Most natural materials contain a number of different components; for example, wood is a composite made up of cellulose fibres, which are strong in tension, within a lignin matrix. The earliest attempts to exploit metals by man involved the use of copper; adding tin was found to improve performance, leading to the so-called bronze age of human development. As we have already seen, even the simplest polymer is, in reality, a mixture of different molecular forms. The properties of these materials result from the range that is present and the desirable characteristics we exploit rely critically on the “right mix” being present.

Polymer Blends

Deliberately mixing together different polymers is a technically and economically attractive way of producing new material systems; these are termed polymer blends. Alternatively, a non-polymeric second phase can be added to produce a composite.

Polymer blends can, practically, be divided into two distinct classes of material:

(i) Miscible Blends
(ii) Immiscible Blends
Polymer Blends

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Miscibility

The extent to which different polymers mix with one another is of great significance when it comes to designing materials to meet specific ends. It is also a fundamental problem when it comes to recycling the polymers that are abundant today, because of “cheap” oil. In the future, landfill sites may become important “plastic mines.” In discussing the extent to which mixing can occur, it is necessary to consider the Gibbs free energy of the system, \( G \):

\[
G = H - TS
\]

In thermodynamic terms, two components will mix intimately provided this results in a reduction in the total free energy of the system:

\[
G_1 - G = G_1 + G - G_1 + G_1 = G_1 + G - G 
\]

where \( G_1 \) = Gibbs free energy of mixture
\( G_1 \) = Gibbs free energy of component A
\( G_2 \) = Gibbs free energy of component B

From this relationship, it is possible to define a quantity, \( \Delta G_m \), called the Gibbs free energy of mixing:

\[
\Delta G_m = G_1 - (G_1 + G_2)
\]

Provided \( \Delta G_m < 0 \), mixing will be favoured thermodynamically. Also, from the general definition of \( G \) or \( \Delta G \) (e.g. equation (M.1)), it is possible to consider \( \Delta G_m \) in terms of two components:

\[
\Delta G_m = \Delta H_m - T \Delta S_m
\]

where \( \Delta H_m \) is the enthalpy of mixing
\( \Delta S_m \) is the entropy of mixing.

These two quantities can now be considered separately, but first it is necessary to review some of the underlying mathematical concepts that are required.
The Mathematics of Permutations and Combinations

This topic involves the selection of \( r \) objects from a set of \( n \) mutually distinguishable objects, e.g., a, b, c, d, e, etc.

A permutation of a set of \( n \) mutually distinguishable objects, \( r \) at a time, is an arrangement in which their order counts. That is:

\[
\text{The total number of different permutations can be written:}
\]

\[
M.5 \quad \frac{n!}{(n-r)!}
\]

A combination of a set of \( n \) mutually distinguishable objects, \( r \) at a time, is a selection of \( r \) objects from the \( n \) without regard to their arrangement. That is:

\[
\text{Since, once selected, these } r \text{ objects can be arranged in } r! \text{ ways (each combination being equivalent), the number of such combinations can be written:}
\]

\[
M.6 \quad \binom{n}{r} = \frac{n!}{r!(n-r)!}
\]

Alternatively, the above can be considered to be a selection from \( n \) mutually indistinguishable objects, a, a, a, a, a, etc. Clearly, then:

\[
\text{bca} \neq \text{abc}
\]

Entropy of Mixing

The entropy of mixing can be evaluated by representing the system as a distribution of particles (A and B) arranged on a lattice, as shown:

In this model, it is assumed that there are \( N_1 \) molecules of component A and \( N_2 \) molecules of component B. Using the above mathematics, the number of combinations that are possible for this system, \( \Omega \), can be written:

\[
\Omega = \frac{(N_1 + N_2)!}{N_1!N_2!}
\]

Since the number of possible arrangements can be evaluated, the entropy of mixing can be found using the Boltzmann's equation:

\[
\Delta S_m = k \ln \Omega
\]

where \( k \) is known as Boltzmann's constant. Combining equations (M.7) and (M.8):

\[
\Delta S_m = k \ln \left( \frac{(N_1 + N_2)!}{N_1!N_2!} \right)
\]
In mathematics, there is a relationship termed Stirling’s approximation, which can be applied to this sort of equation, where $N$ is large:

$$\ln N! \approx N \ln N - N$$

Using this, equation M.9 can be rewritten:

$$\Delta S_m = \frac{1}{2} \left[ \sum \frac{N_i}{N} \ln \frac{N_i}{N} + \sum \frac{N_i}{N} \ln \frac{N_i}{N_i + N_f} \right]$$

Although this equation is usually modified somewhat, this form is adequate for our purposes in that it conveys the significance of this calculation.

What it shows is that the entropy of mixing varies monotonically with the number of molecules present. So, for say a mixture of 0.5 g of A and 0.5 g of B, the larger the molecules, the fewer will be present.

Since polymers are very large molecules, compared with other materials, $N_1$ and $N_2$ will be very small, in which case, the entropy of mixing will also be small. Indeed, it is generally insignificant.

**Enthalpy of Mixing**

In this case we need to take a rather “higher magnification” view of the problem and remember that polymer molecules are long strings of repeating units:

<table>
<thead>
<tr>
<th>Component</th>
<th>A</th>
<th>aaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaaa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td>B</td>
<td>bbbbbbbbbbbbbbbbbbbbbbbbbbbbbbbbbb</td>
</tr>
</tbody>
</table>

Then, three types of interaction need to be considered when evaluating the enthalpy of mixing:

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>A–A</td>
<td>$w_{11}$</td>
</tr>
<tr>
<td>A–B</td>
<td>$w_{12}$</td>
</tr>
<tr>
<td>B–B</td>
<td>$w_{22}$</td>
</tr>
</tbody>
</table>

Consider two square lattices, one containing component A and the other containing component B.

In removing ONE polymer molecule from A, for each segment along the chain, two a-a contacts will be lost and one new contact will be formed.

In inserting the molecule of A into B, one B-B contact is lost and two new A-B contacts will be formed.
In inserting the molecule of A into B, one B-B contact is lost and two new A-B contacts will be formed, per segment, such that the change in enthalpy can be written:

$$\Delta \nu = 2\nu_{12} - (\nu_{11} + \nu_{22})$$  \hspace{0.5cm} \text{(M.11)}

where $\Delta \nu$ is the energy change per A-B polymer contact. Although the above equation has been derived using square lattices, the above approach works irrespective of the assumed geometry. As in the case of the entropy described above, it is conventional to go further with this analysis and, here, $\Delta \nu$ is conventionally expressed in terms of another quantity, the so-called interaction parameter, but M.11 is sufficient for our purposes.

(i) The term involving the quantities $\nu_{11}$ and $\nu_{22}$ is associated with the enthalpy it takes to break bonds.

(ii) Conversely, the term involving $\nu_{12}$ is associated with forming a bond.

(iii) Thus, the sign of $\Delta \nu$ will depend upon the relative magnitudes of $\nu_{11}$, $\nu_{22}$ and $\nu_{12}$.

(iv) Since $\Delta S$ is small, the sign of $\Delta G$ is therefore determined by the sign of $\Delta \nu$, which equates to $\Delta H$.

(v) For polymers to mix, there must be strong positive interactions between the two components. Otherwise, as is generally the case, A and B will be immiscible.

This general result represents a major problem in connection with the recycling of polymers. If you were to attempt to use a mixed polymer waste stream in an engineering application, then the various different components would separate during manufacture to give distinct phases with extremely weak boundaries. Mechanically, such a material would exhibit extremely poor properties, in that failure would occur easily between the various polymers. As such, it is essential that different polymers are separated from one another and recycled separately. However, telling different polymers apart is far from simple such that artefacts intended for recycling are now routinely marked with the relevant polymer type.

Unidentified polymer waste is currently most commonly sent to landfill. Even recovering the energy value is problematical, due to the possible presence of toxic additives included, for example, to reduce flammability.
**Miscible Blends: Polyethylene**

Miscible blends are, generally, about producing a material with some property that is intermediate between that exhibited by each of the components.

Polyethylene and polypropylene are the two most important bulk commodity plastics. Since there are no strong interactions between these two polymers (they only differ in terms of the replacement of one H with a CH₃ group on every second carbon along the chain), they are immiscible.

However, if, say, a H is replaced with a CH₃ group on average on every 40th carbon along the chain, then we have a low density polyethylene, which is miscible with linear HDPE. Blending together different polyethylene grades can be a very effective way of tailoring properties.

Recent research work in Southampton has used this strategy to design the mechanical properties of polyethylene for use in high voltage cable applications. The objectives of the work were:

(i) To develop a clear spherulitic structure.
(ii) To remove weak inter-spherulitic boundaries.
(iii) To retain good low temperature (~20 °C) flexibility.
(iv) To achieve high rigidity at high temperatures (~120 °C).

<table>
<thead>
<tr>
<th>HDPE</th>
<th>YES to (i) and (iv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>YES to (iii)</td>
</tr>
<tr>
<td>Southampton PE</td>
<td>YES to all</td>
</tr>
</tbody>
</table>

The trick was to make a blend composed of 20% HDPE and 80% LDPE and arrange for the HDPE to crystallize first, at about 115 °C, and only later for the LDPE to crystallize. The structural consequences of this are illustrated below.

---

The mechanical properties of this material are shown below as a function of temperature.

1. This material has been designed such that the spherulite boundaries are not weak, as a result of the sequential crystallization process.
2. The good high temperature properties are a consequence of the framework of dominant HDPE crystals, which act as a structural "skeleton" after the LDPE has melted.
3. The low temperature flexibility is a consequence of the regions of "spongy" LDPE that exist between the relatively rigid HDPE crystals.
Immiscible Blends: HIPS

Polystyrene (PS), in its commonly encountered form, is a clear, amorphous thermoplastic, with a glass transition temperature, \(T_g\), around 115°C. As such, at room temperature, it exhibits typical glassy mechanical properties of brittleness and a low elongation at break of ~4%.

The addition of rubbers is a commonly employed method of improving the mechanical properties, in particular its impact resistance, hence the term high impact polystyrene (HIPS).

Conventional rubbers interact only weakly with PS and, therefore, there is no thermodynamic drive for mixing, which means that they form a dispersed second phase. Generally, the rubber is dissolved in the styrene monomer before polymerization. The greatest improvement in toughness is observed if rubber latex particles (sizes 0.1-1.0 \(\mu\)m) are first coated with a chemical that will react with the polymerizing styrene, such that the rubber phases become covalently bonded to the PS matrix. The idea of this is to prevent interfacial failure, such that failure involves deformation of the rubber phase. In this case, a process termed cavitation occurs, which dissipates energy. Although a number of different theories have been proposed for this, the basic idea is shown.

Production

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If the latex, at 10-20%, is added to the styrene and polymerization is initiated, the structure shown below then results. In such a material, the good processing characteristics of PS are retained in the final rubber-toughened blend, although the presence of the rubber results in a considerable increase in impact toughness, albeit at the expense of some deterioration in the softening temperature and a significant reduction in rigidity.

The utility of this approach relies upon a process termed cavitation occurs, which dissipates energy. Although a number of different theories have been proposed for this, the basic idea is shown below.

(i) The top image shows the progressive growth of a crack around a well-bonded rubber particle.
(ii) The rubber inclusion becomes stretched as the cracks, shown at different magnifications in the lower two images, grow.
(iii) Energy is absorbed by the rubber in deforming it (i.e. the area under the stress strain curve).

More complex theories consider the effect of the local stress fields, which serve to cause many small cracks to form, rather than just a single large one.
The properties of HIPS are compared with polystyrene below.

<table>
<thead>
<tr>
<th></th>
<th>PS</th>
<th>HIPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength / MPa</td>
<td>42</td>
<td>35</td>
</tr>
<tr>
<td>Elongation at break / %</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>Impact strength / J m⁻¹</td>
<td>15</td>
<td>55</td>
</tr>
<tr>
<td>Softening temperature / °C</td>
<td>94</td>
<td>85</td>
</tr>
</tbody>
</table>

Another polymer where rubber toughening finds important technologically applications is polycarbonate (PC).

In this case, blends with materials such as ABS (acrylonitrile/butadiene/styrene) have excellent impact performance combined with good optical clarity and improved high temperature stability compared with HIPS. As a result they are commonly used as protective shields and as glazing in hazardous areas.

<table>
<thead>
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<td>94</td>
<td>85</td>
</tr>
</tbody>
</table>

Block Copolymers

A wide range of different block copolymers have been produced using, either two or three chemically distinct blocks.

Diblock Copolymer: AAAAAAABB BBBBBB

Acrylonitrile/butadiene/styrene (ABS)

Triblock Copolymers: AAAAAAABB BBBBBBBBAAAAA AAAAAAAAABBBBBBBBBBCCCCC

These materials exploit the immiscibility of the constituent components and the fact that they are chemically linked to give materials which exhibit a rich variety of phase structures.

Since the components are unable fully to phase separated, structural dimensions in block copolymers tend to be smaller than in immiscible blends and depend upon the relative dimensions of the two blocks.
ABS, for example, is a copolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. Typically, it contains 15% to 35% acrylonitrile, 5% to 30% butadiene and 40% to 60% styrene.

(i) The butadiene gives rubbery properties.
(ii) The nitrile groups are polar and tend to increase interchain interactions.
(iii) The polystyrene provides rigidity.

The resulting material has outstanding impact resistance, albeit stiffness and strength that are too low for its use in structural applications. It is easily moulded and retains its desirable mechanical characteristics down to about -25°C. As such, ABS is commonly used to make light, rigid, moulded products such as luggage, automotive body parts, protective equipment and golf club heads, where its excellent shock absorbing characteristics are exploited.

<table>
<thead>
<tr>
<th>Property</th>
<th>ABS</th>
<th>HIPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate Tensile Strength</td>
<td>28-65</td>
<td>50 – 60</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>2-11</td>
<td>1-5</td>
</tr>
<tr>
<td>Charpy Impact strength (notched)</td>
<td>0.4-14.0</td>
<td>0.1-2.5</td>
</tr>
<tr>
<td>Max. Service Temperature °C</td>
<td>77-109</td>
<td>84-98</td>
</tr>
</tbody>
</table>

An outstanding resource for finding such data is:  

SUMMARY