



# **Polymer Blends**

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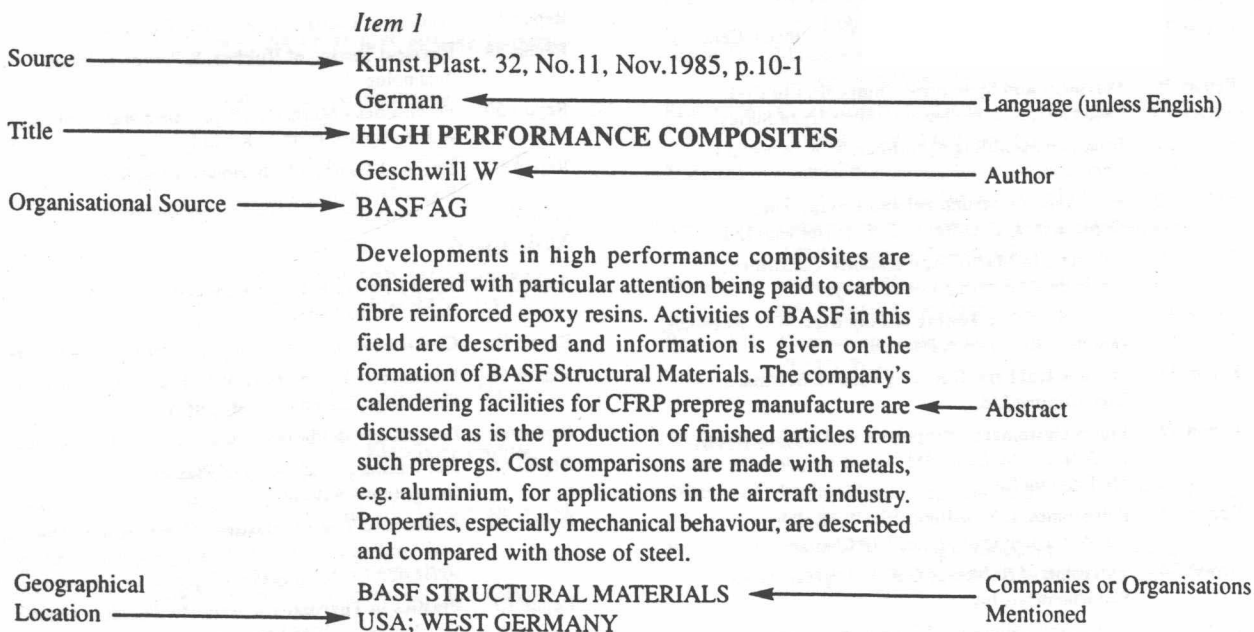
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# 1 INTRODUCTION

## 1.1 A Historical Perspective

Alexander Parkes, an artist from Birmingham, patented the first polymer blends in the ninth year of the reign of Queen Victoria (a.1, a.2). The document describes reactive blending of two isomers, soft *cis*-1,4-polyisoprene (natural rubber, NR) and rigid *trans*-1,4-polyisoprene (gutta percha, GP). These components were softened in a mixture of CS<sub>2</sub> with SCl<sub>2</sub>, then milled with SCl<sub>2</sub> in a hot rubber mill. The blending resulted in partially crosslinked (co-vulcanised) materials whose rigidity was mainly controlled by composition. The blends had many applications, viz. picture frames, tableware, ear trumpets, sheathing of the first submarine cables, fabric waterproofing, etc. This very first patent on polymer blends is evidence that the fundamentals of the blending strategy and methods have changed little during the last 150 years. Today it is also based on the selection of components with complementary properties, then generation of the desired, stable morphology by means of reactive compatibilisation.

The polymer industry started in the beginning of the 19th century with rubbers and thermosets as the main materials. The next century witnessed growth of synthetic polymers unprecedented in the history of materials (from 30 kton in 1900 to 151,000 kton in 1999), dominated by thermoplastics. The growth of consumption and that of demand for better products led to new polymers as well as to prominence of the multiphase systems: alloys, blends and composites. During the 1990s about 38 wt% of all plastics was used in composites and from 36 to 75 wt% in blends. The latter estimate is more difficult as it depends on certain assumptions. For example, usually polyolefin manufacturers blend different lots of materials to maintain specification. Furthermore, often alloying takes place in a reactor(s), viz. thermoplastic olefinic elastomers (TPOs), polyolefin (PO) with bimodal molecular weight distribution (MWD), etc. These products are sold as single resins, while they actually comprise several macromolecular specimens (a.3). Treating dry and reactor blends as homopolymers leads to the lower estimate, when these are considered blends the upper estimate is obtained.

Historically the emphasis on the type of blends produced has varied. The first commercial thermoplastics (e.g. polystyrene (PS) in 1915,

polymethacrylate (PMA) in 1927, polyvinyl acetate (PVAc) in 1928, polyvinyl chloride (PVC) in 1931) had poor mechanical properties. The initial reason for blending was to toughen the rigid resins or to enhance rigidity of the soft ones. The discoveries of high impact polystyrene (HIPS, polystyrene toughened with rubber) and polymeric plasticisers for PVC were the important steps in the evolution of the industry (3, a.3).

In the 1960s, after the accidental discovery of polyphenylene ether (PPE) by Allan Hay, and the subsequent commercial success of this polymer with HIPS (by General Electric under the trade name Noryl), the emphasis for blending shifted to improving processability of the emerging, high temperature polymers. In the 1980s, under the influence of the automotive industry, the aim was to balance the performance characteristics, i.e. not only the mechanical properties and processability, but also cost, paintability, solvent and scratch resistance were important. As a result, complex blends with up to six polymeric components have been developed (111, a.3).

This review focuses on developments in the last six years or so, i.e. from 1995 onwards. The earlier work has been discussed in several monographic and edited books (e.g. 3, 552, 553, 554, a.3 - a.12). As will be evident from the remaining part of this review, during this last part of the 20th century there was a significant evolution in the technology of blends. There is progress in understanding the behaviour of polymer blends, especially the thermodynamics and rheology. From the technological point of view, the reactive compatibilisation of multicomponent blends dominates. Blending technology can improve resin performance by generating optimal properties at lower cost, extending expensive engineering resins with less costly polymers and reducing the number of grades that need to be produced and stored. Commercially, blends of metallocene resins, liquid crystal polymers and biodegradable resins have moved to the forefront. There is also a growing need for polymer recycling: for this purpose, the technology of blends offers well-developed methods (a.13).

## 1.2 Terminology

In this review the following terminology will be used (a.3, a.5, a.10, a.12):

- *Polymer blend*: A mixture of at least two polymers or copolymers, comprising more than 2 wt% of each component.

- *Miscible polymer blend*: Polymer blend, homogeneous down to the molecular level. In thermodynamics a miscible blend is one associated with a negative value for the free energy of mixing:

$$\Delta G_m \approx \Delta H_m \leq 0$$

and a positive value of the second derivative of concentration:

$$\partial^2 \Delta G_m / \partial \phi^2 > 0.$$

(where  $\Delta G_m$  is the free energy of mixing,  $\Delta H_m$  is the heat of mixing and  $\phi$  is the volume fraction of the matrix polymer)

Microscopically, a miscible blend is a blend whose domain size is comparable to the dimension of the macromolecular statistical segment.

- *Compatible polymer blend*: Term to be avoided! At best a utilitarian, non-specific term indicating a marketable, visibly homogeneous polymer mixture, with enhanced performance over the constituent polymers.
- *Polymer alloy*: Immiscible, compatibilised polymer blend.
- *Compatibilisation*: A process of modification of the interfacial properties in an immiscible polymer blend, resulting in reduction of the interfacial tension coefficient, stabilisation of the desired morphology against the processing stresses and improving interaction between phases in the solid state, i.e. formation of a polymer alloy.
- *Reactive compatibilisation*: Compatibilisation accomplished during reactive processing, e.g. mixing, compounding, extrusion forming, injection moulding, etc.
- *Interphase*: Third phase in binary polymer alloys, enhanced by inter-diffusion or compatibilisation. Thickness of this layer varies with the blend components and compatibilisation method from 2 to 60 nm.

## 2 THERMODYNAMICS

The thermodynamic description of polymer blends has its origins in observations of hydrocarbon polymers

dissolved in hydrocarbon solvents, which phase separate at high temperatures. A lattice theory of molecule arrangements in a polymer solution, combined with factors allowing for the heat of mixing approach, resulted in what became known as the Huggins-Flory theory of polymer solutions, later extended to blends. The key element of the theory is the binary polymer-polymer interaction parameter,  $\chi_{12}$ , which effectively is a complex function of all variables: polymer structure, molecular weight and distribution, blend composition, pressure, temperature, stress field, etc. In spite of the complexity of this 'parameter' conceptually it is simple to understand and it has been incorporated into several newer theories (a.3, a.5, a.12).

In the late 1980s Painter, Coleman and their collaborators modified Huggins-Flory theory by explicitly incorporating the effects of specific interactions (hydrogen bonding, ion-ion, ion-dipole, charge transfer,  $\pi$ - $\pi$ -electron interactions, etc.), which provide a negative contribution to the free energy of mixing. Interactions of the van der Waals type are accounted for by the solubility parameter difference. The magnitude of the specific interactions was determined by Fourier transform infrared spectroscopy (FTIR). Furthermore, it was demonstrated that low molecular weight mixtures could be used to predict the phase behaviour of analogous polymer blends. For example, poly(4-vinylphenol) PVPh/PVAc and PVPh/ethylene-vinyl acetate (EVAc) blends were studied (47).

More satisfactory is the lattice-hole theory, which, for liquid mixtures, provides a good description of the thermodynamics across the whole range of variables. This theory allows for a temperature and volume dependent fraction of vacancies or holes in a lattice of sites. The theory employs two binary parameters: energetic  $\epsilon_{12} = \delta_\epsilon \sqrt{\epsilon_{11}\epsilon_{22}}$  and volumetric  $v_{12} = \delta_v [v_{11}^{1/3} + v_{22}^{1/3} / 2]$ , where  $\delta_\epsilon$  and  $\delta_v$  are characteristic constants of the system, usually equal to  $1 \pm 0.13$  (383, a.14). The subscripts 1 and 2 indicate the first and the second components of the mixture. The interaction parameters  $\epsilon_{ij}$  and  $v_{ij}$  are inherent to the Simha-Somcynsky model. (Note: these authors assumed validity of the Lennard-Jones '6-12' potential function. Thus the two parameters correspond to the characteristic constants of the '6-12' potential.)

More recently there has been a growing emphasis on numerical simulation (Monte Carlo or molecular dynamics) of the behaviour of polymer blends (61). These are based on the atomistic approach that considers the configuration of macromolecules. A similar approach has been adopted for modern theories, e.g. the polymer reference interaction site model

(PRISM, 472) or the lattice cluster theory (331). By contrast to the older theories, the new approaches take into account the structural details of polymeric molecules, viz. bond lengths and angles, chain conformation statistics, interaction potentials of one type or another, etc. (549).

For example, lattice cluster theory (originally developed for di-block copolymers) can be generalised to include the effects of trans-gauche energy differences, chain stiffness, monomer molecular structures, energetic asymmetries and non-random mixing on the miscibilities of binary polymer blends. The combination of these factors within one theory was used to evaluate the dominance of different physical factors on the miscibility of PO blends. The lattice cluster theory computations demonstrated the importance of entropic (stiffness disparities) and enthalpic factors (solubility parameter models), combined with other factors arising from monomer structure (236).

Extensive work has also been carried out at Exxon and collaborating laboratories to resolve the intricacies of miscibility in PO blends. The data were determined using either small angle neutron scattering (SANS), cloud point curve determination, or pressure-volume-temperature (PVT) measurements (74, 98, 126, 127). The cloud point is the temperature at which phase separation commences generating a cloudy appearance, this can be plotted against the wt% of one polymer in the binary blend to give a cloud point curve.

## 2.1 Miscibility

Miscibility is a thermodynamic concept, pertinent to the liquid or glassy state. Its thermodynamic definition is unambiguous. However, there is a significant amount of discussion as to methods of detecting miscibility and the size of heterogeneity in the phase dispersion of miscible blends. In polymer blends immiscibility is a rule while miscibility is a rare and precarious state, determined by a well defined range of variables, viz. molecular parameters, concentration, pressure, temperature, stress level, etc.

Opacity provides limited information - light scattering can be detected when the size of heterogeneity (i.e. at what scale the continuum shows compositional disunity) is already relatively large, viz.  $\geq 100$  nm, and the difference in refractive index of the polymer components of the blend is greater than about 0.01.

The glass transition temperature ( $T_g$ ), is relatively simple to measure. Detection of a single  $T_g$  in a blend

has been used as a test for miscibility. However,  $T_g$  is an insensitive measure when the amount of the dispersed component is less than about 10 wt%. This method is also not reliable for blends containing polymers whose  $T_g$ s differ by  $\leq 10$  °C. Furthermore, it has been shown that the  $T_g$  is not sensitive to the thermodynamic miscibility of components, but rather to the degree of dispersion. Thus, a single  $T_g$  has been detected in immiscible blends when the domain size was small enough,  $d \leq 30$  nm. This degree of dispersion may indeed lead to blend processability comparable to that of homopolymers, but domain size is larger than that observed in blends that obey the thermodynamic definition of miscibility:  $\Delta G_m \approx \Delta H_m = 0$ , and  $\partial^2 \Delta G_m / \partial \phi^2 > 0$ , viz.  $d = 2 - 3$  nm.

For detecting miscibility advanced scattering methods have been used, such as high resolution nuclear magnetic resonance (NMR) techniques, NMR-spin diffusion, non-radiative energy transfer, excimer fluorescence, thermally stimulated depolarisation current, SANS and FTIR. For example, simple NMR measurement of the spin-lattice relaxation times is able to distinguish a domain size of 2-3 nm. Thus blends of PVC with polymethyl methacrylate (PMMA) were found to be homogeneous at 20 nm scale, but heterogeneous at 2 nm. After deuteration of PMMA the miscibility improved to 1-2 nm. Blends of styrene-acrylonitrile copolymer (SAN) with PMMA were found to be heterogeneous at a scale of 2 to 15 nm. Homogeneity down to the 2 nm level was reported in polyvinylidene fluoride (PVDF)/PMMA and polycaprolactam (PCL)/PVC blends (a.12, a.15).

During the last few years the miscibility of older systems has been investigated further, viz. PS/polyvinylmethylether (PVME) (14, 96, 183, 207, 212, 220, 253, 259, 284, 419, 534), PS/poly(2,6-dimethyl 1,4-phenylene ether (PPE) (115, 359, 454, 498), PVC/PMMA (44), polyamide (PA)/PA (431, 432, 500), polycarbonate (PC)/acrylonitrile-butadiene-styrene copolymer (ABS) (271), or polyethylene glycol (PEG)/PMMA (367, 368, 438).

Small molecule probes can be used in gas/vapour sorption experiments to determine the polymer-polymer interaction parameter  $\chi_{12}$ . CO<sub>2</sub> sorption was used in PS/PPE blends to confirm its small negative values, that change with blend composition (359).

Blends of PS with PVME were reported to phase separate when spin cast into films of thickness comparable to the radius of gyration (207, 212, 534). In the latter paper phase separation by spinodal decomposition (see **Section 2.2**) was observed.



Similarly, the effect of polymer orientation on miscibility has been studied for PS/PVME blends (419).

Miscibility of several other blends has been analysed, viz. polyethersulfone (PES)/phenoxy resins (437), polyetherimide (PEI)/polyimide (PI) (251), PVPh/PVAc (256), PVPh/PMMA (317), PC/polyvinylpyrrolidone (PVP) (229), ethylene-vinyl acetate copolymer (EVAc)/PVAc (26), PMMA with alternating ethylene-tetrafluoroethylene copolymer (245), PMMA with cellulose acetate-phthalate (8), PS/poly(cyclohexyl methacrylate) (396), amorphous polyethylene terephthalate (PET)/polyethylene naphthalate (PEN) (99), PEN/PEI (148), PS/poly(styrene-co-4-bromostyrene) (206), PS/poly( $\alpha$ -methylstyrene) (96), PC/liquid crystal polymer (LCP) (289, 369), polyvinylidene fluoride (PVDF)/PMA (456), PMA/PVAc (515), poly-phenyl vinyl sulfoxide with PVAc, polymethyl-oxazoline or PVP (166), PVAc/poly(hydroxybutyrate-co-hydroxyvalerate) (152), polyvinyl alcohol (PVAI)/poly(hydroxybutyrate) (533), poly(cyclohexyl acrylate) with poly(2-bromostyrene) (235), PEG/PVAI (57), poly(cyclohexyl methacrylate) with poly(4-methylstyrene) (58), etc.

It is known that addition of a polymeric co-solvent may lead to formation of single-phase blends, viz. phenoxy (polyhydroxyether of bisphenol A) for PC/thermoplastic polyesters (PEST) systems (see also (37)). Miscibility data for three-component blends were recently reported for PEG/poly(epichlorohydrin)/poly(3-hydroxybutyrate) (30) and PC/PVDF/PMMA (311).

Due to the benefits of metallocene technology, it is possible to prepare polyolefin molecules with well-defined configuration, molecular weight and relatively narrow molecular weight distribution ( $M_w/M_n \approx 1.9$ ). Furthermore, the technology has moved towards the production of reactor blends and POs with bimodal molecular weight distribution that require homogenisation. For these reasons there is an intensive international effort for better understanding the fundamentals of PO miscibility. It has been found that a small change in the copolymer composition may lead to a large effect on morphology, and thus properties (viz. around 1996 Montell introduced a PP High Alloy comprising 65 wt% of elastomer (ethylene-propylene copolymer, EPR) and polypropylene (PP), that contains 3% of ethylene). For example, miscibility of PP with PO block copolymers or with polyethylene (PE) has also been investigated (163, 203). Metallocene-type copolymers of ethylene-hexene and ethylene-butene were reported miscible (127, 252).

The effects of pressure and temperature on PO blend miscibility have been studied. For blends with upper critical solution temperature (UCST), (that is phase separation on cooling) or lower critical solution temperature (LCST) behaviour (phase separation on heating), generally the critical temperature ( $T_c$ ) increases with pressure. Therefore increasing pressure usually reduces miscibility in UCST blends and increases it in LCST blends. Increasing pressure increases density which in turn decreases intermolecular separation and increases the interaction between polymers, which may or may not favour mixing. The effects of pressure and temperature on the interaction strength in PO blends was found to differ for the systems with UCST and LCST behaviour. For UCST systems, the interaction strength was found to depend on density. For LCST systems a more complex relation was found (126).

High pressure and temperature miscibility of PP with high density polyethylene (HDPE) was postulated on the evidence of the spinodal structure of injection moulded blends (138). Blends of polyisobutylene (PIB) with head-to-head PP were examined using solid-state NMR and found to be miscible, with the segmental concentration fluctuation on the scale of  $\leq 3.5$  nm (74).

It is noteworthy that independent of the nature of the blend, for the optimum performance, a level of microheterogeneity is necessary to preserve the individual performance characteristics of the polymeric components. Nearly all commercial blends (excepting PVDF with PMMA) are immiscible. One tends to study miscibility not to develop single-phase commercial blends, but rather to control the level of heterogeneity, most often by designing better compatibilisers and compatibilisation strategies.

## 2.2 Phase Separation

Miscibility is rarely observed in polymer blends. When a miscible system is subject to a large enough change of independent variables (e.g. composition, temperature or pressure) it phase separates entering either: (1) the metastable or (2) the spinodal region. In case (1) the phase separation occurs by a mechanism resembling crystallisation: a nucleation followed by growth of the phase separated domains, hence known as nucleation and growth (NG). In case (2) the phases separate spontaneously with concentration fluctuations throughout the whole volume, which results in the formation of co-continuous morphology. This process is known as spinodal decomposition.



The spinodal decomposition structure offers ultimate control of the degree of dispersion. The properties of blends with spinodal decomposition provide an ideal way of combining the inherent properties of both polymeric ingredients. Furthermore, owing to the lock-in structure (the structure is immobilised by entropic effects of the phase co-continuity), these blends require less compatibilisation. There are several routes to cause spinodal decomposition: casting from a co-solvent solution (68, 73, 212, 464); changing temperature or pressure (51, 83, 128, 198, 255, 385, 395, 424, 544, 543); imposition of stresses (5, 51, 83, 128, 138, 198, 385, 543); surface energy in thin films (2, 67, 212, 548); or a chemical reaction (135, 198, 209, 544).

For phase separations caused by variation of temperature, two major types of phase diagram are recognised: with either UCST or LCST. In the former case, lowering temperature worsens the miscibility, whereas in the latter it improves. Most polymer blends show LCST behaviour, while UCST behaviour dominates solutions. The difference originates in the type of inter-species interactions. Since miscibility in most blends (excepting PO) originates from specific interactions that decrease with increasing temperature, LCST behaviour is expected. In solutions, the miscibility is entropy driven, thus relatively weak intra-species interactions by dispersive forces suffice. As the temperature increases the magnitude of these dispersive, intra-species interactions is reduced and the miscibility improves (552, a.5).

Phase separation with LCST behaviour in PS/PVME has been studied by one- and two-dimensional  $^{129}\text{Xe}$  NMR spectroscopy (the  $^{129}\text{Xe}$  is dissolved in the blend) (259), as well as by rheology, optical and electron microscopy, and solid state NMR (14, 51, 96, 253). Blends of PVDF/PMA show miscibility that decreases as the head-to-head content of the PVDF increases up to 24% – above this limit the blends are immiscible (456). The miscible systems show LCST. Blends of poly( $\alpha$ -methyl styrene) with poly(cyclohexyl methacrylate) were studied by thermal analysis, optical microscopy and scanning electron microscopy (SEM). The results showed them to be miscible with non-specific intermolecular interactions, but showing LCST (58). Blends of poly( $\alpha$ -methyl styrene-co-acrylonitrile) with PMMA were extensively studied in the IUPAC Working Party Round Robin project. These blends also show LCST (95).

As well as varying temperature, the effects of pressure variations on miscibility can also be measured. Two factors must be considered: the free volume and the heat of mixing. Since pressure reduces the free volume

contribution, for most blends the miscibility increases with pressure. When  $\Delta H_m < 0$  the miscibility is enhanced by compression, whereas when  $\Delta H_m > 0$  it is reduced. The effect is usually measured as a change of the critical temperature with pressure. For polymer blends the gradient is usually positive, e.g. in PPE/styrene-fluorostyrene copolymer (F-PS)  $d(\text{UCST})/dP = 64$  to  $108\text{ }^\circ\text{C/GPa}$ , and in PS/PVME  $d(\text{LCST})/dP = 300\text{ }^\circ\text{C/GPa}$ . In polyetheramide (PEA)/polyvinyl fluoride (PVF) the LCST showed a complex dependence.

Interesting aspects of phase separation have been discussed in several other papers (10, 18, 25, 36, 39, 51, 59, 68, 73, 82, 84, 90, 148).

There is growing commercial interest in the new polymeric systems comprising nano-size reinforcing particles, the so-called nanocomposites. The current experimental nanocomposites usually comprise exfoliated clay particles. However, research is being conducted on multi-component polymer blends as a means of producing this type of material with specific properties, e.g. electrical or optical. Controlled phase separation (mainly from a solution) has been explored (7, 19). For example, blends have been produced with nanoscale fibrous liquid crystal domains which give improved mechanical properties (140). Blends of diverse polyhedral oligomeric silsesquioxanes (POSS) having 1-2 nm large  $\text{Si}_8\text{O}_{12}\text{R}_8$  cages are also being explored (54, 81).

## 2.3 Interfacial Properties

The simplest dispersed binary blend is characterised by the presence of one interface and three phases: the dispersed phase, the matrix and the interphase between them. The interface is a mathematical concept, a boundary between two phases characterised by the interfacial tension coefficient,  $\gamma_{12}$ . The interfacial tension (surface energy/area) determines the ease of dispersion and often the shape of the dispersed phase. By contrast, the interphase is a well-defined volume where the segmental concentration of either polymer varies from 100 to 0%. Theories and experiments demonstrate that the thickness of the interphase ( $\Delta l$ ) = 2 to 60 nm, and varies with the magnitude of the thermodynamic interactions, and with the contact time as well as with the compatibilisation method. In well-compatibilised blends the volume of the interphase may exceed that of the dispersed phase. Compatibilisation controls  $\gamma_{12}$  and the properties of the interphase and is thus of paramount importance in the technology of polymer blends.

Owing to the high viscosity ( $\eta$ ) of industrial polymer melts there are only a few methods for the measurement of  $v_{12}$  in polymer blends. These are usually divided into equilibrium and dynamic techniques. Equilibrium methods (e.g. pendant, sessile, and spinning drop) have been used with low molecular weight homologues of the polymer blend components. The methods are based on the analysis of the drop shape at equilibrium of one polymer dispersed as threads in a matrix polymer and subject to disturbance until a drop forms. Depending on the ratio of  $v_{12}/\eta$ , the equilibrium shape is obtained after minutes or days. In the spinning drop method the equilibrium deformation imposed by the centrifugal forces requires less time. However, the technical difficulties of constructing an apparatus suitable for handling high viscosity polymer melts make it too elaborate for common use. In short, the equilibrium methods are too slow or too elaborate for the measurements of  $v_{12}$  in industrial polymer blends (155).

The dynamic methods are based on the time evolution of a fluid element shape from deformed toward an equilibrium form; the thread break-up (290) and the deformed drop retraction method (199, 273, a.16) are of main interest. In both cases  $v_{12}$  is calculated by fitting the observed shape evolution to theoretical equations. The capillary break-up method is based on Tomotika's theory (the zero-shear viscosity of the polymers under the processing conditions must be known).

The deformed drop retraction method requires an optical microscope with a hot stage and the means to deform a drop either in shear or (preferably) in elongation. This method is particularly useful for the binary polymer blends, e.g. polymer-1 in polymer-2 or polymer-2 in polymer-1. Measurements of industrial polymer mixtures led to a good agreement with values obtained from the thread break-up method. For the first time the deformed drop retraction method enables the measurement of  $v_{12}$  in polymeric blends as a function of the contact time between the two polymers ( $t_c$ ), hence unambiguously determining dynamic and equilibrium values of  $v_{12}$ . For example, in low density polyethylene (LDPE)/PS  $v_{12}$  decreased from 6.9 to 5.2 mN/m as  $t_c$  increased from 12 to 75 min. The reduction of  $v_{12}$  follows the theoretically predicted  $v_{12}(t_c) \propto t_c^{1/4}$  dependence (27). The change originates in the thermodynamically driven migration to the interphase of chain-ends, low molecular weight fractions and additives, as well as thermal degradation products. The contact time dependence of  $v_{12}$  explains some of the differences reported for the data obtained using different measuring methods, viz. pendant drop, capillary break-up, or the ellipsoid retraction technique (199, 273, a.16).

Less information is available on the determination of the interphase thickness,  $\Delta l$ . Several techniques have been used to determine its value, such as electron microscopy (mainly transmission electron microscopy (TEM) or atomic force microscopy (AFM)), ellipsometry, X-ray and light scattering.

The most successful has been the ellipsometric method developed by Takashi Inoue (100, 141, 269, 441, 511). The measured values of  $\Delta l$  varied with the system and compatibilisation from 2 to 60 nm. In agreement with theory, in immiscible blends  $\Delta l = 2$  to 3 nm. Compatibilisation by addition of a compatibiliser increases  $\Delta l$  to 4 to 6 nm. Reactive compatibilisation is responsible for very large values of  $\Delta l = 20$  to 60 nm (confirmed by several techniques).

Interphase thickness has also been studied by small angle X-ray scattering in PE/ABS and PS/PMMA blends (213). Interphase characterisation by other means, e.g. by neutron reflectivity with low-energy forward-recoil spectrometry, has also been discussed (25, 206).

## 2.4 Crystallisation

In polymer blends crystallisation adds an extra layer of complexity to morphology and thus performance.

### 2.4.1 Miscible Blends

In the simplest case, a crystallisable miscible blend, the system can comprise amorphous (A) with crystalline (C) polymers in the combinations A-1 with C-2, A-2 with C-1, or C-1 with C-2. In this nomenclature, a polymer with index '1' indicates a higher transition temperature (either  $T_g$  in A or melting point ( $T_m$ ) in C) than one with index '2'. Thus in an A-1/C-2 blend, polymer A-1 will vitrify before polymer C-2 has a chance to crystallise. In the second case C-1 will crystallise before A-2 has a chance to become glassy. In the third case C-1 starts crystallising first, modifying the crystallisation of C-2.

The presence of an amorphous component can either increase or decrease the tendency of component C to crystallise, depending on the effect of the composition on the  $T_g$  and  $T_m$  of the components. Furthermore, the morphology of A/C blends is influenced by the crystallisation conditions, chain mobility and microstructure, and blend composition (82, 99, 152, 164, 187, 456, 457).