

# **ENGINEERING WITH BLENDS AND ALLOYS**

**Papers from a one day seminar  
organised by  
RAPRA TECHNOLOGY LIMITED**

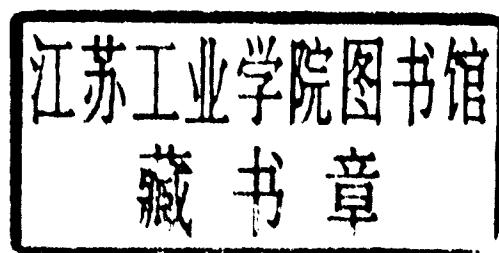
**29th November 1989**

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TECHNOLOGY LTD.

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## INTRODUCTION

Anyone who attended K89 in Dusseldorf will have been impressed by the speed with which plastics technology has recently advanced from simple application of standard polymers and compounds to the careful matching of materials to performance requirements. This rapid transition owes much to the polymer industry's developing skills in synergistically combining and blending their materials to meet specific market needs.

As a result it is becoming increasingly possible genuinely to engineer with polymeric systems. However continued success in these developments will depend on an ever closer understanding of them and their implications. This conference is part of this process of interaction between those who, like ourselves, are involved in the developments and others for whom they represent enabling technologies for further advances in their own fields.

G. Christopher Karas\*  
Conference Chairman

\*Mr. Karas is Manager of Rapra's Business Development Consultancy

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# Recent Developments in Polymer Blends

Jan Czerski

Market Development Manager,  
BASF UK Ltd.

It has for sometime been appreciated that blends of otherwise well-known plastics offer an economic route for arriving at new materials with attractive properties, these may be thermodynamically miscible or multi-phase systems.

Obviously, the aim is to combine the properties of the constituent thermoplastics so that the benefits of each are drawn into the foreground and the drawbacks are minimised. Thus the pattern of the properties obtained for the blend may differ entirely from some of the properties of the constituents.

Developments in polymer blends have been so hectic that time permits discussion of only a few, particularly successful groups or their main representatives, viz. PMMA/SAN, ASA/PC, ASA/PBT, PPE/HIPS and PPE/PA. Some of these blends and the corresponding sales trends are shown in Figure 1. The tradenames and suppliers are listed in Table 1.

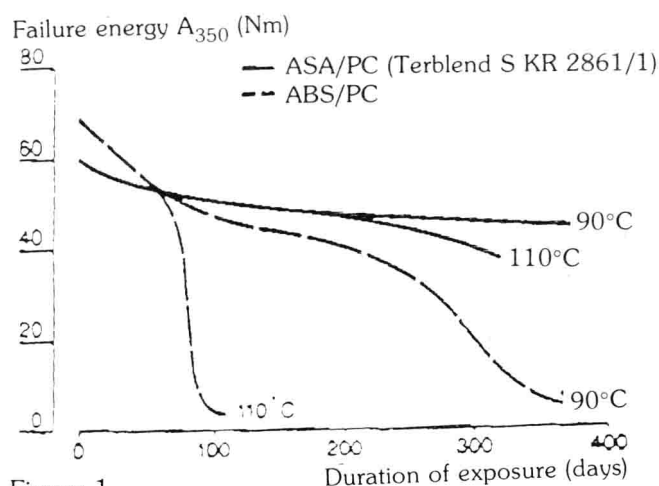


Figure 1

## IMPACT-MODIFIED PMMA/SAN blends

The beneficial properties of ABS polymers are well appreciated. A disadvantage is that they are not transparent, but there has been no lack of efforts to obtain transparent products with properties similar to those of ABS. Two-phase systems, such as ABS, can be made transparent if the refractive index of the rubber phase is reconciled with that of the matrix. An example of how the refractive index of the matrix can be brought into line with that of the dispersed phase would be to incorporate methyl methacrylate in the matrix, i.e. to disperse the rubber phase in a styrene-acrylonitrile-methyl methacrylate terpolymer. However, blend technology offers a simpler means of obtaining transparent products. For instance, it is well-known that optically clear blends can be obtained from methyl methacrylate and SAN polymers containing a defined mass fraction of acrylonitrile.

Typical properties for a MABS polymer obtained are shown in Table 1. This class of product attains the target of clarity combined with properties similar to those of ABS. Although the impact resistance lies in the lower to medium range for ABS, it is decidedly higher than that for SAN or PMMA. The range of these beneficial properties also secures the viability of MABS polymers in competition with other transparent materials in interesting market segments.

## ASA/PC BLENDS

One of the great advantages of impact-modified styrene-acrylonitrile copolymers, e.g. ABS or

Table 1 Properties of MABS, SAN and PMMA

| Property                               | Unit              | Test method | MABS<br>Terluran (R)<br>2802 TR | SAN  | PMMA |
|--|-------------------|-------------|---------------------------------|------|------|
| Impact resistance                      | kJ/m <sup>2</sup> | DIN 53453   | 80                              | 15   | 15   |
| Modulus of elasticity in tension       | N/mm <sup>2</sup> | DIN 53457   | 2000                            | 3700 | 3300 |
| Vicat softening temperature (VST/B/50) | °C                | DIN 53460   | 91                              | 105  | 108  |
| Melt index MFI 200/21.6                | g/10 min          | DIN 53735   | 4                               | 25   | 3    |

Table 2 Resistance to heat deformation and impact resistance of a general-purpose ABS/PC blend, a general-purpose ABS/PC blend, a general-purpose ABS, and an ABS/AMS with high resistance to heat deformation

| Property                               | Unit              | Test      | ABS | ABS/AMS | ABS/PC |
|--|-------------------|-----------|-----|---------|--------|
| Vicat softening temperature (VST/B/50) | °C                | DIN 53460 | 99  | 114     | 120    |
| Heat distortion temperature Method A   | °C                |           | 98  | 106     | 108    |
| Method B                               | °C                |           | 102 | 112     | 125    |
| Notched impact resistance              | kJ/m <sup>2</sup> | DIN 53453 | 11  | 7       | 40     |

ASA, is the ease with which they can be processed. Also, their resistance to heat deformation is sufficiently high for many applications, e.g. radiator grilles and coffee makers. Thus the vicat softening temperature (VST/B/50), which is a measure of the resistance to heat distortion is almost 100°C for a general-purpose ABS. Values as high as 115°C can be attained by ABS polymers with alpha-methylstyrene incorporated in the molecules. If, as is the case in a number of applications, even this resistance is not high enough, it can be raised by blending with polycarbonate.

The effect of this is shown in Table 2, in which the Vicat softening temperature, the ISO heat distortion temperature, and the notched impact strength of a general-purpose ABS/PC blend are compared with the corresponding figures for a general-purpose and a heat-resistant ABS. The superiority of the ABS/PC blend is clearly evident from these figures.

Great success has been achieved in developing ASA/PC blends to meet the demands imposed in automotive and electrical engineering for products with high resistance to heat deformation, ultra-violet radiation, and heat. A particular wish that has also been realised is high colour retention on exposure to heat or ultra-violet radiation.

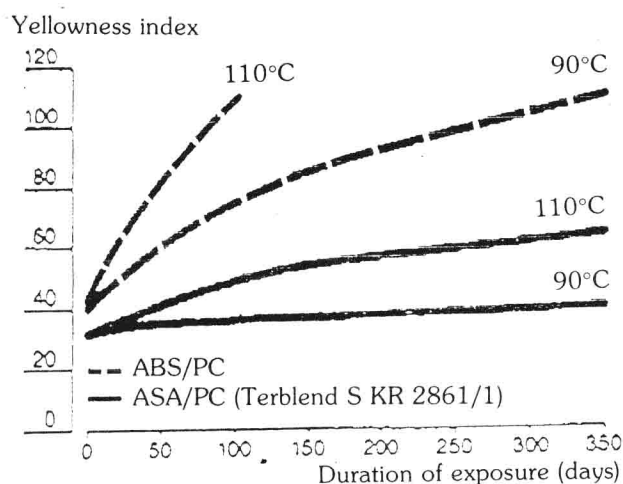


Figure 2

## PERFORMANCE CHARACTERISTICS OF ASA/PC BLENDS

Figures 1 and 2 demonstrate the superiority of ASA/PC over ABS/PC on long-term exposure to heat. The great resistance to high-temperature ageing is evident from Figure 3; and the outstanding resistance to yellowing, from Figure 4. Exposure for more than one year to a temperature of 90°C has hardly any effect on the natural colour of ASA/PC. Even at a temperature of 110°C, the yellowness index of ASA/PC articles is decidedly less than that of ABS/PC articles exposed for the same period to a temperature of only 90°C.

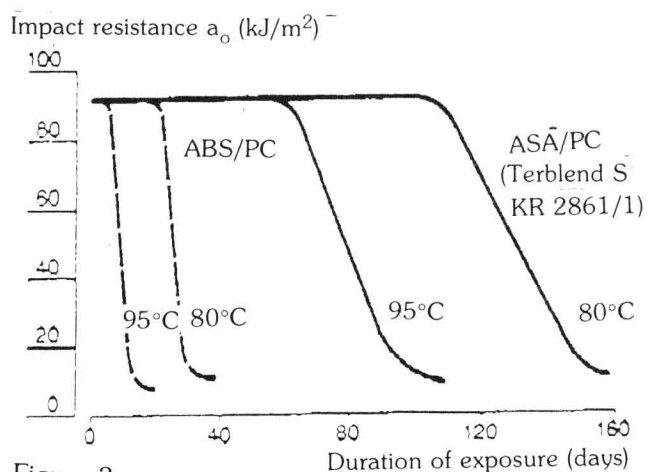


Figure 3

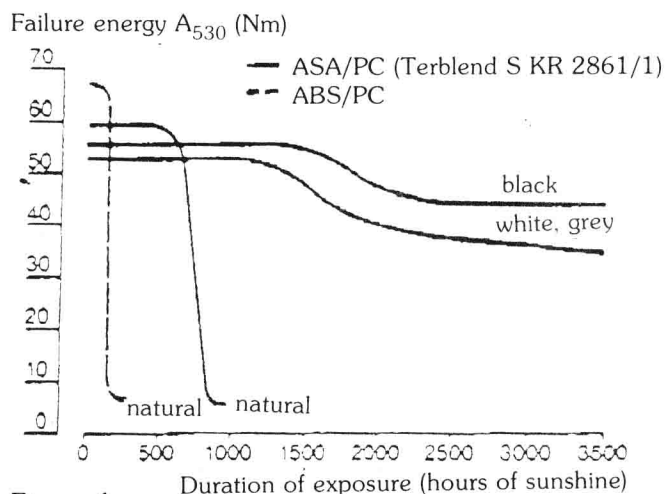


Figure 4

Table 3 Resistance of ASA/PC and ABS/PC to environmental stress cracking determined by the steel ball impression method (DIN 53449), i.e. the ball oversize at which the failure limit is reached in the test medium. The failure limit is taken to be a 5% decrease in strength at break OB or at 20% decrease in ultimate elongation on ER

| Test medium                             | Ball Oversize               |                             |
|---|-----------------------------|-----------------------------|
|   | ASA/PC<br>( $\mu\text{m}$ ) | ABS/PC<br>( $\mu\text{m}$ ) |
| Air, 24 hours                           | >500                        | >500                        |
| Olive oil:oleic acid (1:1), 1 hour      | 140                         | 80                          |
| Premium gasoline, 1 hour                | 15                          | 15                          |
| Isopropanol, 1 hour                     | >500                        | 105                         |
| Wetting agent, 10% (Laventin V), 1 hour | >500                        | >500                        |

ASA/PC has even more other advantages over ABS/PC. For instance, it is more resistant to hot water. This was demonstrated by immersing  $50 \times 64$  mm standard bar specimens in water at temperatures of 80 and 95°C respectively and determining the impact resistance as a function of the duration of immersion.

Although ASA/PC cannot be recommended for applications involving long-term contact with hot water, its short-term performance, e.g. is dishwashing, is better than that of ABS/PC to environmental stress cracking. The failure limits, as determined by the steel ball impression method for specimens immersed in various test media are listed in Table 3. Experience has shown that there is very little likelihood of environmental stress cracking if the ball oversize required to reach the failure limit is higher than 120  $\mu\text{m}$ .

### FLAME-RETARDANT ASA/PC BLENDS

The strong emphasis placed on safety in specifications for electrical equipment has heightened interest in flame-retardant products with high resistance to heat deformation and to yellowing. Typical properties for a general purpose and a flame-retardant ASA/PC are listed in Table 4. Examples of

potential applications for flame-retardant ASA/PC are transformer housings, hot-air fan shrouds, cable duct corner pieces, and parts for fume extractor hoods.

### GLASS-REINFORCED ASA/PBT

ASA polymers also form interesting blends with polybutylene terephthalate. The beneficial properties of PBT include high resistance to heat deformation and good resistance to environmental stress cracking. One of its disadvantage is the high shrinkage and tendency to warpage that result from its partially crystalline nature. This drawback can be considerably alleviated by blending with ASA polymers. Obviously, it can be further offset by reinforcing with glass fibres.

### PERFORMANCE CHARACTERISTICS AND APPLICATIONS FOR GLASS REINFORCED ASA/PBT BLENDS

A comparison of the properties of glass-reinforced ASA/PBT with those of glass-reinforced PBT reveals that, as intended, the incorporation of the ASA polymer greatly reduces shrinkage and

Table 4 Typical values for the properties of ASA/PC blend

| Property  | Unit              | Terblend (R) S<br>KR 2861/1 | Terblend (R) S<br>KR 2862 WU* |
|---|-------------------|-----------------------------|-------------------------------|
| Vicat VST/B/50  | °C                | 120                         | 131                           |
| Modulus of elasticity<br>in tension                         | N/mm <sup>2</sup> | 2300                        | 2500                          |
| Failure energy determined on<br>60 mm $0 \times 2$ mm discs | Nm                | 55                          | 50                            |
| at 23°C   |                   |                             |                               |
| at -40°C  | Nm                | 50                          | 35                            |
| Izod notched impact<br>resistance                           | kJ/m <sup>2</sup> | 60 (no break)               | 40                            |
| at 23°C   |                   |                             |                               |
| at -40°C  | kJ/m <sup>2</sup> | 15                          | 12                            |
| Mass density  | g/cm <sup>3</sup> | 1.15                        | 1.25                          |
| UL 94 Fire  | Rating            | 94 HB                       | 94 V-O                        |

\*Containing a flame retardant



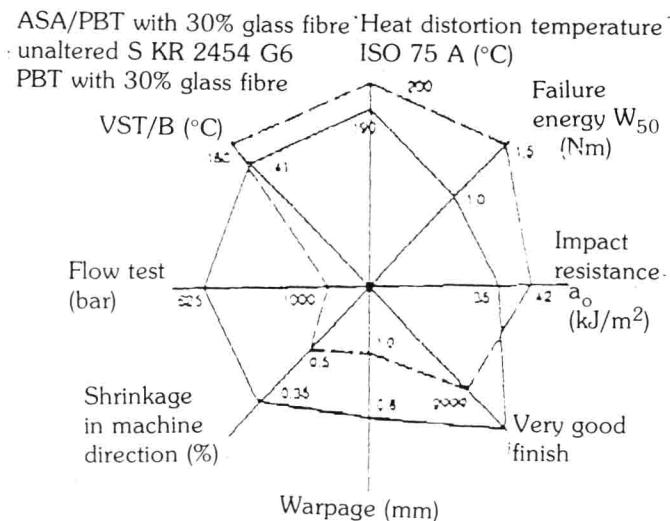


Figure 5

warpage. It also improves the flow (Figure 5), whereas the high resistance typical of PBT are retained. A surprising feature of glass-reinforced ASA/PBT is that it can be moulded to an excellent finish of a quality previously unknown for glass-reinforced products. As a result of this high quality, parts exposed to view do not require any further finishing.

The properties of glass-reinforced ASA/PBT also stand up well to a comparison with other materials. For instance, the mechanical and thermal properties and the finish are decidedly better than those of glass-reinforced ABS or ASA. Its finish is vastly superior to that of glass-reinforced ABS/PC or polycarbonate, and its resistance to environmental stress cracking and its processing characteristics are also better.

Glass-reinforced ASA/PBT is intended for highly stressed housings in automobiles, electrical equipment and the household; examples are circuit breaker mountings and housings, luminaires, and camera cases. A flame-retardant type is being developed to meet demands on fire resistance.

## BLENDS OF POLY(PHENYLENE ETHER) AND HIGH-IMPACT POLYSTYRENE

A motive force in the development of PPE/HIPS blends has been the wide demand for materials, preferably amorphous, with high resistance to heat deformation. Innumerable materials (e.g. ABS/PC, ASA/PC, PBT/PC, PBT, PC, PA and PES) could meet the demand on high resistance to heat deformation, but each has its own particular drawback. For instance, high water absorption, shrinkage or warpage should exclude many heat-resistant materials for applications in which great dimensional stability is specified. In other cases, a tendency to hydrolysis or even the price may prohibit certain products.

PPE has very high resistance to heat deformation, and its glass transition temperature is about 215°C. However, it cannot be processed by the conventional techniques adopted for thermoplastics. This disadvantage can be overcome by blending with Polystyrene. The PPE/PS system represents the seldom case in which the components are miscible (at temperatures below 350°C) in the form of a molecular dispersion over the entire range of compositions; in other words, the blend is single-phase. However, the ductility is inadequate and must be boosted by incorporating rubber in the blend. A very convenient means of achieving this is to use high-impact polystyrene.

## PERFORMANCE CHARACTERISTICS OF PPE/HIPS

The main properties of PPE/HIPS blends include high resistance to heat deformation and great ductility combined with good rigidity. Very rigid products can be obtained by reinforcing with glass fibres.

PPE/HIPS blends are not self-extinguishing and are classified as HB according to UL 94. However, they can quite easily be made self-extinguishing by the incorporation of flame-retardants because of the high proportion of PPE, which itself is self-extinguishing. Thus all the UL fire resistance ratings that are so important in electrical engineering can be attained ranging from HB through V2, V1 and V0 to 5V. A feature of PPE/HIPS blends is that these fire resistance ratings can be achieved by adding comparatively small proportions of organic phosphorus compounds. They can thus entirely dispense with the controversial flame-retardant systems adopted for many other thermoplastics, i.e. those based on halogens and antimony trioxide.

A property that attracts interest in any material is its rigidity at room temperature and on exposure to heat. In Figure 6, the rigidity of unreinforced

Rigidity of unreinforced and glass-reinforced PPE/HIPS blends  
(Polycarbonate for comparison)

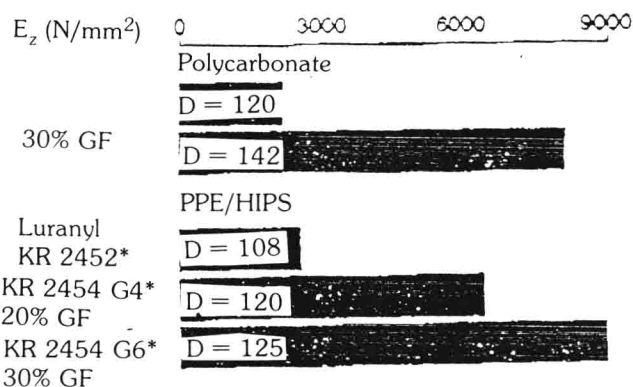


Figure 6

\*Flame-retardant

and glass-reinforced PPE/HIPS is compared to that of the corresponding polycarbonates. In view of the fact that the density of the PPE/HIPS blends is about 10% less, the similarity in rigidity is remarkable. Another advantage that PPE/HIPS has over polycarbonate is its good resistance to hydrolysis.

## **APPLICATIONS FOR PPE/HIPS BLENDS**

We have seen that PPE/HIPS blends are amorphous materials with very high resistance to heat deformation, very low water absorption and good resistance to hydrolysis. As a consequence, they find an extensive field of application in the automobile industry and in electrical engineering. The field is widened by specialties, e.g. glass-reinforced, impact-modified and flame-retardant products. Typical applications in the automobile industry are instrument panels, rear view mirror housings, hot-air ducts, interior trim and wheel caps. In electrical engineering, the applications include housings for office machines, television chassis frames and baseplates, pump casings and transformer housings.

A recent innovation consists of flame-retardant products that are particularly immune to environmental stress cracking. An example is Luranyl KR 2453, a typical application for this is capacitor cases.

The market is currently showing great interest in PPE blends containing modifiers other than HIPS; examples are special block rubbers and partially crystalline polymers, e.g. polyamides. The rubber-modified blends resist heat distortion at temperatures up to 160°C. Their main application is in parts exposed to high temperatures, e.g. shrouds and rotors for hot-air fans.

As will be demonstrated, PPE/PA blends have even higher resistance to heat distortion.

## **POLY(PHENYLENE ETHER)/POLYAMIDE BLENDS**

Nylon is an engineering material of good ductility and resistance to chemicals and can be readily processed. It has the disadvantage that its rigidity decreases drastically on absorption of water. The reasons for this is that the water causes the glass transition temperature in the amorphous zones to drop from 60°C to below 10°C. As a consequence, only the crystalline zones are available to meet any demands on strength and rigidity at the temperatures normally encountered in practice. Another disadvantage of water absorption is its adverse effect on dimensional stability.

Once again, blend technology offers a means of

escaping the predicament. The answer in this case would be to find a suitable amorphous component with a high glass transition temperature and low water absorption; and, one more, poly(phenylene ether) fits the bill. However, nylon and PPE are completely incompatible. The PPE particle size will be much higher than 10  $\mu\text{m}$ , even if the components have been intensively mixed in the form of their melts.

If the products thus obtained are conditioned in the melt, microscopic separation occurs; in other words, the products are of no use as engineering materials. Hence the problem is to obtain a finer, stable phase distribution and to establish a bond between the phases.

It is well known from work on the impact modification of nylon with olefin copolymers that the elastomer components can be readily dispersed in the nylon and bonded at the phase interface if it contains acid groups. The bond may be ionic or effected through amides.

On the other hand, since PPE/PS is a thermodynamically miscible system, recourse may be taken to compatibility promoters, e.g. graft copolymers of nylon and styrene/maleic anhydride (SMA) copolymers.

## **APPLICATIONS FOR PPE/PA BLENDS**

No other thermoplastic engineering materials can touch this extremely interesting blend for its combination of resistance to heat distortion, impact resistance, and rigidity. The main applications of interest are in the automobile sector, particularly for parts of extensive area. The range of applications for this group of products, too, can be greatly widened by specialties, e.g. impact-modified types and products reinforced with minerals, glass fibres, and carbon fibres.

A particularly beneficial property of PPE/PA blends is the outstanding resistance to most solvents. As a result, one or more coats of various types of paint applied to them will adhere firmly and not detract from the high level of mechanical performance. Their high resistance to heat deformation permits them to be admitted after the cationic electrodeposition stage onto coating lines in the automobile industry. It is current practice to apply a very flexible intermediate coat between the plastic and the automotive finish in order to avoid any deterioration in the mechanical properties.

Applications for PPE/PA blends on the automobile sector include wheel caps, radiator grilles, bumpers, spoilers, rearview mirror mountings and air louvers. PPE/PA blends reinforced with carbon fibres are interesting materials for high-quality sports gear (e.g. tennis racquets, golf clubs and fishing rods).

## **OUTLOOK**

New applications, more complicated designs, and more rational or new production methods imposed growing demands on polymer materials. It has been demonstrated that the most rapid and economic means of engineering products to meet market requirements is to modify existing materials or to produce polymer blends. It has given rise to materials that have different, yet attractive properties and they have already secured a firm foothold on the market.

## **ACKNOWLEDGEMENT**

Jan Czerski would like to thank Dr. G. Lindenschmidt, BASF AG for all his help and assistance in compiling this paper.

The development potential inherent in modification and blending is by no means exhausted. On the one hand, the comparatively new products are still open to further optimisation, e.g. by means of processing auxiliaries. On the other hand, the scope available for further development by varying the morphological structure is unusually wide. Thus research and development workers are faced by extremely interesting tasks for the future.

# Specific Intermolecular Interactions in Polymer Blends

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## SUMMARY

The formation of miscible quasi-binary polymer blends is not a commonly observed phenomenon. With a few exceptions, one phase blends will only form if there are some specific intermolecular interactions (SII) between the two components such as hydrogen bonding, ion-dipole, dipole-dipole,  $\pi$ -bonding, or charge transfer interactions. In certain copolymer blends, however, miscibility can be achieved by making use of repulsion effects rather than SII.

## 1. INTRODUCTION

It is rather unfortunate from a technological point of view that attempts to form miscible blends from the commonly available polymers usually results in two phase systems which rarely display any advantageous properties. As the formation of miscible polymer blends is an attractive goal, methods of overcoming the difficulties in producing one phase polymer mixtures have been explored by applying fundamental principles. A suitable point of departure is to consider the simple Flory-Huggins equation for the free energy of mixing  $\Delta G^M$ ,

$$\Delta G^M/NRT = (\phi_1/m_1) \ln \phi_1 + (\phi_2/m_2) \ln \phi_2 + \chi \phi_1 \phi_2 \quad (1)$$

which is the sum of a combinatorial entropy of mixing contribution and an interaction parameter,  $\chi$ , related to the enthalpy of mixing  $\Delta H^M$ . Here  $\phi_i$  is the volume fraction and  $m_i$  the number of chain segments of component  $i$ . For polymers,  $m_i \gg 1$ , and so the favourable entropy term is very small. this means that the sign of  $\Delta G^M$  will depend largely on  $\chi$  (or  $\Delta H^M$ ). Formation of one phase polymer mixtures will then be restricted to systems for which  $\Delta H^M$  is a very small positive, zero, or negative value. For many polymer pairs  $\Delta H^M$  is positive, and stable one phase mixtures are either impossible to obtain or can only be formed from low molar mass components where the residual entropy of mixing is sufficient to overcome the unfavourable  $\Delta H^M$ . The majority of blends which are miscible over a wide concentration and

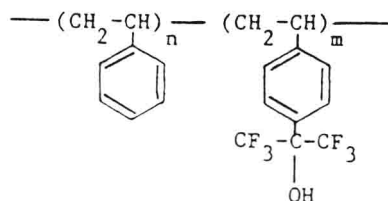
molecular weight range, have an exothermic heat of mixing resulting from some specific intermolecular interactions (SII) operating between the components. A number of these have not been identified and used to enhance polymer miscibility.

## 2. SPECIFIC INTERMOLECULAR INTERACTIONS

### 2.1 Hydrogen bonding

Pearce et al<sup>(1)</sup> have demonstrated that if polystyrene (PS) is modified by introducing a number of hexafluoro dimethyl carbinol groups into the phenyl rings then miscible blends can be formed with polymers containing proton acceptor groups, which are normally immiscible with the unmodified polystyrene.

The modification means that the polystyrene is actually a copolymer (MPS) with the structure (I), but when there are less than 10% of the hydroxyl groups present the glass transition temperatures,  $T_g$ , are similar to polystyrene. Miscible blends of MPS with poly(vinyl acetate), poly(vinyl methyl ether), (PVME), poly(alkyl methacrylate)s and poly(2,6-dimethyl-1,4-phenyleneoxide) (PPO) have been reported.



The main evidence for hydrogen bonding in the blends has come from FTIR spectroscopy. The MPS has two absorption peaks at  $3600\text{ cm}^{-1}$  and  $3520\text{ cm}^{-1}$ , characteristic of the hydroxyl group, which disappear on blending with, for example, poly(alkyl methacrylate)s and are replaced by a new absorption at  $3400\text{ cm}^{-1}$ , see Figures 1 and 2. Similar shifts are recorded in other blends and indicate that H-bonding takes place between the -OH of the MPS and either the carbonyl or the ether groups in the acceptor polymers.

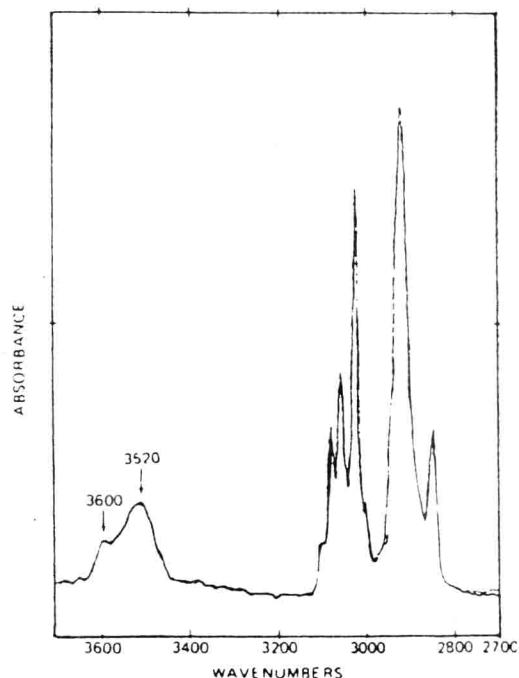


Figure 1 The FTIR spectrum of copolymer MPS with 9.7 mol. % of hydroxyl groups (Reproduced from ref. 1 with the kind permission of Marcel Dekker Inc.)

Examination of the lower critical solution cloud point curves (LCST) for the blends, shows that the temperatures of phase separation are raised as the hydrogen bonding sites are increased. Thus introduction of only 0.4 mol.% hydroxyl into the MPS raises the LCST by about 50°C in the MPS/PVME blends as seen in Figure 3, while 4 mol.% is

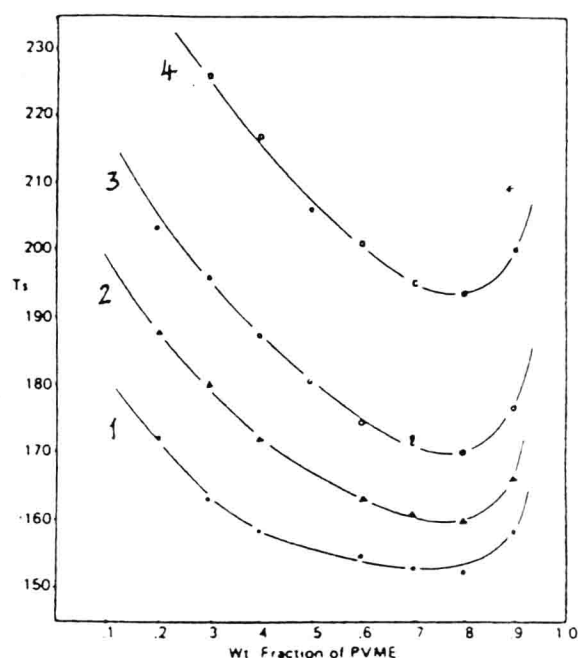


Figure 3 LCST curves for blends of PVME with pure polystyrene (curve 1) and MPS samples: curve 2 - MPS (0.1); curve 3 - MPS (0.2); and curve 4 - MPS (0.4) (Reproduced from ref. 1 with the kind permission of Marcel Dekker Inc.)

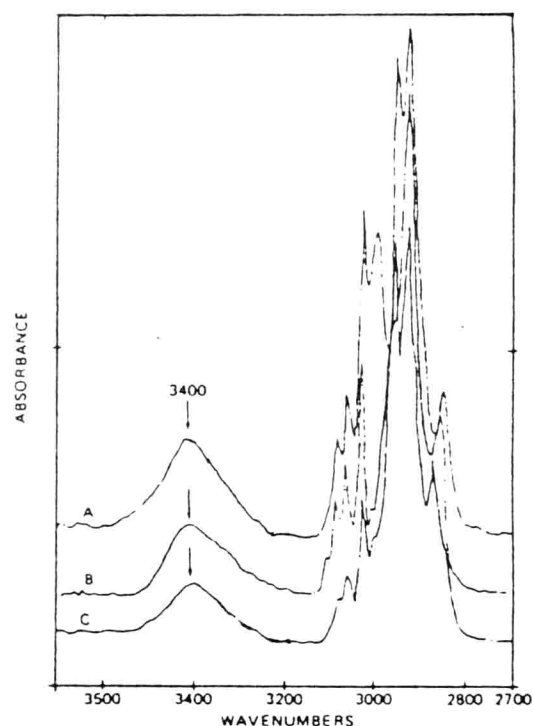


Figure 2 FTIR spectra of blends of MPS (9.7) with A - poly(methyl methacrylate); B - poly(ethyl methacrylate); C - poly(butyl methacrylate) (Reproduced from ref. 1 with the kind permission of Marcel Dekker Inc.)

sufficient to change the immiscible PS/poly(methyl methacrylate) system into one with an LCST >200°C. Thus remarkably low levels of H-bonding sites in the MPS are sufficient to produce miscibility in these systems.

Coleman and his associates<sup>(2,3)</sup> studied blends of poly(vinyl chloride), (PVC), with poly( $\epsilon$ -caprolactone)<sup>(2)</sup>, (PCL), and ethylene/vinyl acetate copolymer, (EVA)<sup>(3)</sup>, using FTIR. Spectral shifts detected for the carbonyl groups in PCL and EVA indicated that this unit was involved in the SII, but it could not be determined unequivocally that the interaction was hydrogen bonding with the methine proton of PVC ( $C=O \cdots H-C-Cl$ ) as the C-H stretching vibration is weak and often submerged in the methylene absorbances, although this was thought to be the most likely explanation. This was resolved by deuteration of the  $\alpha$ -hydrogen in PVC to allow the C-D stretching vibrations to be observed; these were seen to shift in the blends, substantiating the hydrogen bond hypothesis<sup>(4)</sup>. This does not rule out the possibility of dipole-dipole interactions also operating in such systems involving the (C-Cl) and (C=O) groups or perhaps even H-bonding involving the  $\beta$ -hydrogens in PVC.

## 2.2 Ionic and dipolar interactions

Eisenberg and coworkers<sup>(5-8)</sup> have taken a lead



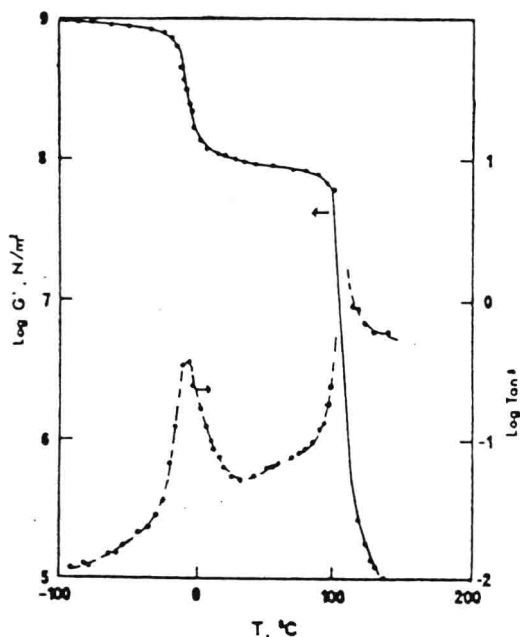


Figure 4 Temperature dependence of the shear storage modulus  $G'$  and the loss tangent  $\tan \delta$  for a 50/50 blend of polystyrene and poly(ethyl acrylate) (Reproduced from ref. 6 with the kind permission of John Wiley and Sons Inc.)

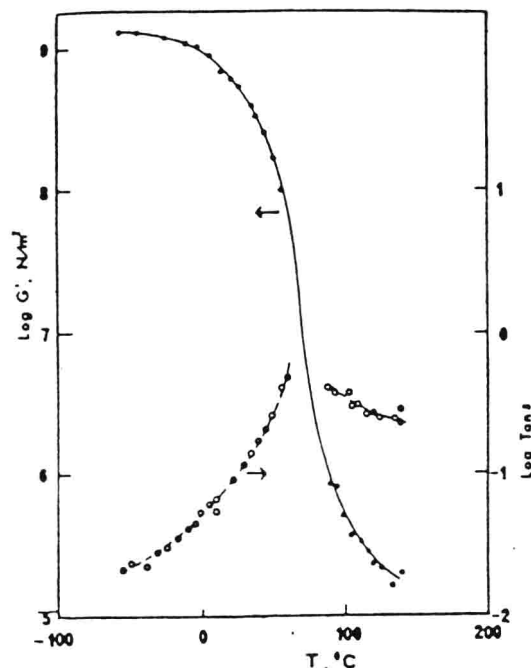
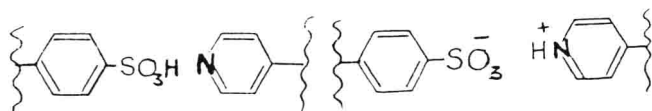


Figure 5 Temperature dependence of the storage modulus  $G'$  and the loss tangent  $\tan \delta$  for a blend of the modified polystyrene and poly(ethyl acrylate) (see text) (Reproduced from ref. 6 with the kind permission of John Wiley and Sons Inc.)

from observations by Michaels and Miekka<sup>(9)</sup> that polymer complexes can form through ionic interactions. They have examined the effect of introducing groups into polymer chains capable of ion-ion, ion-dipole, and dipole-dipole interactions, on the miscibility of normally immiscible polymer pairs.

Poly(ethyl acrylate), PEA, and PS are normally immiscible, but if PS is modified by inclusion of styrene sulphononic acid units in the chain and ethylacrylate is copolymerised with small quantities of 4-vinyl pyridine, then the two resulting copolymers form miscible blends<sup>(5)</sup>. This can be achieved as can be seen from the dynamic mechanical spectra in Figures 4 and 5 of unmodified and copolymer blends, by incorporating at least 5 mol.% of the ( $-\text{SO}_3\text{H}$ ) and 4-vinyl pyridine units respectively in each copolymer. The SII in this system is a coulombic attraction, but the mere introduction of any coulombic force into the polymer can be insufficient to promote miscibility. This was demonstrated by mixing poly(styrene-co-methacrylic acid) with poly(ethyl acrylate-co-acrylic acid) which proved to be an immiscible system, so introduction of carboxyl groups only did nothing to enhance the miscibility.



Strong coulombic interactions between an acidic group and a non ionic basic group provide an effective means of increasing the miscibility in polymer blends, but weaker ion-dipole interactions can also prove useful<sup>(7)</sup>. Poly(ethylene oxide), (PEO), and PS form two phase mixtures but this can be improved by incorporating up to 10 mol.% of the lithium salt of methacrylic acid in the polystyrene chain. A greater level of miscibility is obtained when this ionomer is blended with PEO which is encouraged by the ion-dipole interactions in the system.

Dipole-dipole interactions<sup>(10-12)</sup> have also been identified as SII in certain blends. Challa and Roerdink<sup>(13)</sup> found evidence for the interaction between the carbonyl groups in poly(methyl methacrylate) and the dipoles of the poly(vinylidene fluoride) segments, in blends of these two components. A similar interaction has been suggested as the operative SII in blends of poly(vinyl chloride) and several other polymers containing carbonyl units<sup>(8,10,12)</sup>.

### 2.3 Interactions with $\pi$ electron systems

FTIR has been found to be a useful tool in identifying SII in polymer blends. The digital subtraction method leaves a residual spectrum from which band broadening or shifting can provide information on the groups involved.

Studies on PS/PPO blends<sup>(14)</sup> have revealed the presence of strong favourable dispersion forces between the phenyl rings of PS and PPO. Several workers<sup>(15-18)</sup> have used the technique to examine PS/PVME blends and have found evidence for an interaction between the  $\pi$  electrons of the phenyl ring in PS and the lone pairs of the ether oxygen in PVME. Garcia<sup>(17)</sup> demonstrated the involvement of the latter by observing spectral changes when the temperature was raised above the LCST. The ether absorption bands at  $1183.6\text{ cm}^{-1}$  and  $1107.6\text{ cm}^{-1}$  increased in intensity above the LCST after remaining essentially constant at lower temperatures. This indicated that the ether group had gained rotational freedom above the LCST due to elimination of the SII. The strength of the interaction was estimated to be  $6300\text{ Jmol}^{-1}$ .

Similar conclusions concerning the origins of the SII in PS/PVME blends have been arrived at by Porter et al<sup>(19)</sup> from  $^1\text{H}$  nmr and  $^{13}\text{C}$  nmr studies. The miscibility in PS/PVME blends is known to be solvent dependent and casting from  $\text{CHCl}_3$  results in a two phase structure with no evidence of SII<sup>(15)</sup>. Porter's work has shown that there could be competitive interaction between the  $\pi$ -electron system and the electron deficient hydrogen in  $\text{CHCl}_3$  which would prevent efficient mixing of the two polymers. This is certainly a possibility and highlights the importance of solvent in such cases.

## 2.4 Charge-transfer complexes

The use of electron donor-acceptor groups to form intermolecular charge-transfer complexes in polymer blends was first studied by Sulzberg and

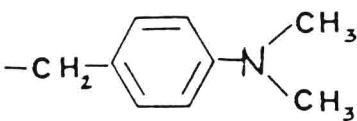
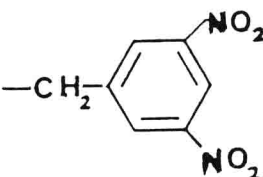
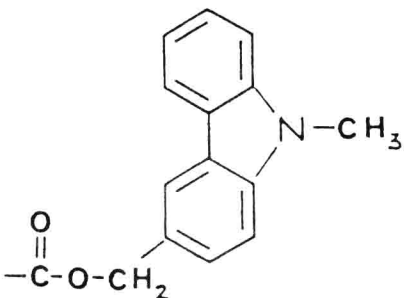
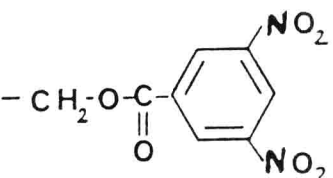
Cotter<sup>(20)</sup> who incorporated donor and acceptor residues into the main polymer chain. More recently polymers containing pendant donor and acceptor groups have been prepared<sup>(21,22)</sup> using the type of group shown in Table 1.

Blends of type 1 polyesters, each containing high levels of donor and acceptor groups were not completely miscible but did show some improvement due to the formation of charge-transfer complexes. Melt mixing of type 2 polyacrylates was not successful, but (1:1) mixtures cast from tetrahydrofuran solutions gave homogeneous one phase blends. Dynamic mechanical studies indicated that crosslinking, through the charge-transfer complex, had occurred in the blend.

## 3. INTRAMOLECULAR REPULSIVE INTERACTIONS

The systems mentioned so far have relied on the presence of intermolecular interactions to promote miscibility. In blends where the components are statistical copolymers one should also consider the effect of intermolecular interactions between the different monomeric units comprising the copolymer. Interesting examples have been reported where a homopolymer such as PMMA, which is neither miscible with PS nor polyacrylonitrile, forms miscible blends with a styrene/acrylonitrile copolymer<sup>(23)</sup> within a restricted range of copolymer compositions. This 'miscibility window' has been reported in several systems; PPO blends with copolymers of o- and p-chlorostyrene and other halogenated styrenes<sup>(24,25)</sup>, PVC with EVA<sup>(26)</sup> and with butadiene/acrylonitrile copolymers<sup>(27)</sup>, are a few. Karasz and MacKnight<sup>(28)</sup>, Kambour et al<sup>(29)</sup>

Table 1

| Type | Donor   | Acceptor   | Polymer    |
|------|---|--|------------|
| 1    |  |  | Polyesters |
| 2    |  |  | Acrylates  |

and Paul and Barlow<sup>(30)</sup> all agree that the restricted miscibility in these systems is a result not of SII but of the repulsive forces in the copolymer, which cause it to 'dissolve' in a polymeric solvent when the net forces of interaction are most favourable. This is in many ways similar to the dissolution of a polymer in a liquid co-solvent pair where the co-solvent liquids often have an unfavourable free energy of mixing<sup>(31)</sup>. For a binary mixture of two statistical copolymers, one composed of monomers (1) and (2), and with a composition  $[(1)_\alpha (2)_{(1-\alpha)}]$ , and a second with monomers (3) and (4) of composition  $[(3)_\beta (4)_{(1-\beta)}]$ , where  $\alpha$  and  $\beta$  are volume fractions, the interaction parameter for the blend is given by<sup>(28)</sup>,

$$\chi_{\text{blend}} = \alpha\beta\chi_{13} + \beta(1-\alpha)\chi_{23} + \alpha(1-\beta)\chi_{14} + (1-\alpha)(1-\beta)\chi_{24} - \alpha(1-\alpha)\chi_{12} - \beta(1-\beta)\chi_{34} \quad (2)$$

Here  $\chi_{ij}$  are the component binary interaction parameters.

This can be simplified for the special case of a homopolymer (1) and a copolymer (3) and (4) to

$$\chi_{\text{blend}} = \beta\chi_{13} + (1-\beta)\chi_{14} - \beta(1-\beta)\chi_{34} \quad (3)$$

These equations have the same general form as those proposed by Kambour<sup>(29)</sup>, and Paul and Barlow<sup>(30)</sup> and they show that it is possible to obtain a favourable value of  $\chi_{\text{blend}}$  from a combination of  $\chi_{ij}$  parameters each of which can be unfavourable to mixing. Obviously a large (repulsion) value for  $\chi_{34}$  in equation (3) will make the existence of a 'miscibility window' more likely. A more sophisticated version of equation (2) has been developed by Koningsveld and Kleintjens<sup>(32)</sup> which introduces parameters to account for the interacting surface areas of the repeat units. This appears to be a very promising development and a fruitful area for further work.

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