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PROBLEMS IN COMPATIBILITY STUDIES

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I. GENERAL DISCUSSION

For various reasons interest in multi-component polymer systems exhibiting what is variously termed compatibility of miscibility (but usually not solubility) has greatly expanded in the last few years. Though as a result, the understanding of the properties of such systems has significantly grown, a number of fundamental problems remain. Several such problems will be discussed, in certain cases with a degree of unavoidable subjectivity, below. Illustrative examples in nearly all cases will be taken from the binary system consisting of poly(2,6-dimethyl phenylene oxide) and polystyrene, and/or derivatives (e.g. copolymers) of the latter.

Reluctance to adopt the term "solubility" in a discussion of polymer-polymer systems is in itself revealing for it immediately indicates the first problem we shall consider, the difficulty of establishing a meaningful criterion (or criteria) for favorable polymer-polymer interactions leading to compatibility, and the corollary to this, the question of the molecular conformational state of the polymer which correlate with such a criterion. As is well known, "compatibility" in polymer-polymer systems has historically been based on strictly pragmatic criteria and it is only in the most recent past that, in a very few systems, some progress in understanding the state of the macromolecule on a molecular level has been achieved. Thus the original compatibility criteria--mechanical integrity and (for amorphous-amorphous systems) optical transparency--have long been rejected as providing any more than superficial

information concerning the conformational state. It is also generally realized that the other criterion commonly employed, the presence of a single glass transition in an amorphous-amorphous polymer pair, is also not yet meaningfully correlated with molecular conformation. There is at least one report in the literature of a compatible system which displays a single T_g , calorimetrically determined, and yet in which electron microscopic studies clearly demonstrate the presence of separate phase domains on a 100-150A level, (1). A related problem concerns the measurement technique used in assessing the presence or absence of the single T_g held to denote compatibility. Commonly used are so-called thermodynamic methods (calorimetry and dilatometry) and relaxational techniques (dynamic mechanical and dielectric relaxation measurements). It is by no means obvious that in a marginal case all of these techniques will yield the same result, and indeed there is again at least one example in which a system appeared to be substantially compatible on the basis of DSC measurements displayed some evidence for phase separation in dynamic mechanical measurements, (2). A further difficulty arises when this criterion is applied to binary systems in which the T_g 's of the constituents are relatively close.

An additional problem concerning T_g determinations is related to the fact that such measurements necessarily reflect the state of the system at a temperature substantially removed than T_g itself. An increasing number of systems is being found that display a lower consolute point and in which, therefore, depending on the thermal history of the sample, phase separation may or may not have occurred. In such instances it will be possible to observe single or double T_g 's in binary samples of identical composition. A related observation concerns certain binary systems whose preparative history may have included removal of a solvent by precipitation from, or evaporation of, the low molecular component(s). In these cases the phase state of the polymer mixture presumably reflects the detailed path from dilute solution to solid sample.

The general difficulty of attaining an equilibrium state stemming, clearly, from the long relaxation times associated with polymer melts, is also reflected in the virtual absence of thermodynamic data for polymer-polymer mixtures in terms of solubility theory. For example very few pertinent heats of mixing have been reported and there is

no complete thermodynamic analysis as yet available for any system in which both components are of high molecular weight, (3). A number of interaction parameter studies have appeared, the data mostly obtained from ternary polymer-polymer-solvent studies, (4), but a general correlation of such parameters (using well established polymer-solvent precepts) with compatibility is not available. This then brings us to a final problem--the prediction of mutual solubility in polymers. It is well known that the latter is a relatively rare phenomenon, and a simple explanation of this fact is associated with the difficulty of obtaining the requisite negative free energy of mixing for any polymer-polymer pair. (A negative ΔG is a necessary but not sufficient condition for the formation of a single homogeneous phase). It is apparent from experimental results on several systems that the free energy balance is a delicate one and that in many if not all cases a small change in the chemical structure of either or both components of a compatible system is sufficient to cause phase separation. It may be presumed that this criticality is accentuated by an increase in the molecular weight of the constituents (though it may in this limiting case be masked by non-equilibrium effects). Thus any a priori attempt to predict mutual solubility on the basis of the properties of the proposed components is inherently a formidable one. None of the methods, empirical and semi-empirical, which have in the main been successful for predicting polymer solubility in potential low molecular weight solvents, have been found to be applicable to the polymer-polymer case. Some progress has been achieved using equation of state concepts, (5), but it appears here again that physical parameters such as bulk thermal expansivity which may be presumed on theoretical grounds to have some predictive value in this regard will require "matching" to a degree which is beyond their experimental determinability. It would seem that polymer-polymer solubility is necessarily as yet explored on a somewhat empirical basis.

II. A MODEL SYSTEM:

POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)-POLYSTYRENE

Introduction. A system with which most of the problems and effects discussed above may be rather effectively illustrated is poly(2,6-dimethyl-1,4-phenylene oxide)-polystyrene (PPO-PS), and systems derived from this. In the following section we shall briefly review the principal results

obtained by the authors and co-workers relating to this versatile system.

1. Order. PPO-PS is unique amongst all known compatible polymer pairs in that it is possible to obtain, by appropriate selection of the tacticity of the PS component, and of the thermal and solvent exposure history of the intimately blended components, blends which are either totally amorphous (using atactic PS), in which one or other of the two components are partially crystalline (using PPO and isotactic PS) or, finally, in which both components (PPO, i-PS) exhibit substantial degrees of crystallinity. Conditions necessary to obtain each of the conditions delineated above have been explored in detail, (2,6). A principal area of interest in the systems containing either or both components in discrete (and, of course, separate) crystalline regions concerns the melting points of the respective crystallites. In systems considered here substantial melting point depressions were observed as the fraction of "diluent" increased. Such depressions are predicted to occur in polymer-polymer systems in recent theoretical treatments of this problem, (7), (though it was originally believed that a high molecular-weight diluent should be incapable of causing such a decrease). Nevertheless it is clear that a melting point depression in a polymer-polymer system can be a consequence of either or both thermodynamic and kinetic effects. The former would result essentially from free energy decrease upon mixing, the latter from the potential failure of the crystallites to attain substantial size. In the PPO-i-PS system wide- and small-angle x-ray studies were conducted to further investigate this point. The analysis of these results, using as a basis a paracrystalline model, for blends in which only the i-PS had been allowed to crystalline found that the lamellae thickness of the i-PS component did indeed decrease with the increasing PPO content, thus explaining, in part, the observed m.p. depression, (8). The results of the complementary study, in which m.p.'s are determined as a function of annealing conditions (and in which the effect of crystal size can, therefore, in effect, be removed from consideration by extrapolation) are not yet complete in this system.

2. Chemical Modifications and Compatibility. The PPO-PS system (using either atactic or amorphous isotactic PS) is compatible, by all known criteria, over the entire com-

position range. However, and in parallel with empirical observations in other compatible binary mixtures, relatively small changes in chemical structure of either polymer component are sufficient to render the resulting system entirely incompatible. For example, both the 2-methyl-6-phenyl or the 2,6-diphenyl phenylene oxide polymers are incompatible in mixtures with PS, (9). Similarly neither p-chloro nor the o-chlorostyrene homopolymers are compatible with PPO. However, certain copolymers within a strictly defined range of composition are compatible; thus p-chlorostyrene (pClS) and styrene copolymers containing up to 67 mole % pClS are compatible. The compatibility-incompatibility transition in the latter system has received extensive study with respect to solid state transitional and mechanical properties. The incompatibility transition in the copolymer is an extremely sharp one, with a half-width of the order of 1 mole %. The same criticality is exhibited with respect to copolymer-PPO blends. Thus, as far as is experimentally ascertainable a given compatible copolymer is compatible in all proportions with PPO; for any incompatible copolymer the converse is true, (10).

Further consideration of the sharpness of the compatible-compatible transition along the copolymer composition axis, however, needs to be made taking into account the possibility of non-equilibrium effects. It is recalled that the criterion of a single T_g necessarily reflects a thermodynamic pseudo-equilibrium at some temperature other than the measured T_g itself; in samples prepared by melt blending presumably at temperatures close to or at the processing temperatures. This important point is illustrated by recent observations concerning the compatibility of p-ClS and o-ClS copolymers with PPO. A compatibility "window" exists in this system, but the width of the "window" is highly dependent on the thermal history of the sample. It has been deduced that a lower critical consolute point exists for mixtures of the copolymer and PPO. For the "most compatible" copolymer i.e. with compositions near the center of the "window", the critical temperature is substantially higher than any normally employed processing temperature, hence all blends exhibit compatibility. However, for copolymer compositions nearer to the edges of the "window", the LCST curve intersects the processing temperature regions. Thus samples of a given composition with respect to copolymer and PPO quenched from a higher temperature will exhibit incompati-

bility, whereas samples processed at an appropriately lower temperature appear to be compatible. The fullest exploration of the edges of the transition is compromised, of course, by rapidly increasing equilibrium times as the temperatures of interest approach the respective T_g 's, (11). These studies provide further evidence of the subtlety of the compatibility---incompatibility phenomenon with respect to chemical composition for high molecular weight components and the evident difficulty in accounting for such effects in terms of any bulk properties of individual constituents. Although in the pClS-PS copolymer system we have been able to correlate compatibility with respect to mixtures with PPO with a densification of the respective compatible copolymers (of the order of 1% at most, compared to a simple additivity prediction), some preliminary analogous measurements in the pClS/oClS copolymer compatibility "window" have failed to show such an effect.

3. The Glass and Other Solid State Transitions. The PPO-PS system and compatible derivatives thereof all exhibit what has become the standard criterion of miscibility in polymer-polymer blends: a single glass transition temperature coupled with the absence of any manifestation of the T_g 's of the component polymers. Additionally, the single T_g varies in a monotonic manner with the composition of the blend, and may be functionally defined by any of the semi-empirical relations that have been derived to account for the composition dependence of T_g for a polymer-diluent mixture. Somewhat more subtle aspects are revealed when a comparison is made of the T_g phenomenon observed by different experimental techniques.⁸ Thus in an early investigation of this system it was found that in PPO-PS blends prepared under a given set of conditions (not necessarily representing "asymptotic" equilibrium behavior) a single T_g was observed in DSC measurements whereas some evidence⁸ of less than complete miscibility in the same samples could be inferred from dynamic mechanical considerations, (2). The resulting question, could there be a difference in the sensitivity to compositional inhomogeneity in the two respective techniques, has not been definitively answered and this, together with other aspects of glass transition behavior, remain important unknown factors in the comprehensive understanding of the complete phenomenon.

The effect of compatibility on solid state relaxations

other than these associated with the glass transition in PPO-PS is somewhat obscured by the coincidental overlap of the major sub- T_g relaxations in the two components. The respective β -peaks are both broad and, in the dynamical mechanical domain, relatively weak. There is some evidence that blending causes a suppression of the β peak and this has been attributed to a specific interaction, (12), but it seems that this particular phenomenon may be more fruitfully investigated in a compatible system in which the sub- T_g relaxations in the individual components occur at substantially different temperatures.

Finally we discuss in this section the special problem of assessing compatibility in amorphous binary mixtures in which the T_g 's of the individual constituents happen to lie comparatively close. A possible solution to this problem lies in observations, now confirmed in both PPO-PS and PPO-pClS/PS copolymers, regarding large deformation properties of such blends. It has been found that these properties, particularly the tensile strength, offer a sensitive additional criterion. Thus for compatible systems a pronounced maximum is observed in measurements of tensile strength as a function of blend composition. In incompatible systems, conversely, a minimum is found, (10,13). Additional tests of the general applicability of this suggested criterion particularly with respect to brittle-brittle polymer systems is under way.

4. Level of Miscibility. A question of prime interest in all compatible systems naturally concerns the level of dimensional homogeneity in such a system. Although it is possible to assert from electron microscopic observations, for example, that discrete phases with an average characteristic dimension of greater than, say, 50-100Å are not likely to be present in PPO-PS blends (or, most probably, in any system displaying a single T_g) experimental limitations (electron density contrast, for example) do not permit any more definitive statement in this regard. Neither, as has been mentioned above, is it known, how the single T_g phenomenon may be correlated with dimensional homogeneity. Whether or not a "true" solution in terms of a macromolecular--low molecular weight solvent concepts exists in polymer-polymer systems has not been readily ascertainable. Recent results from small angle neutron scattering measurements have provided evidence, for those systems examined, which strongly support the concept of a

molecular, segmental, level solution in which the R.M.S. end-to-end distances of the chains of the constituents are mutually expanded with respect to their respective unperturbed values, a situation, therefore, to be anticipated for any polymer in a thermodynamically favorable solvent, (14). We have reached a similar conclusion in the compatible PPO-pClS/S copolymer system from dielectric relaxation measurements, which provide, again, strong evidence, in this particular system, for an extended pClS/S chain in the PPO "solvent", (15).

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DISCUSSION

N. DODDI - ETHICON, INC. The subject of polymer compatibility you discussed here, can you extend this to processing of polymer mixtures? Are they compatible from the processing point of view? Can we use this information presented by you to predict the processibility of polymer mixtures? F. KARASZ - U. MASSACHUSETTS. That's a many faceted question. First of all to answer the simple part. Yes, if a material is compatible, and if one knows the phase boundaries, the kind of information I gave can give you an indication of what temperature one should process. For example, in the p-chlorostyrene/o-chlorostyrene/PPO system that I discussed, we have a compatibility window. Clearly if one were interested in developing a material which was compatible ultimately at room temperature one would process at a temperature A. If, on the other hand, for reasons of one's own, there was interest in producing a system consisting of a matrix containing discrete phases one would process in the range B and cool quickly. This kind of diagram thus does indeed give one potentially very important information about processing conditions for the desired end product. As I said, it might well be that for other systems the L.C.S.T. is either nonexistent or is at such a high temperature that it doesn't make any difference. One would have to examine each situation individually. See Phase Diagram Figure on following page.

ELI PEARCE - POLYTECHNIC INSTITUTE OF NEW YORK. I'm wondering whether you've also given any consideration to the variation of copolymer structure with conversion. I believe when you prepared your copolymers they were run to rather high conversions. Therefore, they are really a polymer "blend" themselves, and how does this affect the results? Perhaps if low conversion copolymers were used, such difficulties would be minimized. F. KARASZ. Yes, we were very aware of this problem and the potential dangers. It just happens that in the particular copolymer that we used, reactivity ratios are such that product composition changes only 1% with conversions from 20 to 60%. We showed this experimentally and theoretically. In other cases it might be more crucial.

Phase diagram for a blend of a *p*-chlorostyrene/*o*-chlorostyrene copolymer (*p*-chlorostyrene content 47 mole %; $\bar{M}_v = 2.2 \times 10^5$) with poly(2,6-dimethylphenylene oxide) as a function of weight fraction (w_{PPO}) of the latter polymer.

J. LANDO - CASE WESTERN RESERVE U. Have you given any consideration to the fact in your tensile experiments that as you vary the compositions you may get a different mechanism for tensile failure? F. KARASZ. Yes. As the amount of PPO increases there is a transition from brittle to ductile failure.

J. LANDO. One last point. Have you ever thought of using corresponding fluorinated polymers because then you could perhaps separate the effect on compatibility of size and polarity? F. KARASZ. Yes, we are starting to look at such systems.

T. W. HUSEBY - BELL LABS. My comment refers to the previous question on processibility, and I wanted to reinforce what Frank had said about predicting processibility from some of these studies. In our own work we have found compositions of PPO and polystyrene in which the zero shear viscosity scales with concentration of polystyrene in a very predictable manner and in which the shape of the viscosity-shear rate curve also scales in a very predictable manner.

RICHARD CHEN - BAUSCH AND LOMB. In your presentation, it is interesting to see the correlation between T_g 's and the compatibility of two blended polymers. I wonder, do you do any work using electron microscopic sectioning techniques to correlate the domain size of blended polymers and the T_g 's? F. KARASZ. Yes, with the exception of the last system I discussed: the *o*-chloro and *p*-chlorostyrene where we have not yet examined the edge of compatibility. With the other systems, i.e., the PPO-polystyrene and the PPO-*p*-chlorostyrene/styrene copolymers we have looked at the systems electron microscopically. We do not observe anything that is inconsistent with T_g measurements. In other words we do not observe an effect such as I mentioned Matsuo had found where he saw discrete phases and yet found a single T_g . In other words, in our case we go from a discrete phase to a homogeneous phase situation at exactly the same point as our T_g measurements indicate. All that means, of course, is that we are possibly too insensitive in our visual observations to the subtleties of the transitional region.

RICHARD CHEN. Some people have been working on the so-called interpenetrating polymer network (IPN) systems. There have been some arguments about the T_g values too. Do you think they should obtain the separate T_g 's as you said, even if the IPN samples are transparent? How small should the domain size be in order to obtain a single T_g ?

F. KARASZ. It depends on two things. (1) How discrete are the phases? The components are presumably not compatible in the sense that I am talking about. They are forced into proximity but not compatibility. (2) It also depends on the answer to the fundamental point you raised. How small a region do you have to have before it shows a single T_g ? There is evidence that a region as small as 50 or 60 Å can show a single T_g but if you get down to 10 Å (even if that has a real meaning) I don't know whether that would show a single peak.

I. SKEIST - SKEIST LABORATORIES. With regard to predicting compatibility from the properties of the constituents, how useful are solubility parameters, either the single value suggested by Hildebrand or the triple values of Hansen and the Tennessee Eastman people (Crowley and coworkers)? F. KARASZ. Well, it is perhaps good for predicting noncompatibility, but, in my opinion, not very productive for predicting compatibility simply because the subtleties of the problem are a couple of orders of magnitude greater than those reflected in the solubility parameter. For example, if we talk about, as a very obvious example, the systems I discussed, any method of predicting solubility parameters that I know for the *p*-chloro and *o*-chlorostyrene copolymers will give essentially the same value. There is no way, therefore, in which a solubility parameter argument will predict the observed compatibility window in such a system.

R. PORTER - U. MASSACHUSETTS. T_g is, of course, just one position on the viscoelastic spectrum and in a study that you know about, Frank, we have shown that the full viscoelastic spectrum is additive for the PPO-polystyrene system, which is germane to the comment by Dr. Huseby that viscosities are additive, so that we can literally predict the rheological properties as long as we are working in an area where the two materials are fully compatible.

FRED BAILEY - UNION CARBIDE. One system on which I have worked is the p-chlorostyrene/styrene isotactic copolymer system. Here the isotactic conformation can be made but only the styrene portion will crystallize; the chlorostyrene segments are amorphous. Thus, the degree of crystallinity can be closely controlled. The chlorostyrene dipoles can then be measured in a system which is crystalline: polystyrene-PP0 and varying degrees of polystyrene-poly-p-chlorostyrene crystallinity.