit for the SMA copolymers lies around this temperature. As is well known, at elevated temperatures the disruption of specific interactions by the thermal motion makes a blend unstable giving rise to a LCST behaviour. Indeed in the case of PGI/SMA14 that we studied previously [14], a LCST-type phase behaviour was found with an LCST equal to 246°C. Owing to the relatively low content of SMA14 in MA in this system, the Ma–glutarimide interactions are expected to be sparse and a less effective stabilisation of the system occurs. However, the LCST is still quite high, close to the thermal stability limit of SMA copolymers. For the SMA25, SMA33 and SMA50 copolymers, which are richer in MA, the interactions are more abundant and a greater stabilisation of the system occurs. This raises the miscibility limits to temperatures higher than the degradation point. On the contrary, in the SMA8 blends the interactions are sparser and not sufficient to ensure micibility at ambient conditions. Of course, one may not overlook the fact that the molecular weight of SMA8 is significantly larger than that of the other SMA copolymers. It is a well established fact that increasing the molecular weight causes a decrease in the miscibility of the system as combinatorial entropy is diminished. In similar blends of PGIs with SAN copolymers it has been shown that for two PGIs with similar degrees of imidization, the one with the higher molecular weight gave lower LCSTs whereas the one with the lower molecular weight gave consistently higher LCSTs which in some cases were too high to measure [12]. It is generally difficult to assess to what extent the molecular weight affects miscibility in our case. It must be noted however that the SMA 14 (Dylark 332) copolymer has a molecular weight ($M_n = 9\ 000$, $M_w = 18\ 000$) very similar to that of SMA8, but it shows miscibility up to very high temperatures.

FTIR spectroscopy has proven to be a valuable method in the detection and study of miscibility in polymer blends and, especially, of the interactions developing between the blend components. In this case, changes in absorbance frequencies and/or intensities of the interacting groups are expected. In our case most of the interest is focused upon imide and anhydride carbonyls which are the polar units and are expected to be capable of interacting. In SMA copolymers, the vibrational coupling between the two cabonyls gives rise to two stretching vibrations, one weak antisymmetric vibration peak and one strong symmetric vibration peak centred

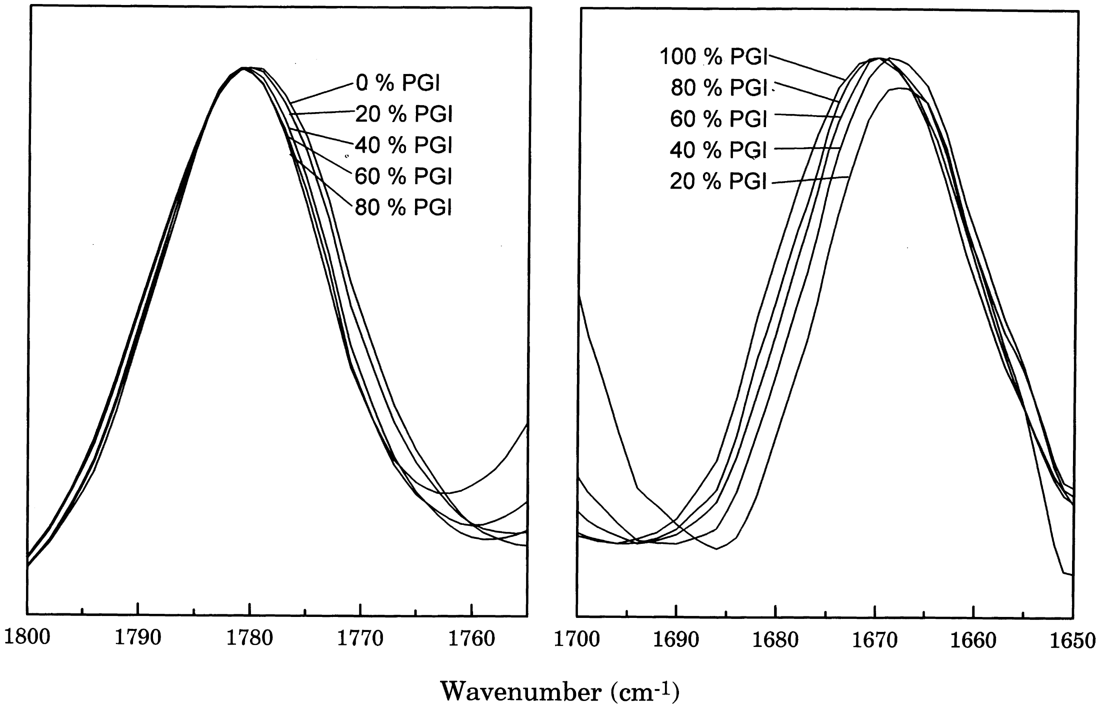


Fig. 4. Carbonyl region FTIR spectra of PGI–SMA50.

around 1856 and 1780 cm^{-1}, respectively, as shown in Fig. 3.

A similar coupling in the imide carbonyls of PGI creates two vibrations at 1728 and 1670 cm^{-1}, respectively. As can be seen, there is a partial overlap of the 1780 and 1728 cm^{-1} peaks of the SMA and PGI peaks, respectively. The 1728 cm^{-1} peak also contains a significant contribution from the PMMA unit of the copolymer which absorb at around 1730 cm^{-1}. This makes this peak inappropriate for analysis of either PGI or PMMA unit interactions with SMA. On the contrary, the 1670 cm^{-1} peak of PGI is free from any contribution. For the SMA copolymers, the 1780 cm^{-1} band, in spite of its partial overlap, is preferred for study as the peak at 1856 cm^{-1} is weak and asymmetric.

Fig. 4 shows the FTIR spectra in two regions of the carbonyl area for various PGI–SMA5 blends. The blends of PGI with SMA25 and SMA33 show similar frequency shifts.

A gradual shift of the 1670.5 cm^{-1}, imide peak towards lower frequencies is observed for increasing SMA50 content in the blend. Thus, for a PGI–SMA 50 20 : 80 blend the respective frequency is 1668 cm^{-1}. As SMA50 does not absorb in this region, this shift to lower frequencies indicates a gradual weakening of the imide carbonyl bond. This weakening comes possibly as a result of its interaction with SMA50 which leads to a redistribution of the charges within the molecules. The band at 1780 cm^{-1}, attributed to anhydride carbonyl stretching, shows a similar shift but towards higher frequencies. A similar shift of the anhydride carbonyl stretching has been found in SMA–SAN blends, but it was not definitely assigned to specific interactions [23]. Shifts were also detected in mixtures of low molecular weight analogues [24]. All these reported shifts however were towards lower frequencies whereas in our case a shift to higher frequencies occurs. Such shifts to higher frequencies have been reported by Jo et al. in poly (styrene-co-acrylic acid) blends with PMMA [25]. Generally, in this case two alternative explanations for this behaviour can be given.

The first and most obvious one is that a donor–acceptor interaction develops between the imide and anhydride carbonyls, respectively. Similar interactions have been invoked to explain frequency shifts in mixtures of polycarbonate with dioxane and tetrahydrofuran [26]. In these mixtures, it was speculated that a lone pair of electrons from the oxygen atom of the solvents is donated to the electron poor carbon of the polycarbonate carbonyl, leading to a strengthening of this bond and to shift to higher IR absorbance frequency. In the case of an analogous carbonyl–carbonyl interaction, Kamide [27] has shown using ^{1}H and ^{13}C-NMR measurements that, in order for a carbonyl to act as a donor it must be attached to a polar atom such as S or N. indeed, in our case the imide carbonyls of PGI are bonded to nitrogen atoms and therefore are able to act as electron donors. The already discussed shift of the PGI imide carbonyl absorbance to lower frequencies further substantiate our assumption.

A second explanation can be given if we assume that in the case of compounds containing polar groups such as carbonyls, a significant amount of dipole–dipole

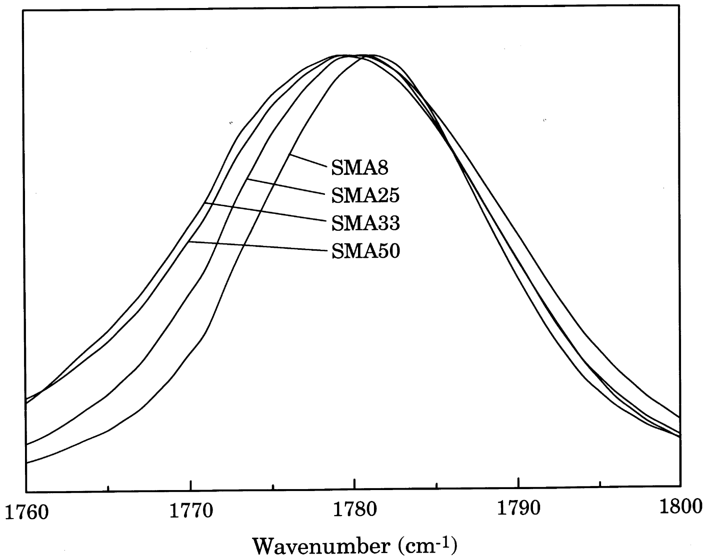


Fig. 5. Anhydride carbonyl region spectra of the SMA copolymers.

interactions develop when the compound is in the pure state. Thus, it can be assumed that two distinct populations of carbonyls exist, namely ''free'' and ''interacting'' (associated). These populations absorb at very similar, but still different, frequencies, with the interacting carbonyls absorbing at lower wavenumbers. The exact position of the carbonyl peak depends on the relative amounts between these two populations. Upon dilution of the compound with an inert component a disruption of interactions occurs and the population of free carbonyls increases. Unfortunately in the case of polymer blends this dilution is not easily carried out, as in the absence of interactions most polymer pairs are immiscible. An alternative approach is to use low molecular weight analogues of the polymers as suggested by Jo et al [25]. Using low molecular weight analogues of PS and PMMA, they showed that indeed, upon diluting the PMMA analogue with the inter-PS analogue a well defined 5 cm^{-1} shift of the carbonyl peak towards higher frequencies was observed. Fortunately, in our case such a procedure is not necessary; the styrene units in the SMA copolymers already act as an ''internal'' diluent. If the previous assumption is correct, then a monotonic increase of maleic carbonyl absorbance frequency should be observed on going from SMA50 to SMA8. This is indeed the case, as shown in Fig. 5.

An upset in the trend is observed for the SMA33 copolymer which absorbs at a slightly lower frequency than expected. The origin of this behaviour is unknown,

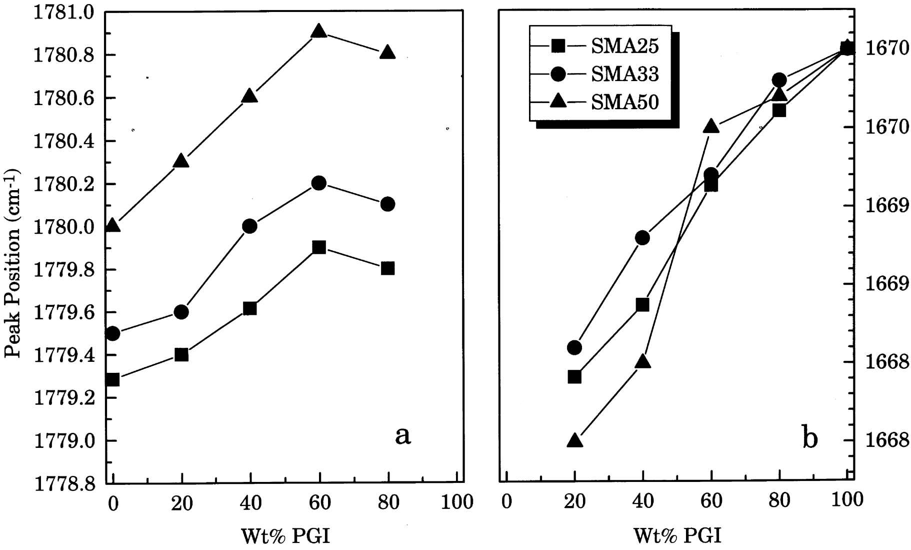


Fig. 6. Peak positions of: (a) anhydride; and (b) imide carbonyl as a function of blend composition.

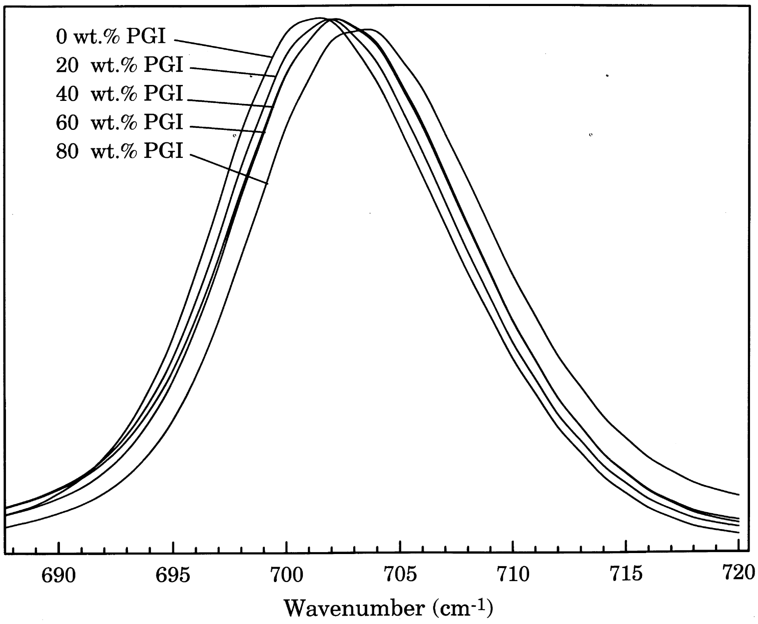


Fig. 7. FTIR spectra of SMA33/PGI blends in the aromatic C–H out of plane vibration region.

but perhaps it is related to the low molecular weight of this sample. This may permit a better chain packing which leads to an increased degree of interactions of this particular polymer. Irrespective of this, the general trend suggests that indeed, the MA carbonyls self-interact to a certain degree and the disruption of these interactions by dilution should lead to an increase in absorbance frequency.

Upon blending with PGI the picture becomes more complicated as three phenomena take place simultaneously, namely:

(a) Disruption of self-interacting SMA carbonyls through simple dilution and production of ‘free’ carbonyls.
(b) Disruption of self-interacting SMA carbonyls and a concurrent formation of a donor–acceptor type ‘complex’ between an imide and an anhydride carbonyl when the two groups are in appropriate spatial orientation.
(c) Formation of the same complex between a previously ‘free’ anhydride carbonyl and an imide carbonyl of PGI.

Irrespective of the relative extent to which these three phenomena occur, the net result is the formation of products which all absorb at a higher frequency than the self-interacting anhydride carbonyls.

The peak position of the studied groups (amide and imide) as a function of composition in the case of miscible blends is shown in Fig. 6. It is evident that the frequency shifts observed are increasing with increasing amounts of the second polymer. These shifts are more intense in the case of the amide carbonyl peaks. For blends of the same composition, the imide peak shift generally increases in the order SMA50 > SMA33 > SMA25. This is expected as for higher amounts of MA groups in the SMA copolymer, the possibilities for interactions with PGI increase and a greater number of ‘‘interacting’’’’ imide groups is produced (Fig. 7). A similar trend in the case of the anhydride peak is more difficult to establish, as the shifts observed are much smaller.

In previously studied SMA14/PGI blends we also detected some shift in the 700 cm^{-1} band of styrene which are also observed in the current blends as well. This shift is observed in the current blends as well. A typical behaviour is shown in Fig. 7. The peak shift was regarded as a clue of possible interactions between the phenyl ring and the glutarimide units. Given the observed immiscibility of polystyrene with PGI, we postulated that the styrene moieties are in a different environment within the SMA copolymers, due to their adjacency to the strong electron withdrawing maleic anhydride units. The changes in electronic density of the phenyl ring may in turn enhance the ability for complex formation, possibly of n-π type with the glutarimide and methyl methacrylate units.

In a recent paper, Feng et al. studied the SMA50/PMMA system [28]. They showed using CPMAS ^{13}C NMR spectroscopy that copolymerization of styrene with maleic anhydride results in a marked change of the electron density in the styrene monomer unit compared to pure PS homopolymer. This was reflected by changes in the chemical shifts (both to higher and lower fields) of the aromatic and main chain carbons. Furthermore, significant changes in the electron environment of the SMA phenyl groups upon blending with PMMA were detected using the same technique. A study of the T_1 relaxation times showed an increase in the motion rate of the phenyl group and a concurrent decrease in the motion rate of the carbonyl group compared to the pure polymers. This unambiguously indicates a strong

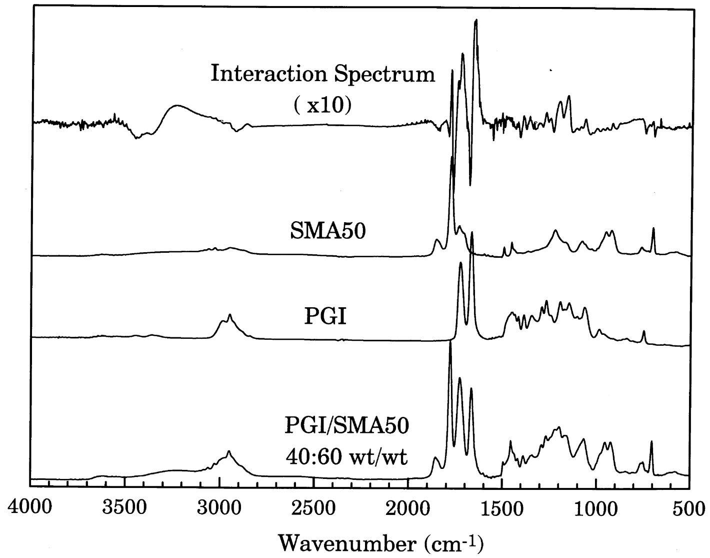


Fig. 8. Interaction spectrum for 40 : 60 PGI/SMA50 blend.

interaction between the phenyl ring and the PMMA carbonyl, which was further corroborated by the positive deviations observed in the T_g-composition curves of the SMA/PMMA blends and the frequency shifts observed in the IR spectra of the blends compared to those of the pure components. Most interestingly, both the phenyl 700 cm^{-1} band and the anhydride 1780 cm^{-1} band also moved to higher frequencies upon blending, which is the case with our blends as well. The authors ascribed this shift to the disruption of electron transfer complexes formed between the styrene and maleic anhydride comonomers in SMA and a concurrent partial formation of a similar complex between phenyl and carbonyl groups. In fact, the authors concluded that it is this interaction, instead of the intermolecular repulsion force within the SMA copolymer, that makes the SMA/PMMA system miscible. In our case both the methyl methacrylate and glutarimide units within the PGI copolymer are capable of forming such complexes. Unfortunately the 1730 cm^{-1} band of PMMA units is as already mentioned badly overlapped by the 1728 cm^{-1} asymmetric vibration band of anhydride group and thus such an interaction cannot be unequivocally established. On the other hand, the shift of the imide band to lower frequencies can be attributed to a certain extent to interactions with phenyl groups.

The interaction spectra of the blends can give a more general view of spectral changes taking place upon

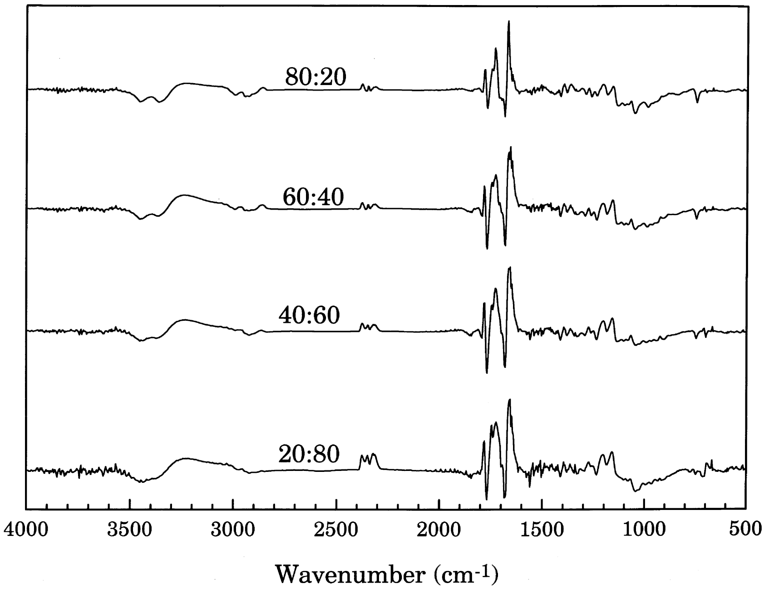


Fig. 9. Interaction spectra for various PGI/SMA50 blends.

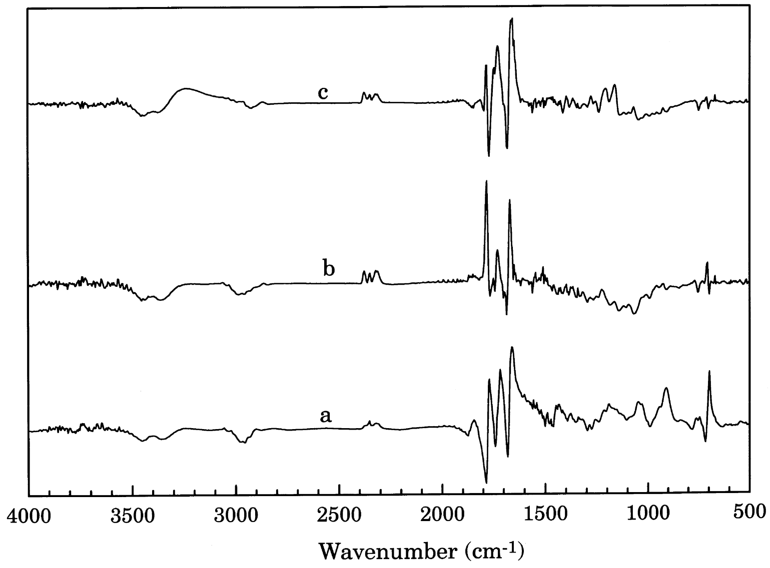


Fig. 10. Interaction spectra of 40 : 60 wt./wt. blends of: PGI with (a) SMA25 (b) SMA 33 and (c) SMA50.

mixing [29]. A typical interaction spectrum along with the spectra of pure constituents and their blend is given in Fig. 8.

Both positive and negative peaks appear in the interaction spectra, with changes located mainly in the carbonyl region of the spectra. The peaks in this region are of the derivative type (a positive lobe immediately followed by a negative one or vice versa), indicating that spectral changes involve mainly peak shifts rather than changes in intensity. A broad derivative type peak also appears between 3600–3000 cm^{-1}. In our previous publication [14], the weak absorbances appearing in this region were attributed to carbonyl overtone stretching bands. In this sense, these bands are also expected to give shifts during mixing and, thus, a derivative-type peak appears in this region. The interaction spectrum is fairly consistent throughout the composition range as well as the between SMA copolymers (Figs. 9 and 10).

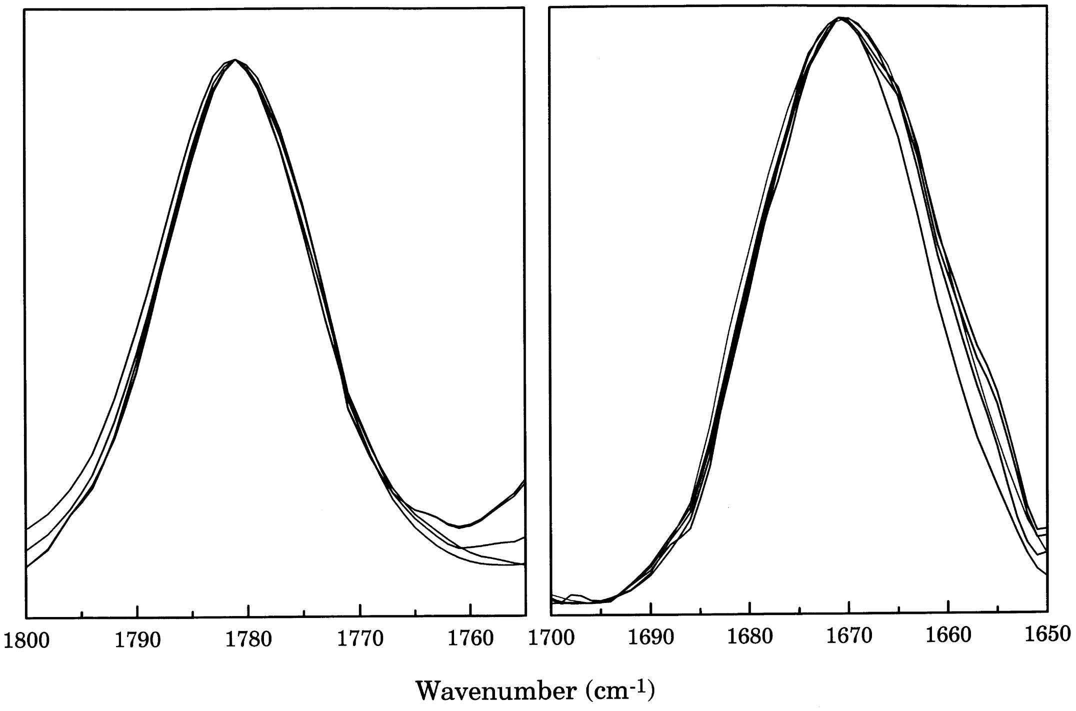


Fig. 11. Carbonyl region FTIR spectra of PGI/SMAR8 blends.

In the respective carbonyl region spectra for the PGI/SMA8 blends (Fig. 11) no significant shifts nor changes in peak shape are observed. This is not unexpected, as in phase separated blends each phase consists essentially of pure polymer with only minor amounts of the other polymer dissolved in it. As a result, the overall spectrum is expected to be the sum within experimental error of the pure components spectra [30].

From the aforementioned facts it becomes clear that interactions developing between PGI and SMA (Figs. 8–10) is a major factor leading to miscibility. However, as already mentioned in Section 1, the intramolecular repulsion effect is another cause of miscibility in many systems. According to the binary interaction model, [3], the net Flory–Huggins interaction parameter for the SMA/PGI system (Fig. 11) is given by:

$$\begin{aligned}\chi_{\text{tot}} = {} & (1-\varphi_{\text{GL}})\varphi_{\text{MA}}\chi_{\text{MMA/MA}} + (1-\varphi_{\text{GL}}) \\ & \times(1-\varphi_{\text{MA}})\chi_{\text{MMA/ST}} + \varphi_{\text{GL}}\varphi_{\text{MA}}\chi_{\text{GL/MA}} \\ & + \varphi_{\text{GL}}(1-\varphi_{\text{MA}})\chi_{\text{GL/ST}} - (1-\varphi_{\text{GL}})\varphi_{\text{GL}}\chi_{\text{GL/MMA}} \\ & -(1-\varphi_{\text{MA}})\varphi_{\text{MA}}\chi_{\text{ST/MA}}, \qquad (4)\end{aligned}$$

where GL, MMA, MA, and ST stand for glutarimide, methyl methacryate, MA and styrene units, respectively, ϑ_1 is the volume fraction of unit i in the copolymer and $\chi_{i/j}$ is the respective binary interaction parameter between units i and j.

Even though the formula is quite complicated, what becomes apparent is that a sufficiently large positive $\chi_{i/j}$ parameter in the last two terms can render the total interaction parameter negative, even the positive $\chi_{i/j}$ parameter in the last two terms can render the total interaction parameter negative, even though all of the individual binary interaction parameters are positive. The last two terms represent the intramolecular interactions developing in the two respective copolymers.

Indeed, in the SMA copolymer a high repulsive interaction develops between styrene and MA segments owing to the large dissimilarity in their polar nature. Thus, it is not surprising that the χ value for this pair is 034 [31]. This is quite a high value compared for example with that of the styrene–methyl methacrylate pair which is 0.01. Even for styrene–acrylonitrile copolymer which also shows a highly repulsive interaction this value is only 0.12. As a result of this, SMA shows miscibility with a variety of polymers such as styrene–acrylonitrile copolymers [23–24] and methacrylates [32] over a certain composition range. Miscibility behaviour in these systems has been explained quite satisfactorily in terms of the binary interaction model. The glutarimide–methyl methacrylate interaction has also been reported to be repulsive [12] (i.e. $\chi_{\text{GL–MMA}}$ has a positive value), but no value for the interaction parameter was reported.

In our system, given the results of the FTIR study which indicate the presence of interactions, it is not unjustified to assume that the binary interaction parameters $\chi_{\text{GL–MA}}$ and $\chi_{\text{GL–ST}}$ are also negative. This is another favourable contribution to the χ_{tot}parameter. The aforementioned favourable contributions are partially counterbalanced by the large positive value of the $\chi_{\text{MA–MMA}}$ parameter which is about 0.20 [27]. Taking into account the composition of the PGI copolymer and by replacing the appropriate χ values (wherever available) in Eq. (3) we finally obtain:

$$\begin{aligned}\chi_{\text{tot}} = {} & 0.058\varphi_{\text{MA}} + 0.71\varphi_{\text{MA}}\chi_{\text{GL/MA}} + 0.71(1-\varphi_{\text{MA}})\chi_{\text{GL/ST}} \\ & -0.206\chi_{\text{MMA/GL}} - 0.34\varphi_{\text{MA}}(1-\varphi_{\text{MA}}). \qquad (5)\end{aligned}$$

In the previous formula the term involving $\chi_{\text{MMA–ST}}$ was omitted, as it is very small. Unfortunately as the exact values are not known, we cannot have any quantitative information about the behaviour of χ_{tot} as a function of the SMA copolymer composition. This would permit the evaluation of the optimum MA content which maximises χ_{tot}. The determination of the individual χ parameters is usually done by fitting the experimental miscibility data of a series of copolymer blends to the Flory–Huggins theory predictions [33]. This procedure however requires an extensive series of both copolymers with comparable molecular weights which in our case is not available (only one PGI copolymer was used). In fact Paul et al. who studied PGI–SAN blends with a series of both copolymers, considered that the range of copolymers was not adequate to obtain reliable results [12].

In view of the lack of any quantitative information we can only make qualitative predictions about the variation of χ_{tot} with SMA copolymer composition. One can observe in Eq. (5) that an increase in MA content of the SMA copolymer simultaneously increases both the favourable second and fifth terms and the unfavourable first term. The fourth term does not depend upon SMA composition and, thus, it is a constant favourable contribution to χ_{tot}. The magnitude, even the sign of the $\chi_{\text{GL–ST}}$ parameter is not known. Even if, however, it is unfavourable it is obvious that the contribution of the third term diminishes with increasing MA content. One must also observe that in low to moderate MA content, the magnitude of the first term is smaller than that of the fifth term. The two terms become equal at $\varphi_{\text{MA}} = 0.82$. However in practice, owing to the already mentioned strong alternating character of the SMA anhydride radical copolymerization, the preparation of SMA copolymers with a MA content greater than 50 mol.% is infeasible [34].

Therefore, within the attainable SMA compositions, the fifth term will always overwhelm the first term. Most interestingly, the fifth term is at a maximum at $\varphi_{\text{MA}} = 0.5$, as the quadratic $\varphi_{\text{MA}}(1-\varphi_{\text{MA}})$ coefficient is then maximised. Thus within the frame of the binary interaction model, SMA copolymers with a content close to 50 mol.% are expected to have a more negative total interaction parameter with PGI and thus a greater miscibility.

A similar combination of specific interaction between ethylene oxide and acrylic acid segments and intramolecular repulsive force in styrene–acrylic acid copolymers has been suggested to explain the miscibility in the poly(ethylene oxide)–poly(styrene–co-acrylic acid) [35] as well as in the poly (4-hydroxystyrene)–poly(*n*-butyl acrylate–co-tert-butyl acrylate) and poly(styrene-co-4-hydroxy-styrene)/poly(tert-butyl acrylate) [36] blends. On the contrary, in the previously mentioned SMA–SAN and SMA–methacrylates blends where interactions are absent or are very weak, miscibility is observed only within a limited composition range.

4. Conclusions

In the present study, blends of PGI with a series of SMA copolymers containing 8, 25, 33 and 50 wt.% MA were prepared and studied. The last three copolymers showed complete miscibility with PGI over the entire composition range. On the contrary SMA8 was immiscible with PGI, irrespective of the blend-preparation method used.

The positive deviations in the T_g-composition data and the peak shifts in the FTIR spectra of the blends compared to those of the pure components, indicate the presence of significant specific interactions between the two polymers and especially between MA and *N*-methyl glutarimide segments. These interactions are possibly of dipole–dipole type as both these units are strong dipolars as shown by quantum mechanical calculations. Interactions between the phenyl ring with both comonomers in the PGI are also possible as indicated by FTIR measurements.

The strong intramolecular styrene–MA repulsion is another factor contributing to miscibility. Application of the binary interaction model has shown that copolymers containing almost equimolar amounts of styrene and MA (which are also the most easy to prepare) are expected to show the greatest miscibility. This assumption was not possible to be verified, as all miscible blends studied were stable up to the degradation point of SMA copolymers. Perhaps the use of higher molecular weight polymers may lower the separation temperatures and allow the testing of this assumption.

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