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POLYMER BLENDS : FROM MOLECULAR STRUCTURE THROUGH MORPHOLOGY TO CONTROLLED BULK PROPERTIES

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Summary - It is shown how the morphology and the bulk physico-mechanical properties of polymer blends and alloys may be tailored, by using proper physical and processing conditions for homogeneous systems, and molecular engineering of the interfaces for heterophase ones.

That approach, which has been substantiated by a physical study of the miscibility situations at molecular level, has been applied successfully to commodity and engineering polymer-polymer blends, but also to polymer-filler and polymer-liquid heterophase systems.

INTRODUCTION

Polymer blends undoubtedly represent one of the most fascinating and fast moving chapters of polymer science today. First of all, they constitute the best technological answer to the economical challenge raised by the increasing difficulties in lanching new monomers and polymers; they allow indeed the designing of new higher performance materials based on available well-known products, hence their success and an impressive growth rate of about 15% a year over the last decade (1), leading soon to a 1 billion U.S. $ market (2). Second, but not less , they offer a still largely open and extremely fruitful field to scientific investigations, at three different levels: development and clever application of suitable physical techniques for the study of their morphology, thermodynamics and processing; those control of their structure and behaviour by a careful and imaginative "molecular engineering"; in-depth attempts to correlate chemical and preparative methods with morphology and physico-mechanical properties (3).

This paper aims at presenting a short summary of the state of the subject, including typical examples illustrative of its main trends; the readers interested in having more details are refered to more comprehensive recent reviews(3)(4)(5).

I. HOMOGENEOUS, "MONOPHASE" BLENDS

In blending different polymers, one may encounter two extreme situations: a gross phase separation, or an homogeneous mixture at the molecular level. However, the reality is more complex, and many intermediate situations can be characterized: increasing separation at the intermolecular level only, formation of a cocontinuous morphology, dephasing into dispersed heterophase morphologies of increasing phase size (typically from a few tens of Å up to hundred μm).

Moreover, one must be conscious of the size-scale comprehended by the method used: only particular techniques such as high resolution (S)TEM, bulk relaxation NMR, non-radiative energy-transfer (NRET) and other fluorescence techniques will really give general information at the molecular level, although other ones may prove more practical and valuable at higher scales.

That being said, so-called homogeneous blends represent a first attractive class of mixtures. Of course, in this class of materials examplified by General Electric "Noryl", final macroscopic properties are most often intermediate between those of the corresponding homopolymers (although there are noticeable exceptions to that statement). Such a "mediation" of properties is somehow a limitation to the overall spectrum of properties displayed by a blend of different polymers; however, it already offers an interesting way to broaden the "processing temperature window" of a given product (i.e. poly(phenylene oxide)), and to generate a continuum of properties in a given polymer blending process.

However, it has now been realized that such situations offered more potentialities than previously envisioned. Indeed, many of the "homogeneous" blends (at room or use temperature) undergo a so-called "lower critical solution" transition (LCST) at higher temperatures (see fig. 1), in a range where

processing may possibly be performed while taking advantage of the different morphology (now heterophase) and physico-mechanical or rheological characteristics of the material.

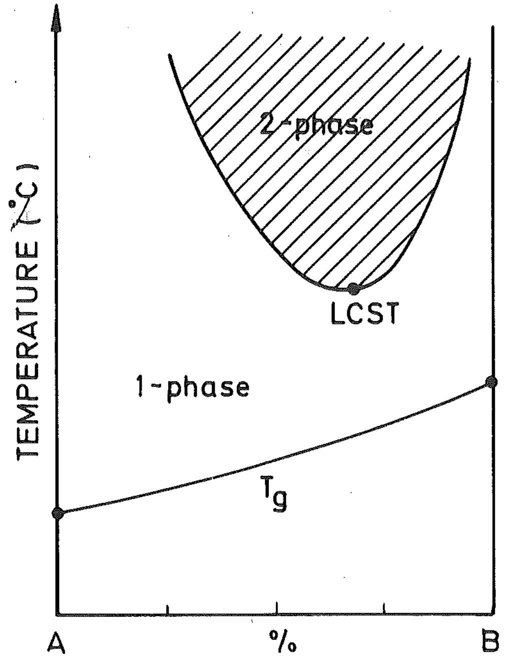

Fig. 1. A Typical LCST (and Tg) Behaviour for some "Homogeneous" Polymer Blends

Moreover, these new characteristics can be easily quenched in a controlled cooling process provided that the Tg value were not located at a much lower temperature than the LCST one. These are exciting possibilities which should be further explored.

II. HETEROPHASE POLYMER ALLOYS

1. The general problem

Blending non-miscible polymers (a general situation) leads to a material in which additivity of properties can now be obtained. However, two demanding structural characteristics have to be achieved to avoid gross phase separation and ensure a good spectrum of final properties: proper interfacial tension providing a small phase size (definitely below the micron scale), and good interphase adhesion preventing deleterious irreversible effects of stresses and strains. The answer of the chemist to that challenge has been to establish strong interactions between phases: covalent bonding (in HIPS or ABS resins), ionic bonding (6,7), or reversible anchorage promoted by the use of a block copolymer and based both on entanglements and/or dipolar interactions with the corresponding homophase (8). Such a systematic molecular engineering of the interfacial situation has led to an experimental optimization justified by the achievement of high-level performances, in these so-called polymer "alloys". The main results obtained are briefly summarized in the following paragraphs.

2. The answers from polystyrene (PS)-polyolefins (PO) model alloys

Melt-blending of stable commodity polymers such as PS and PO (i.e. LDPE, LLDPE, HDPE, PP and EPDM) has been of course an attractive and easy way to produce interesting materials for systematic study: in order to fulfil the structural requirements mentioned above, anionically prepared block copolymers of polystyrene and hydrogenated polydienes (9) have been used allowing the preparation of high-performance alloys.

The main information gained from their study can be expressed as follows:

a. mean phase size can easily be reduced to values as small as (10) a few hundred nanometers (or even lower). Moreover, under particular conditions, dispersion morphologies can be changed into cocontinuous ones (11);

b. these morphologies are stable, even under drastic processing conditions such as extrusion and injection molding (12);

c. compared to a simple blend, bulk physico-mechanical properties of these alloys are strikingly improved: much higher elongation, stress and total energy at break (13,14), much better impact resistance (5), much smoother cold fracture surfaces and gloss (11);

d. if properly designed, most of the diblock additive goes to the interface: moreover, "salami-type" structures can be produced (15); a 1-2 weight-% is sufficient to reach the maximum properties improvement, supporting the economical viability of the approach (11,14);

e. the molecular characteristics of the additive, relative of course to those of the homopolymers (16), are key parameters:

- composition is important, particularly in the case of more polar polymers, but less critical here;
- length of the blocks, somewhat related of course to the former point, is a key parameter; although its influence is a complex problem (14), it may safely be said that the designing of high strength <u>and</u> high toughness alloys implies the use of blocks having M.W.'s close to those of the corresponding homopolymers (this also implies some rheological problems). That M.W. matching is presently studied (17) on other blends, but is probably of decreasing importance when the interactions between the blocks and the corresponding homopolymers become significantly stronger;
- microstructure of the copolymer is the other important feature. The efficiency decreases in the order: diblock, triblock, graft (14); tapered blocks are better than pure ones (9); and isomerism of the monomeric units is an important tailoring tool (5).

3. Extension to other more polar commodity and engineering polymers

In order to apply the same type of approach to other polymers for which the synthesis of the corresponding diblocks was unpractical, a new principle has been developed (18): i.e. A-C diblocks have been synthesized to tailor A and B homopolymers alloys, granted that C would have strong enough interactions with B. A general family of additives has thus been developed, wherein the C block is a poly(meth)acrylate (e.g. anionic PMMA, about 70% syndiotactic, being miscible with many other important homopolymers), while the A block may be a PS, a (hydrogenated)polydiene, etc... (19,20)

Since the basic validity of this approach has been demonstrated by physical miscibility measurements (21,22) (NMR, NRET), interesting alloys of styrenics, polydienes or polyolefins have been prepared with a number of important polar polymers. These exciting possibilities are illustrated hereafter by three typical examples.

a) Super high impact (SHI) materials have been designed by by dispersing an elastomer phase (polydienes or Kratons) into rigid PVC(23) or SAN(24) resins. The use of the proper bridging agent, a poly(butadiene-b-methylmethacrylate), not only promotes a fine phase dispersion and excellent global impact resistance, but also allows an interesting tailoring of the fracture history (as shown by the instrumented fracture profiles).

b) Costly engineering polymers have been blended with cheaper polymers and/or fillers, improving the economics of the final material while preserving most of the valuable properties of the engineering resin (continuous phase) thanks to the good interfacial adhesion provided by suitable block copolymers: an interesting example may be found in poly(vinylidene fluoride) alloys (25).

c) Attractive alloys of polymers displaying very different cohesive energy densities and solubility parameters such as nylon-polystyrene or nylon-polyolefin combinations, can also be optimized thanks to additives ensuring very strong interactions: it has been shown that copolymers containing a hydrocarbon block (PS or HPD) on one side, and a nylon.6(26) or a polycarboxylic acid(27) block on the other one (much like the Zitel material of Du Pont), were both efficient in ensuring phase size and interphase adhesion control.

4. Extension to phases other than polymers

Considering the general scheme in which an A-C block copolymer bridges two non-miscible phases A and B, it was of course a rather straightforward approach to replace B by a non-polymeric phase, also able to develop strong interactions with C. There are presently at least two important areas of development for that concept.

a) Alloys where phase B is an inorganic filler

As yet, the molecular adhesion of a filler phase to a polymer matrix is not a completely well mastered problem: where mediocre results are not acceptable, satisfactory designing implies usually delicate and costly pretreatment of the filler.

It is thus more than desirable that additives were able to fulfil that role during the processing of the alloy, or at least in a simple premixing operation. This goal has been achieved using block copolymers combining an A segment interacting with the matrix (entanglements and/or dipolar interactions), while the C block adheres, or better reacts, with the filler: electrostatic bonding is an easy answer for the latter, and dramatic improvement in the adhesion of a polyolefin matrix to $CaCO_3$ has been demonstrated(5), using a C block containing carboxylic groups (grafted and hydrolyzed maleic anhydride, or hydrolyzed alkyl(meth)acrylate units). Similarly promising results include Al_2O_3 and $Al(OH)_3$(28); inversely, interaction of a block containing basic groups with an acidic-type of filler is also favorable (e.g. vinylpyridine units with acidic silica).

b) Dispersions where phase B is a liquid medium

Another very promising field of application for such diblock copolymers is the stabilization of fine dispersions of an insoluble phase (i.e. polymer or inorganic pigment) in a liquid medium (pure liquid or (polymer) solution): i.e. systems in which the A block interacts with the insoluble dispersed phase (physically or even with chemical bond formation), while the C block is solvated by the liquid and creates a coalescence barrier around the dispersed particles. Further to the important work of Riess on the behaviour of block copolymers in selective solvents(29), interesting applications of the above concept have been developed, both in organic or in aqueous media, as illustrated by the two examples hereafter.

- The problem of stabilizing dispersions of an inorganic pigment, e.g. carbon black particles in the micron range, in a paraffinic liquid (i.dodecane), has been solved by using a suitable block copolymer(30): one of the block, i.e. PS, strongly adsorbs on the surface of the particles (typical adsorption isotherm, of at least one molecular layer), while the other block is a very lipophilic one "dissolving" in the paraffine, i.e. a poly(stearyl methacrylate) (PSMA)(fig.2). That combination results in a very stable, size-homogeneous dispersion of the pigment.

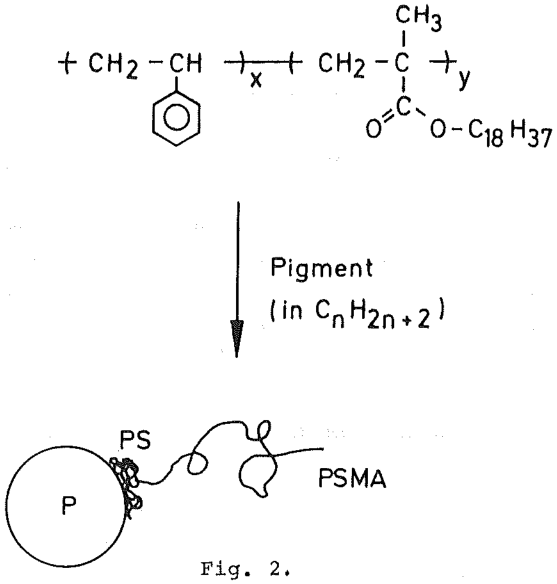

Fig. 2.

Stabilization of a pigment dispersion in a paraffinic medium, using a poly(styrene-b-stearyl methacrylate) diblock copolymer

- Along similar lines, but in a completely different context, very fine dispersions (down to 100 nm) of hydrophobic polymer particles (PS, poly(meth)acrylates,...) have been produced in aqueous medium. A typical additive is a copolymer containing an hydrophobic block A (PS, PA,...) which again adsorbs on the particles, as well as a strongly hydrophilic block containing sulfonic acid groups (obtained by reaction of glycidyl methacrylate units with sulfite) which not only ensure the interaction with the aqueous phase but also create an extremely efficient electrostatic coalescence barrier around these particles (fig.3)

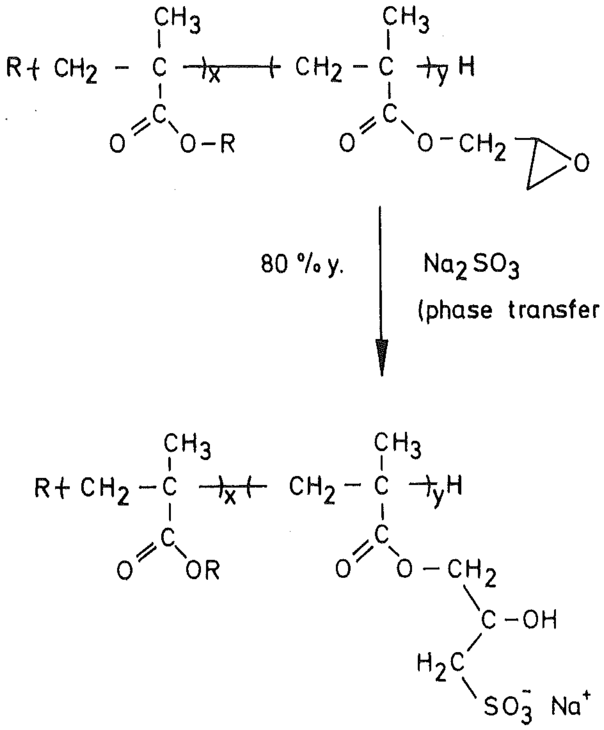

Fig. 3.

Stabilization of a hydrophobic polymer dispersion in aqueous medium, using a copolymer containing a hydrophobic block and a sulfonic acid block

There is no doubt that such approaches will receive more attention and give rise to other fruitful applications in the future.

CONCLUSION

The molecular engineering of interfaces in heterophase blends, leading to high quality alloys, is rapidly becoming a remarkably efficient and versatile tool for the optimization or creation of polymer materials. In that prospect one can rely upon entanglements, dipolar interactions or electrostatic forces developing between phases, using block copolymers (diblock, multiblock or graft, sometimes prepared in situ (32)) and/or functional groups carried by any of the phase-partners(7); ultimately, covalent bond formation (already involved in HIPS and ABS) may freeze-in the favorable morphologies obtained and impart still higher resistance to external sollicitations(5,31).

Such an approach opens the way for a tremendous broadening and diversification in the use of already available polymers; the creation in that context of new families of higher performance useful materials is undoubtedly a very worthwhile scientific, technological and economical goal in a time where polymer-based products and systems pervade all fields of human activity.

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SYNTHESIS, CHARACTERIZATION AND RECENT DEVELOPMENTS OF LIQUID CRYSTALLINE POLYMERS

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Abstract: Recent developments of polymer liquid crystals (PLCs) are reviewed . The virial expansion method of Onsager and the lattice model used by Flory to appreciate the most relevant parameters in establishing mesomorphic behavior in polymeric systems are presented. These and other theoretical predictions are confirmed by numerous experiments. Both lyotropic (polymer solutions) and thermotropic (polymer melts) types of PLCs are considered with emphasis placed on the latter. The general properties of mesophases formed by such polymers are surveyed and some chemical structures capable of producing mesophases are classified in relation to their ability to form lyotropic and thermotropic systems. The synthetic routes, the effects of polymer structure on physical properties, and applications of two major classes of lyotropic systems (polypeptides, polyamides) and of a range of potentially important thermotropic polymers are discussed.

HISTORICAL INTRODUCTION

The observation by REINITZER (1888) of what appeared to be two melting transitions in cholesteryl benzoate is usually cited as the event that initiated the study of mesomorphism or liquid crystalline behavior (Ref.1). His findings were confirmed by LEHMANN (1889) who coined the term "liquid crystal" to denote the partially ordered liquid phase that forms upon melting the crystalline solid (Ref.2). In 1922 FRIEDEL proposed a new nomenclature adopted from the Greek language which included the terms mesomorphic ("Mesos" meaning "intermediate" and "morphe" meaning "form") nematic ("nema" = thread) and smectic ("smegma" = soap) (Ref.3). VORLÄNDER (1923) working with little more than the notion that lath-like molecules are predisposed to form liquid crystalline melts, postulated that "infinitely long mesogens" would be compatible with the supramolecular organizational constraints in liquid crystals (Ref.4). In 1937, BAWDEN and PIRIE reported that, when its concentration was increased, a solution of tobacco mosaïc virus (Lyotropic Polymer Liquid Crystal) separated into two phases, one of which being birefringent (Ref.5). Following this observation ONSAGER demonstrated that a gas composed of ideal, rigid rods will exhibit a spontaneous transformation from an isotropic to a quasi-parallel distribution of rods (nematic) at a threshold concentration that depends on the axial ratio of the particles (Ref.6). Later, it was shown by ROBINSON et al. (Refs.7,8) that poly(γ-methyl L-glutamate) (PMLG) and poly(γ-benzyl L-glutamate)(PBLG), synthesized by ELLIOTT and AMBROSE (Ref.9) at COURTAULDS Ltd, as part of a programme of evaluation of fiber formation in synthetic polypeptides, gave liquid crystalline solutions in a variety of common organic solvents. Fibers were wet-spun by BALLARD (Refs 10,11) but were not commercialised.