Estimation of polymer compatibility from molecular mechanics calculations

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A new computational method is presented for the rapid estimation of polymer miscibility. This algorithm (coined FLEXIBLEND) makes use of molecular mechanics calculations on a pair of polymer segments in order to estimate heats of mixing. Specific interactions between polymer segments of different types are accounted for, as are effects due to local chain flexibility. The many assumptions and approximations of such two-segment approaches are discussed, and the new algorithm is used to investigate how miscibility predictions are influenced by segment size and other parameters of the model. Predictions of polymer miscibility in agreement with experiment are presented for miscible and immiscible blends, and detailed error analysis indicates the statistical significance of the FLEXIBLEND results. Balancing the recognized limitations with the computational speed of the method, it is concluded that the new algorithm should be useful in initial screening of potential blend candidates, and in giving a rough guide as to how changes in chemical structure might alter phase behaviour. The method also provides useful insight as to why two polymers mix or phase-separate. Finally, the FLEXIBLEND results are compared with those of a more rigorous, but computationally more expensive, amorphous cell method for calculating heats of mixing.

(Keywords: polymer miscibility; computer modelling; molecular mechanics)

INTRODUCTION

Polymer chemists and theoreticians alike have devoted much attention to the subject of phase separation of polymer solutions and blends. In the 1940s, Scott[1] and Tompa[2] applied the classical lattice model of Flory[3] and Huggins[4] to polymer mixtures, an approach that has now been further developed and is widely used[5]. Equation-of-state theories to describe lower critical solution temperature behaviour have also been presented[6], and Kleintjens and Königsveld have used a mean-field lattice-gas model for polymer fluids[7]. Whilst these theories provide very useful means for calculating polymer compatibility, they require data that must be obtained from experiment, such as the Flory–Huggins χ parameter. By contrast, the recently developed polymer reference interaction site model holds great promise for first-principles prediction of the phase behaviour of polymer blends and solutions[8,9].

Alongside the theoretically rigorous approaches mentioned above, polymer scientists have traditionally used a much simpler 'rule-of-thumb' technique for estimating miscibility. The method is based upon comparison of Hildebrand solubility parameters for the polymers of interest. Solubility parameters, which are related to cohesive energy density, may be obtained experimentally or using group additive methods[10]. If, for example, polymer A has a solubility parameter of similar magnitude to that of polymer B, this indicates that the strength of the interactions between segments of polymer A is similar to that between segments of polymer B. In the absence of specific interactions (such as hydrogen-bond formation) between A segments and B segments, this clearly makes mixing of segments energetically more favourable than in the case where the A–A interactions are much stronger than the B–B interactions. Thus, comparison of solubility parameters can be used as an approximate miscibility predictor.

Recently, Jacobson *et al.* have described how molecular modelling studies can give a rapid estimate of whether two polymers will form a miscible blend using a method that can account for specific interactions between polymer segments[11,12]. The theoretical foundation of their method relies upon the premise that miscibility is determined by thermodynamic factors alone, and furthermore that these thermodynamic factors are dominated by the energetics of local interactions between segments of the polymer chain[1,3,4,13]. In these original investigations, rigid high-performance polymers were studied, and effects due to local chain flexibility were neglected[11,12]. This two-segment approach to miscibility prediction is modified and extended here so that flexible polymers may also be studied.

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THEORETICAL BASIS OF THE TWO-SEGMENT APPROACH

A necessary condition for the miscibility of a mixture of two polymers is a negative free energy of mixing:

$$\Delta H_{\mathrm{mix}} - T\Delta S_{\mathrm{mix}} < 0 \qquad (1)$$

It has been proposed that entropic contributions to the free energy of mixing are small[14], so that to a first approximation we may ignore the $T\Delta S_{\mathrm{mix}}$ term in the above equation.

In the method of Jacobson *et al.*[11,12], computer models of a pair of segments of polymer chain (each containing about 200 atoms) are built and then 'docked' together using molecular mechanics techniques[15]. The net interaction energy of mixing (ΔE_{mix}) is computed as a good approximation to ΔH_{mix}, volume changes upon mixing being ignored. For example, in a study of the miscibility of polymers A and B, the interaction energies of AA, BB and AB pairs must be calculated (E_{AA}, E_{BB} and E_{AB} respectively). These interaction energies can be defined as the *decrease* in energy of the segment pair if all non-bonded interactions between the two segments are turned off. A negative interaction energy therefore denotes a favourable interaction between the two segments. Miscibility of the A/B blend is indicated by the relation:

$$\Delta E_{\mathrm{mix}} = E_{\mathrm{AB}} - \tfrac{1}{2}(E_{\mathrm{AA}} + E_{\mathrm{BB}}) < 0 \qquad (2)$$

which determines that it is energetically favourable to make two AB pairs from an AA pair and a BB pair.

There are several potential problems with the theoretical basis of such two-segment approaches to estimating miscibility. For example, there are non-combinatorial contributions to the entropy of mixing that may not be small, even for long polymer chains. Furthermore, packing between two polymer segments in a vacuum will only be a very approximate model for the way that polymer chains pack together in a real blend; this is perhaps particularly true for flexible polymers. The effects of temperature and concentration are also ignored. However, the two-segment approach has been found useful as a method for initial screening of likely miscible combinations of polymers[11,12], and some have even attempted to predict phase diagrams using it[16]. Given that the method is computationally fast, we aim to show that the two-segment model can be used in the manner of a 'rule-of-thumb' technique, somewhat more sophisticated than the solubility-parameter approach in that specific interactions between polymer segments can be accounted for in the E_{AB} term.

Aside from the potential problems with the theoretical basis, there are also practical problems with the two-segment approach. Calculation of the interaction energy of a pair of segments is complicated by the very large number of different possible geometries of the interacting pair. Jacobson *et al.* docked the two segments together using the fixed valence geometry molecular-mechanics technique[17], in which the conformation of each segment is held rigid during the docking procedure. This was shown to work well for polymers composed of rigid units[11,12], but is unlikely to be appropriate for determining interaction energies between flexible segments. The interaction energy between two segments of flexible polymers may be significantly decreased as the molecular geometries of the two segments change to enable the most favourable interaction; the chain segments can fold around each other to lower their interaction energy. We illustrate below that in such cases it is important to sample statistically the energetically accessible conformations of the two polymer segments, as well as their different relative orientations and positions.

THE 'FLEXIBLEND' ALGORITHM

A new methodology for estimating miscibility of flexible polymers using the two-segment approach is outlined below, and this procedure will be described hereafter as the FLEXIBLEND algorithm:

(1) A computer model of a short segment of polymer A is built, and a sample of energetically accessible conformations is generated using high-temperature molecular dynamics[18] or rotational-isomeric-state (RIS) Monte Carlo sampling[19]. These conformations are stored in an archive.

(2) Two A segments, with conformations randomly selected from the archive, are placed with their centres of mass coincident. One of the two segments is first randomly oriented in space, and then moved a fixed distance (R_{CM}) in a random direction. If the intermolecular energy of the resulting structure is below a specified threshold value (E_{max}) it is stored for later refinement. If the intermolecular energy exceeds E_{max}, the structure is discarded. This procedure is repeated until a specified number of *starting structures* is obtained, each containing one pair of segments.

(3) Each starting structure is relaxed by molecular-mechanics energy minimization, leading to a set of *refined structures*. The molecular geometries change during the energy minimization, allowing the two segments in the structure to fold around each other.

(4) After refinement, the interaction energy (i.e. non-bond intermolecular energy) for each refined structure is determined from analysis of the energy components[18]. Normalization yields an energy density, and E_{AA} is set equal to the average of these interaction energy densities over the full set of refined structures.

(5) Steps (1) to (4) are repeated using segments of polymer B of similar size to the A segments, and then for a pair consisting of one A segment and one B segment. Finally, the resulting interaction energy densities, E_{AA}, E_{BB} and E_{AB}, are substituted in equation (2) to estimate whether or not the A/B mixture will be miscible.

The interaction energy initially computed in step (4) must be normalized because its value depends upon the number of atoms—it is an energy per mole of structures. Normalization is achieved through division of the interaction energy by the volume of a mole of structures, giving an interaction energy density conveniently expressed in units of cal cm^{-3}. The volume of a mole of structures is calculated by dividing the molar mass of the pair of molecules in the structure by a density. For an AA pair, we use the density of the pure A polymer, whilst for an AB pair we take the density with inverse equal to the average of the inverse densities of the pure A and pure B polymers.

The FLEXIBLEND algorithm as outlined above leaves several parameters yet to be defined. Specifically these are the size of the polymer segments to use, the values of R_{CM} and E_{max}, and the details of the molecular-mechanics energy refinement procedure. The number of structures that must be generated in step (2) is determined by the requirement for statistical significance of the results, and careful error analysis is therefore a priority. All of these parameters will be considered in detail later.

THE AMORPHOUS CELL APPROACH

A second, more rigorous, method is also used below in the study of the poly(ethylene oxide)/polypropylene blend. This involves setting up computer models of the amorphous bulk polymers, A and B, and for the proposed A/B blend, using 'amorphous cell'[20] techniques. The cohesive energy of such an amorphous cell is defined as the *increase* in energy per mole of a material if all the intermolecular forces are eliminated. Note the difference in sign convention compared to the interaction energies defined above; a large positive cohesive energy indicates strongly attractive intermolecular interactions. The cohesive energy density (E_{CED}, cohesive energy per unit volume) is related to Hildebrand's solubility parameter, δ, through the equation:

$$\delta = (E_{\mathrm{CED}})^{1/2} \tag{3}$$

An estimate of the heat of mixing can be obtained in the following way. Several amorphous cells of the pure A polymer are first constructed and thoroughly equilbrated using molecular dynamics and molecular mechanics methods. The cohesive energy density of each cell is then calculated, and an average taken over all the cells. The same procedure is carried out for cells of the pure B polymer, and for cells containing a mixture of A and B chains. The heat of mixing can be estimated from the net change in cohesive energy density (using the equivalent of equation (2)). In this case, a positive value indicates exothermic mixing.

FORCEFIELD

Both the FLEXIBLEND algorithm and the amorphous cell approach require the use of a forcefield to describe how the energy changes as a function of intra- and intermolecular geometry. In this work, the 'cvff' forcefield is used[18]. In addition to describing how the energy of a molecule varies with bond stretching, angle bending and other internal coordinates, the forcefield determines the interactions between two molecules as a sum of atom-pair potentials describing van der Waals and Coulombic interactions:

$$E_{\mathrm{int}} = \sum_{ij} E_{ij} \tag{4}$$

where i is summed over atoms in the first molecule, and j over atoms in the second molecule. In the cvff forcefield, E_{ij} takes the form

$$E_{ij} = \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} + \frac{q_i q_j}{\varepsilon r_{ij}} \tag{5}$$

where A_{ij} and B_{ij} are determined from the forcefield parameters for atoms i and j; r_{ij} is the distance between the two atoms; q_i is the partial charge on atom i, assigned using a simple method of bond increments[18]; and ε is the dielectric constant. For all calculations presented here we use a relative permittivity of 1.

PARAMETERS OF THE 'FLEXIBLEND' ALGORITHM

As mentioned previously, the FLEXIBLEND algorithm has several adjustable parameters. Its usefulness therefore depends upon the sensitivity of its predictions to the values chosen for these parameters; clearly the algorithm will be useless if we can predict on the one hand miscibility and on the other immiscibility by changing the parameters within sensible bounds. The purpose of this section is to consider what these sensible bounds might be. Only general considerations are presented at this stage. More detailed analysis of the sensitivity of the FLEXIBLEND predictions to parameter changes is given later for specific polymer blends.

Effect of polymer segment length

We suggest that the length, L, of the polymer segment must satisfy the criterion $L \gg R_{\mathrm{CM}}$, so that the calculated interaction energies between two segments are dominated by backbone and side-chain atoms and not chain ends. However, L should not be too large. Consider two long chain segments randomly oriented with respect to each other; even when the centres of mass of the two chains are very close, there will be significant regions of each segment that are so far from the other segment that they do not feel its influence (unless the chains happen to be lined up roughly parallel to each other). The molecular-mechanics energy minimization alleviates this problem to a certain extent by folding the chains around each other, but this is inefficient for very long segments.

It is important that the A and B segments are of similar size, otherwise the E_{AB} energy may be estimated incorrectly. The reason is that if, for example, the A segment is much longer than the B segment, then the AB pair will contain large regions of the A segment that extend into a vacuum. These regions increase the volume of the pair, but contribute little to its cohesive energy. We shall return to this point later.

Effect of initial polymer segment conformation

Studies on pairs of polyethylene (PE) segments containing 11 backbone bonds were carried out in order to assess the effect of initial segment conformation upon the calculated interaction energy. Some 150 starting structures were generated, each containing a pair of polyethylene chain segments in the all-*trans* conformation. Use of the parameter values $R_{\mathrm{CM}} = 1.0$ Å and $E_{\max} = 10^8$ kcal mol^{-1} resulted in an acceptance ratio of 0.75 (i.e. 200 trial structures were built in order to generate 150 acceptable structures). The value of $E_{\max}$ was chosen to be quite large because there are likely to be significant atom overlaps in *any* starting structure generated. The molecular mechanics energy minimization very quickly puts each structure into a 'reasonable' conformation, but by using $E_{\max}$ we avoid submitting structures with very bad atom overlaps to this refinement process. Energy refinement of each starting structure was carried out until the maximum derivative of energy with respect to any atomic Cartesian coordinate dropped below 1 kcal mol^{-1} Å^{-1}. The average interaction energy from the 150 refined structures was then calculated as described above.

This procedure was repeated starting with a pair of polyethylene segments each in the 3/1 helical conformation, and then in each of five other conformations generated by RIS Monte Carlo sampling[19,21] at a temperature of

Table 1 The effect of initial segment conformation on the calculated interaction energy for polyethylene structures

Initial conformation	Interaction energy density (cal cm^{-3})	Standard error on the mean (cal cm^{-3})
All-*trans*	−10.91	0.15
3/1 helix	−12.37	0.10
Monte Carlo 1	−15.83	0.23
Monte Carlo 2	−13.55	0.05
Monte Carlo 3	−13.45	0.08
Monte Carlo 4	−13.50	0.08
Monte Carlo 5	−15.00	0.08

300 K. The resulting interaction energies are summarized in *Table 1*.

The standard error on the mean of the interaction energy density for each set of 150 structures is found to depend somewhat upon starting conformation. It can be seen that the variation in the average interaction energies reported in column 2 of *Table 1* is much greater than the estimated statistical error in each average interaction energy. We therefore conclude that it is necessary to generate starting structures using a representative set of polymer segment conformations rather than a single conformation. In the FLEXIBLEND algorithm, these sample conformations are generated in step (1) by high-temperature molecular dynamics or RIS Monte Carlo sampling.

It is worthwhile to consider exactly what we mean by a 'representative' set of polymer segment conformations. Ideally, the conformations should be representative of those found in the homopolymer melt. Such conformations might be selected from a suitable ensemble using a Boltzmann weighting factor appropriate for the temperature of interest. Whilst a sufficiently large ensemble of conformations generated using an RIS approach will have the correct configurational statistics, the segment conformations themselves will not be representative of those found in the melt (for example, RIS chains can self-intersect). Furthermore, the molecular mechanics refinement process itself alters the segment conformations, and thereby also the configurational statistics. We must therefore note that the FLEXIBLEND algorithm approximates that heats of mixing are not very sensitive to the fine details of polymer chain conformation at the scale of short segments. Later we show that statistically significant, reproducible predictions can be made from as few as 200 structures (certainly not enough to ensure accurate configurational statistics), indicating that this approximation is quite reasonable for our purposes.

Effect of molecular mechanics refinement strategy

Once the starting structures have been generated, they are refined by molecular mechanics energy minimization. Complete energy minimization would alter the conformations and relative positions and orientations of the two molecules until they lie at a local minimum in the potential-energy surface described by the forcefield[18]. (The polymer chains in a real blend have thermal kinetic energy, so that a minimum in the potential-energy surface may not be an appropriate place to measure the segment–segment interaction energy. However, we will show that the results are not sensitive to the details of the refinement strategy.) In practice, complete energy minimization is prohibitively time-consuming for use in the FLEXIBLEND algorithm. Instead, we carry out energy minimization until the maximum derivative of total energy with respect to any of the atomic coordinates falls below a predefined minimum value. The total energy contains contributions from internal degrees of freedom (e.g. bond stretching, valence angle bending, etc.) in addition to the intermolecular non-bond (interaction) energy. We therefore seek a maximum derivative criterion for the total energy which balances the requirement for a quick result with the need to ensure that the non-bond interaction energy comes within reasonable range of the limiting value it would obtain upon complete convergence.

In order to estimate a suitable maximum derivative criterion, the FLEXIBLEND algorithm was used to generate 200 polyethylene starting structures, each containing a pair of 11-backbone-bond polyethylene segments. Initial segment conformations were randomly selected from an ensemble generated by RIS Monte Carlo sampling at 300 K. The 200 initial structures were then refined using various maximum derivative criteria. *Figure 1* plots the average interaction energy against the inverse of the maximum derivative criterion for the set of 200 PE structures. When the maximum derivtive of total energy falls below about 1 kcal mol^{-1} Å^{-1} the interaction energy converges close to its limiting value, and we therefore suggest this as a working value for the maximum derivative criterion in the refinement procedure of the FLEXIBLEND algorithm. The sensitivity of FLEXIBLEND predictions to the maximum derivative criterion is further investigated below.

Effects of R$_{CM}$ *and* E$_{max}$

As we might intuitively expect, it turns out that an increase in R_{CM} generally leads to a decrease in the magnitude of the resulting interaction energy. Small

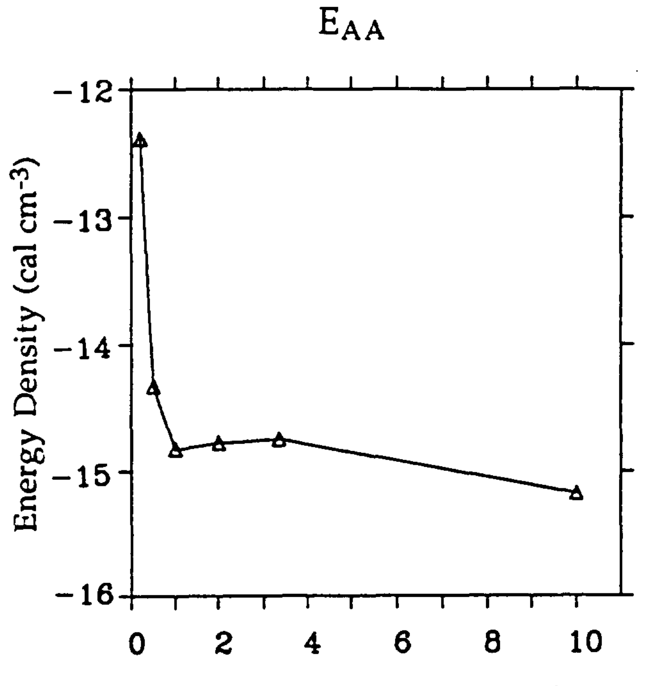

Figure 1 Calculated average interaction energy density for 200 polyethylene segment pairs plotted as a function of the inverse of the maximum derivative of total energy with respect to molecular coordinates used in the energy-minimization procedure

values of R_{CM} give rise to starting structures in which the two segments are initially very close, so that the molecular mechanics refinement procedure pushes them apart. The segments start from a point on a steep repulsive wall of the potential-energy surface, and settle down into a nearby local energy minimum. If larger values of R_{CM} are used, the segments will start further apart, and will therefore end up in local energy minima in which the two molecules are more widely separated. The interaction energy after refinement is correspondingly smaller in magnitude (less negative).

In the bulk polymer, the chain segments will experience compressive forces from surrounding chains, which are absent in the simple FLEXIBLEND model. We therefore aim to generate refined structures in which the segments are close together, and consequently propose the use of a small value of R_{CM} (~ 1 Å). A large value of E_{max} can be chosen to give a reasonable acceptance ratio (something above 0.4). A value of about 10^8 kcal mol^{-1} is normally sufficient to discard structures that will cause problems for the molecular mechanics energy minimization algorithms. The sensitivity of FLEXIBLEND predictions to the value of R_{CM} is investigated below.

'FLEXIBLEND' PREDICTIONS FOR MISCIBLE AND IMMISCIBLE BLENDS

In this section we investigate two polymer blend systems in detail, one immiscible, the other miscible, in order to test the sensitivity of the FLEXIBLEND predictions to the parameters of the model. For an immiscible system we choose poly(ethylene oxide)/polypropylene (PEO/PP); PEO coatings on the metal surfaces of injection moulding machines enable objects made from PP to separate cleanly from the equipment. For a miscible blend we choose poly(ethylene oxide)/poly(acrylic acid) (PEO/PAA)[22]. Densities for the PEO and PP homopolymers are taken as 1.12 and 0.852 g cm^{-3} respectively[23], and the density of pure PAA is estimated using structure–property relationships[24] to be about 1.35 g cm^{-3}.

Interaction energy densities and ΔE_{mix} *for various segment sizes*

We first constructed computer models of small segments of the polymers, PEO$_N$, isotatic PP$_N$ and isotatic PAA$_N$, where $N = 2, 3, 4, 5, 6, 8$. Ensembles of 100 conformations of each PP$_N$ segment were generated from RIS Monte Carlo sampling at 300 K[25], followed by energy minimization of each conformation until the maximum derivative of total energy with respect to atomic coordinates fell below 1 kcal mol^{-1} Å^{-1}. The same procedure was used to generate an archive of 100 PEO$_N$ conformations[26]. Since the appropriate RIS statistical weights are not available, high-temperature molecular dynamics followed by energy minimization to 1 kcal mol^{-1} Å^{-1} was used to generate 100 conformations of each PAA$_N$ segment.

The FLEXIBLEND algorithm was then used to generate and refine 200 starting structures of the segment pairs, PEO$_N$/PEO$_N$, PP$_N$/PP$_N$ and PAA$_N$/PAA$_N$, and to calculate the corresponding average E_{AA} interaction energy densities. Parameters for the FLEXIBLEND algorithm were chosen as $R_{CM} = 1.0$ Å, $E_{max} = 10^8$ kcal mol^{-1}, and energy refinement to 1 kcal mol^{-1} Å^{-1} for the reasons discussed above. *Figure 2* shows how the average interaction energy density changes for each polymer as a function of segment size, N. The error bars on the graphs indicate the standard error on the mean of the 200 structures used for each calculation (error bars are not shown for PP$_N$ because they are smaller than the size of the graph symbol). We have already noted that the interaction energy density must tend towards zero for a pair of very long segments, where interaction can only take place over a small region of the total segment volume. This effect will be particularly noticeable for long, thin segments, such as PEO N-mers that have three backbone bonds per monomer unit and no side groups. *Figure 2* shows a clear tendency for the magnitude of the interaction energy density to be reduced in 5-mers and longer segments of PEO, suggesting that we should use short PEO segments in FLEXIBLEND calculations. Bearing in mind the need to minimize end effects, 3-mers or 4-mers appear to be the most appropriate choice. On the other hand, PAA and PP N-mers are shorter and fatter than PEO N-mers, having side groups and only two backbone bonds per monomer unit. *Figure 2* shows the interaction energy density becoming more negative with increasing N for these polymers (up to $N = 8$), although the trend must eventually reverse as N becomes very large.

Figure 3 shows the calculated interaction energies of PAA$_N$/PEO$_M$ segment pairs for various values of N and M. The FLEXIBLEND algorithm was again used to generate 200 segment pairs for each calculation using the parameters $R_{CM} = 1.0$ Å, $E_{max} = 10^8$ kcal mol^{-1}, and energy refinement to 1 kcal mol^{-1} Å^{-1}. As we have

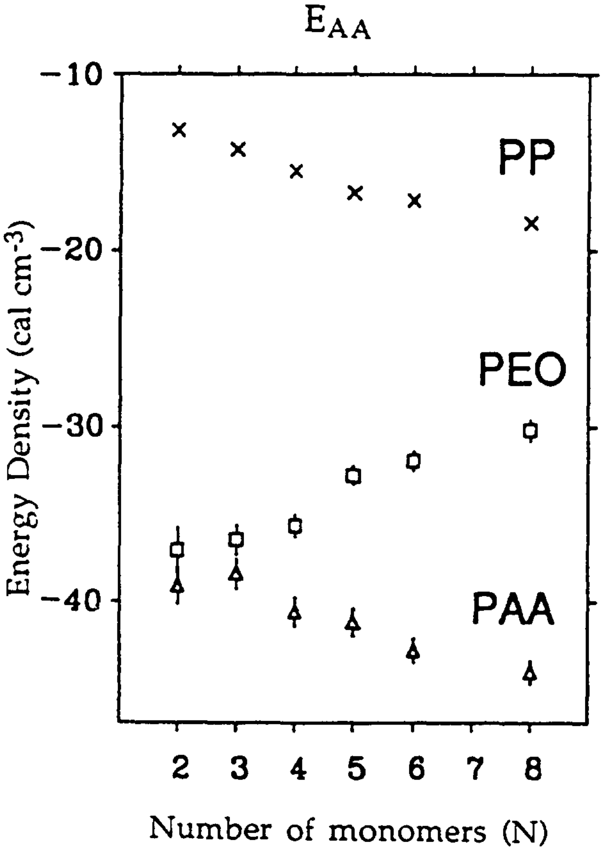

Figure 2 Variation of the average interaction energy density between pairs of like segments of the polymers PP, PEO and PAA as a function of segment size. Error bars indicate standard errors on the mean of the 200 interaction energy values used to obtain each average

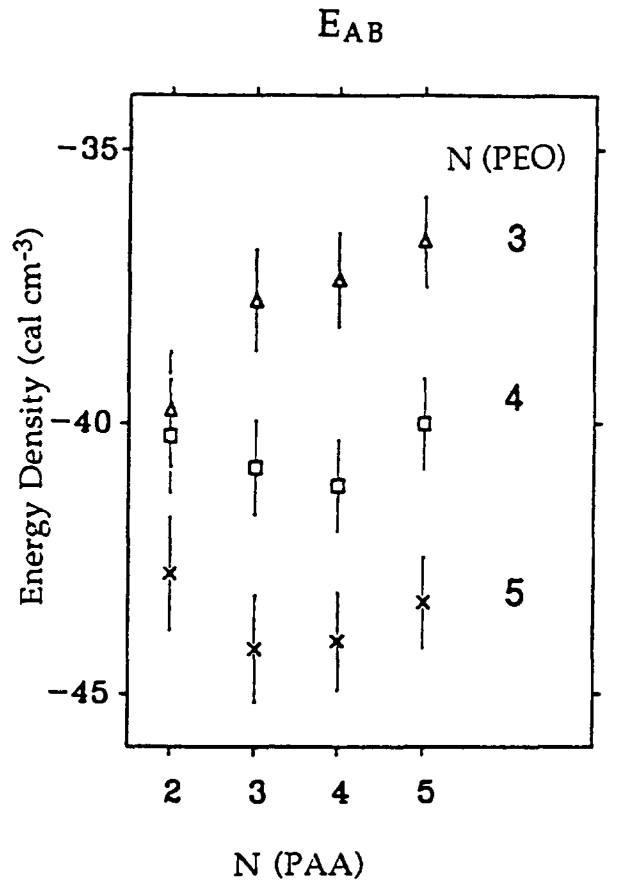

Figure 3 Dependence of the average interaction energy density for PEO/PAA segment pairs upon relative size of the two segments. Each energy density is the average value from 200 structures, and error bars denote the standard error on the mean

already pointed out, the interaction energy density must tend towards 0 when the segments are of greatly differing sizes. Correspondingly, we expect to find a minimum value when the two segments are roughly the same size, and the results in *Figure 3* are in accordance with this expectation. Minima in the interaction energy density could conceivably lie at PAA_2/PEO_3, PAA_3/PEO_4 and PAA_4/PEO_5, although the error bars in *Figure 3* are too large for a definite prediction. An N-mer of PAA is somewhat larger than an N-mer of PEO due to its bulky side groups. On the other hand, an N-mer of PP is of similar size to an N-mer of PEO, the greater length of the PEO N-mer being compensated by the methyl side group on the PP monomer.

Table 2 shows predicted values of ΔE_{mix} for PAA_N/PEO_M and PP_N/PEO_M using different segment sizes, N and M being chosen so that the segments in the mixed structure are of similar size. Each ΔE_{mix} result (involving calculations of $E_{A_N A_N}$, $E_{B_M B_M}$ and $E_{A_N B_M}$) takes between 1 and 4 h on a Silicon Graphics R4000 Indigo workstation, depending upon the size of the segments. The magnitude of the predicted ΔE_{mix} in *Table 2* depends quite strongly upon segment size. However, the results are consistently negative for PAA/PEO, and consistently positive for PP/PEO, in accordance with the experimentally observed compatibility of the respective blends.

It is interesting to consider which is the best value of ΔE_{mix} in *Table 2* for each blend. We have already noted that the E_{AA} interaction energy density for PEO may not be reliable for $N>4$; its magnitude will be too small, leading to values of ΔE_{mix} that are more negative than they should be. On the other hand, very small segments of PAA and PP may also have unreliable E_{AA} values owing to large end effects. On this basis, we choose the PP_4/PEO_4 and PAA_3/PEO_4 cases for further investigation below, even though these cases do not give the most conclusive predictions in *Table 2*.

Figure 4 analyses the PP_4/PEO_4 calculation in detail, showing the calculated interaction energy densities for each set of 200 structures of PEO_4/PEO_4, PP_4/PP_4 and PP_4/PEO_4. Quite large fluctuations are observed in the interaction energies, especially for the PEO_4/PEO_4 structures, although the standard error on the mean of each set of 200 structures is small enough that a statistically significant prediction of ΔE_{mix} can be made. *Figure 4* also gives some insight into the reasons why the two polymers do not mix: although the average interaction energy of the PEO/PP segment pair is more favourable than that of the PP/PP pair (so that the PP segment prefers to be near to a PEO segment), the mixture is predicted to be immiscible because a PEO segment prefers to be near another PEO segment rather than a PP segment, and this latter consideration is dominant. Typical refined segment pair structures are also illustrated in *Figure 4*, showing the way that the two segments fold around each other.

Dependence of predicted ΔE_{mix} on FLEXIBLEND parameters

Before deciding whether the FLEXIBLEND algorithm can make useful predictions, it is necessary to determine how the magnitude of ΔE_{mix} changes with R_{CM} and the maximum derivative criterion in the energy refinement procedure. (E_{max} can be considered dependent upon R_{CM}, its value being chosen so as to give a reasonable acceptance ratio.) *Figure 5* shows how the values of ΔE_{mix} are influenced by the maximum derivative criterion for the PP_4/PEO_4 and PAA_3/PEO_4 cases. The result for PP_4/PEO_4 becomes slightly more conclusive with a decrease in the maximum derivative limit, although this is, of course, achieved at the cost of increased computer time spent in the refinement process. The value of ΔE_{mix} for the PAA_3/PEO_4 case appears to be quite insensitive to the maximum derivative criterion.

Figure 6 shows the variation of ΔE_{mix} with R_{CM} for PP_4/PEO_4 and PAA_3/PEO_4. Again, the results are not very sensitive to the value chosen for the FLEXIBLEND parameter, although the most conclusive predictions are made with the smallest values of R_{CM}. There is a tendency for the magnitude of ΔE_{mix} to decrease with an increase in R_{CM} (for very large values of R_{CM} we would expect to find $E_{AA}=E_{BB}=E_{AB}=\Delta E_{mix}=0$ as the segments are too far apart to interact at all).

Table 2 Predicted ΔE_{mix} for PEO/PP and PEO/PAA blends

Structure	ΔE_{mix} (cal cm^{-3})	Standard error on the mean (cal cm^{-3})
PP_3/PEO_3	+5.55	±0.67
PP_4/PEO_4	+3.55	±0.66
PP_5/PEO_5	+1.64	±0.65
PAA_2/PEO_3	−2.01	±1.97
PAA_3/PEO_4	−3.63	±1.59
PAA_4/PEO_5	−7.37	±1.59

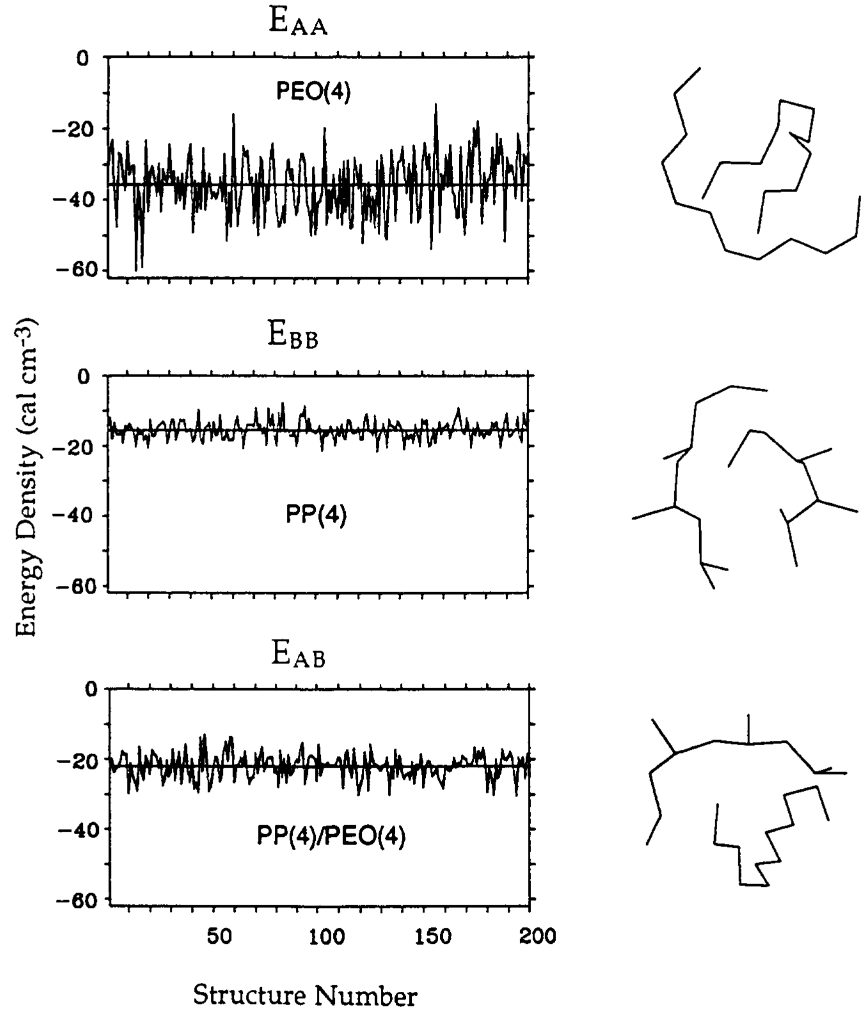

Figure 4 Calculated interaction energy densities for 200 PEO_4/PEO_4 segment pairs, 200 PP_4/PP_4 segment pairs and 200 PP_4/PEO_4 segment pairs generated using the FLEXIBLEND algorithm. Averages of each set of 200 data points are shown as horizontal lines on the graphs. Typical refined structures are shown (heavy atoms only) to the right of the graphs, illustrating the way that the segments fold around each other

AMORPHOUS CELL CALCULATIONS ON THE POLY(ETHYLENE OXIDE)/POLYPROPYLENE BLEND

Amorphous cell methods can be used to generate an atomistic model of a bulk amorphous polymer[20]. The model is periodic, so that if a polymer chain in the central cell passes out through one of the cell faces, an exact copy (or image chain) enters the cell through the opposite face. *Figure 7* shows an amorphous cell of PEO surrounded by eight identical image cells, giving an impression of the way an infinite, bulk model is constructed from an individual cell.

Ten different amorphous cells each of PEO (at a density of $1.12\,g\,cm^{-3}$), isotactic PP (density $0.852\,g\,cm^{-3}$), and a PEO/isotactic PP mixture (density $0.968\,g\,cm^{-3}$) were built using commercial software[19], with each cell containing 1012 atoms. Each cell was constructed from two parent chains of 506 atoms. Thus the PEO cell contains two 72-mers, the PP cell contains two isotactic 56-mers, and the mixed cell contains one 72-mer of PEO and one isotactic 56-mer of PP. The resulting mass fraction of PEO in the mixed cell is 0.574. Each cell was equilibrated for 10 ps of molecular dynamics at a temperature of 298 K, and then cohesive energy densities were calculated using molecular mechanics[19].

Table 3 gives the calculated average cohesive energy densities for the three sets of cells. As expected, the magnitude of the cohesive energy density for the bulk model is much larger than that for a pair of isolated chains (compare *Figure 4* and the values in column 2 of *Table 3*). The calculated net change in cohesive energy density upon mixing is unfavourable at $-5.3\,cal\,cm^{-3}$. The amorphous cell calculation therefore suggests that a mixture of the PEO (mass fraction 0.574) with isotactic PP (mass fraction 0.426) will be immiscible, in agreement with the FLEXIBLEND result and with experimental observation. Again, the amorphous cell calculations show the dominant factor to be the high cohesive energy of the pure PEO polymer.

DISCUSSION

The most important consideration in using the two-segment approach for miscibility prediction appears to be segment size. In particular, if the sizes and shapes of the monomer units of polymers A and B are very different,

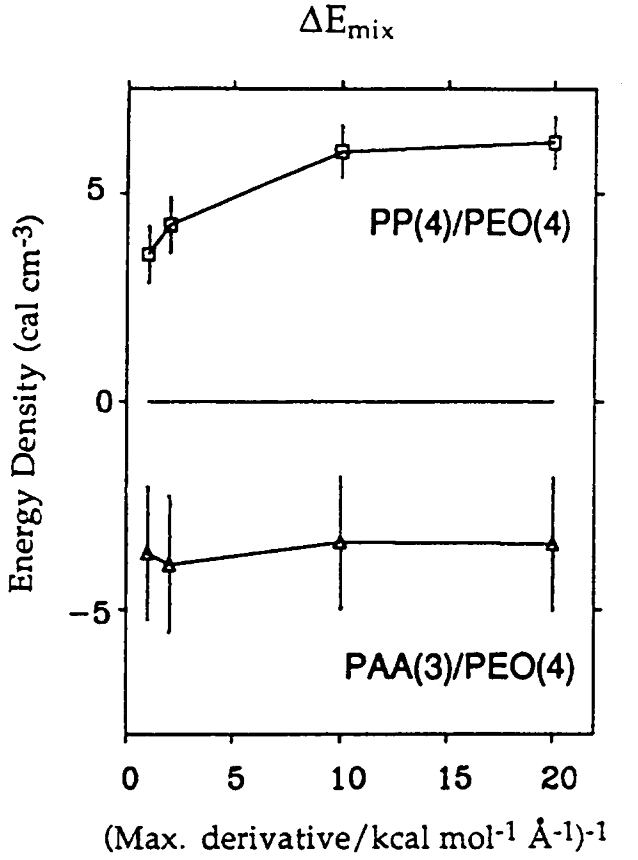

Figure 5 Variation of the calculated value of ΔE_{mix} with the maximum derivative criterion used in the molecular mechanics energy minimization procedure. Results are shown for PP_4/PEO_4 and PAA_3/PEO_4 combinations

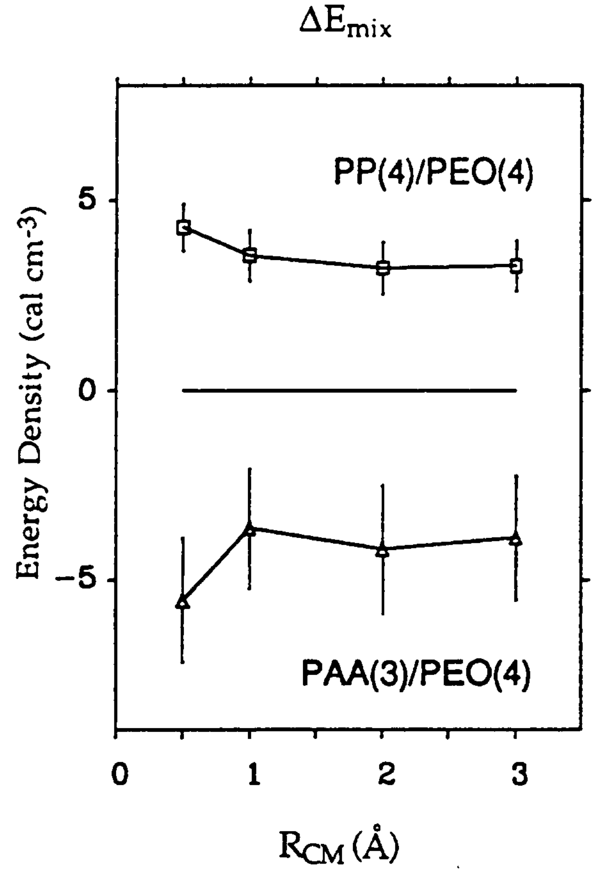

Figure 6 Variation of the calculated value of ΔE_{mix} with the R_{CM} parameter of the FLEXIBLEND algorithm. Results are shown for PP_4/PEO_4 and PAA_3/PEO_4 combinations

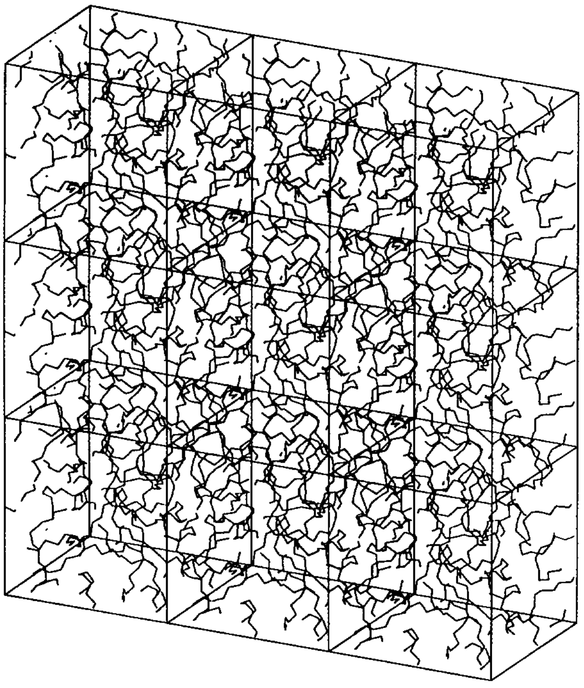

Figure 7 Part of a periodic amorphous cell model of bulk PEO. A 3 x 3 x 1 array of cells is shown, and hydrogen atoms are not displayed

Table 3 Average cohesive energy densities of amorphous cells containing PEO, isotatic PP and a mixture of PEO and isotactic PP

Cell composition	Average cohesive energy density (cal cm^{-3})
PP	50.5
PEO	96.3
PEO/PP mixture	68.1

Table 4 Solubility parameters for PEO, PP and PAA

Polymer	δ (cal cm^{-3})$^{1/2}$		Ref.
PP	~9.2	Experimental	23
PEO	~9.9±1	Experimental	23
	~9.4	Structure–property relationships	24
PAA	~12.6	Structure–property relationships	24

predictions may depend strongly upon the size of segments for which the calculations are performed.

However, with careful attention to the segment size, molecular mechanics calculations on short segments of polymer chains using the FLEXIBLEND algorithm consistently predict that PEO and PP are immiscible, whilst PEO and PAA are miscible. These predictions cannot be made on the basis of comparing solubility parameters, as the values in *Table 4* readily show. Furthermore, the two-segment approach gives some insight into the reasons why two polymers are miscible or immiscible. The method is quick, typically requiring only a couple of CPU hours for each polymer blend studied, and is based upon the premise that miscibility is largely determined by the energetics of local interactions between segments of the polymer chain. Effects of temperature and concentration are ignored, as are volume changes upon mixing.

The spatial correlations between chain segments in the set of refined structures produced by the FLEXIBLEND model are somewhat dependent upon the parameters chosen to generate the starting structures. By contrast, the amorphous cell method creates a realistic three-dimensional model in which the spatial correlations between chain segments can be accurately determined for the bulk, amorphous polymer (within the limitations of the forcefield). This, more rigorous, method requires greater computing resources; calculations on the PEO/PP blend took a total of about three CPU days on a Silicon Graphics 4D/35 workstation. However, using the amorphous cell approach, it is, at least in principle, possible to investigate the effects of concentration by varying the volume fractions of the two components in the mixed cell.

Predictions of cohesive energy density and solubility parameter using the amorphous cell technique are likely to give a more reliable guide to miscibility than are calculations using the FLEXIBLEND algorithm. However, the speed of the FLEXIBLEND method suggests its usefulness for initial screening of potentially miscible combinations of polymers for a given application, and for understanding changes in phase behaviour resulting from modifications in chemical structure. More reliable calculations using the amorphous cell method might then be carried out on promising combinations.

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