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POLYMER BLENDS AND ALLOYS Part-I

COMPATIBILIZERS - A GENERAL SURVEY.

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The ever increasing demand on performance characteristics of polymers to match the application requirements has led the scientists to try the idea of blending the existing polymers as a cheaper alternative to developing an entirely new plastics. Different polymers could be blended together to act in a complementary manner and yield enhanced properties. Thus, low priced polyolefins with low moisture absorption could be blended, for example, with moisture sensitive nylons to reduce moisture absorption and enhance dry impact strength. Similarly polycarbonates can be blended with ABS; ABS or Acrylates with PVC; PBT with PC and so on.

If their dissimilarity is the main attraction for combining these polymers into a blend, the same is often the main obstacle too for making a useful blend with improved properties. The ability to produce blends that have a better combination of properties than that of the individual components, depends on the compatibility of the system.

It is important here to define the two terms, which will be frequently used in this article, i.e., Polymer Blends and Compatibility.

The term polymer blend refers to intimate mixture of two or more polymers. The blends may be homogeneous or heterogeneous on a microscopic scale, but should not exhibit inhomogeneity on a macroscopic scale.

Compatibility refers to the degree of intimacy of blends. From a practical view point, it is most useful to consider a polymer blend as compatible when it does not exhibit gross symptoms of polymer segregation. A blend that is inhomogeneous on a macroscopic level should thus be considered as incompatible. (1,2)

Specific compounds can be used to bring together otherwise incompatible polymers into a stable blend through intermolecular bonding, and thus act as “compatibilizer” for these systems. Compatibilizers are generally polymers themselves, but there are exceptions, like monomeric silanes and organic peroxides. Compatibilizers act through reactive processing, i.e., through various grafting techniques or through hydrogen bonding based on polarity of the materials. In addition, a compatibilizer may function just as a surfactant can stabilize oil-water mixtures-by being soluble in one or both major components of the blend. A compatibilizer often works by a combination of these mechanisms, e.g., by attaching themselves to one blend component through chemical grafting and leaving a polymeric “tail” that is soluble in the other component.

How these compatibilizers can penetrate both phases of an immiscible blend when mixed is shown in figure 1. In these examples, it is assumed that the segment A of the block or graft copolymer is identical to polymer A, and segment B identical to polymer B. The working hypothesis is that segment A penetrates polymer A and segment B penetrates polymer B. Stabilized, more uniformly dispersed domains result because of reduced interfacial energy between phases. In addition, the interfacial adhesion is improved because the compatibilizer segments, which reside in separate phases, are linked covalently.

Use of block copolymers of the same chemical nature as the two homopolymers is an obvious choice which, once optimized, will lead to enhancement of properties. These are cases of non-reactive compatibilization. The disadvantage of this method is, on one hand, their nonavailability and the price, and on the other, the lack of flexibility in tuning the properties to specific applications. In polystyrene-polyolefin blends, block and graft copolymers have been reported to be added as compatibilizers. (3-7) These compatibilizers, which are block copolymers or grafts of polystyrene and polyolefins, are very effective in enhancing the properties of the immiscible polymer blend. In these examples, the compatibilizer polymer segments are identical in chemical composition to the components of the polymer blend. This does not always have to be the case, because the main criterion for enhanced properties appears to be miscibility of the compatibilizing segments in the respective polymer domains.

Compatibilization without the complication of having to control a chemical reaction is often preferable to compounders for sake of simplicity. Non-reactive compatibilizers are often simply a graft of the two base polymers that are desired to be alloyed. A small amount of this graft copolymer should provide the needed miscibility with both components. Using PS/PE grafts for compatibilizing PE and PS, and PS/nylon grafts for combining nylon and PS are examples of this type.

A block copolymer of polycaprolactone (PCL) with PS is particularly useful in blending PVC with PS for improving PVC's temperature performance and processability. Some other examples are: (8)

| Polymer 1 | Polymer 2 | Compatibilizer |
|-----------|-----------|--|
| LDPE | PS | Poly(styrene-b-ethylene) di-block |
| LDPE | PS | (a) EPDM or PVC (b) ABS or PP (c) SBS (styrene-butadiene styrene block polymer) |
| | | (d) CPE (chlorinated polyethylene) |
| | | (e) HIPS (high impact PS) |

Their utility varies from system to system, not only as a function of compatibilizing efficiency but also in relation to the overall performance of the final product, including e.g. the weathering.

Another interesting non-reactive compatibilizer is chlorinated PE (CPE). Dow Chemical have reported some work using the company's CPE materials as compatibilizers for styrenics with polyolefins, in an effort to improve the stress-crack resistance of PS. And the Centre for Polymer Research at the University of Texas has successfully used CPE to blend PVC and PE for scrap-reclaim applications. (9)

Another approach for compatibilization of two normally incompatible polymers is through grafting functional groups on one of the polymers which make it compatible with the other polymer. For example, grafted polyethylene becomes compatible with polyamides such as nylon-6 and -6,6 (10). Micrographs of blends with and without grafted material show gross inhomogeneity in one case and a very fine uniform dispersion of polyethylene in the polyamide matrix in the other. In Table below, properties of a nylon-6,6 are compared to a blend of the same nylon with 30 wt% graft modified polyethylene .

Impact Properties of Nylon and Nylon-PE Blend

| Property | Nylon-6,6 | Blend,70% nylon-6,6/30% graft PE |
|-------------------------------|-----------|----------------------------------|
| Gardner impact, N.m at 26.5°C | 26.5 | >36.1 |
| at -17.8°C | 0.8 | 23.7 |
| Notched Izod,J/m | 53.38 | 1035.5 |

Most popular compatibilizers have been derived from acid or anhydride modified polymers. Thermoplastic elastomers, polyolefins and their copolymers can thus be modified to serve as compatibilizers. The modified material itself is compatible with the base material while the acid and anhydride groups act as chemical hook to link the otherwise incompatible polymer. This has been particularly useful in blending low modulus polyolefins and rubbers to nylon for increasing toughness. The other applications are:

Polyolefin/EVOH, PS/EVOH, PE/Polyester blends, for combining barrier properties with less expensive materials as well as facilitating scrap reclaim.

Shell chemical Company's Kraton FG 1901X, a modified styrenic block copolymer, is a commercially available compatibilizer of this class. Kraton FG is reported to help compatibilize nylon/PP, which combines the heat and chemical resistance of nylon with the moisture resistance and low cost of PP. Kraton FG has also been used successfully to alloy thermoplastic polyester with various polyolefins to upgrade reclaimed materials.

Modified polyolefins and copolymers are also available commercially and used as compatibilizers with a wide range of materials. Du Pont's Bynels and Mitsui Petrochemicals' Admer are examples of this type of polymers.

Imidized acrylics from Rohm and Haas is the other type of compatibilizer commercially available. They are used for among other things, compatibilizing nylon and polycarbonates with other polymers like polyolefins.

In several commercial polymer blends "modifiers" are used. The modifier is usually a copolymer containing a rubbery component with interactive one(s). Acrylic-based copolymers, chlorinated polyolefins, ethylene-propylene-diene, poly (ethylene-covinylacetate), etc. are frequently used. These play a dual role, compatibilizing and toughening the blend. For this reason they are used at much higher loading than pure compatibilizers; while 1 to 2 wt% of the latter is usually sufficient 20 to 40 wt% of a modifier may be needed.

There are several other materials both polymeric and monomeric, that have been used as reactive compatibilizing agents in making alloys and blends. These include peroxides, silanes, organotitanates and phenoxies.

Information about the actual composition of blends and the nature of compatibilizers is closely guarded industrial secret. This introductory article is based on published information. Work in India on polymer alloys, blends and compatibilizers is in its infancy.

A few commercial blends have been introduced into the market. Indigenous manufacturing of some graft modified polymeric compatibilizers has also started. Yet, some more of development effort will have to be put in before the indigenous blends and alloys can make their presence felt. This being the first article in the proposed series on Polymer Blends and Alloys, it gives a general review of the compatibilizers used in the industry. Future articles will cover the specific blends and their applications and present the Indian scene in detail.

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MANAS 16-05-December 93

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