Interactions in Miscible Polymer Blends

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This research has been concerned with learning more about the energetic interactions between the segments of polymers and how they affect the phase behavior and the physical properties of polymer blends. A primary tool for quantitative investigation of these interactions has been the calorimetric measurement of heats of mixing between low molecular weight liquids having structures similar to those of polymers of interest. In this way, it has been possible to simulate both intermolecular and intramolecular interactions that are important in blend phase behavior and properties. Various theories have been employed to utilize this information including one that permits prediction of miscibility by a group contribution method.

Several new miscible blend systems were identified, e.g. polycarbonate/poly(methyl methacrylate), and several ways to use copolymerization to manipulate phase behavior were demonstrated.
Gas permeation in miscible blends was measured for several systems and related to the degree of interaction as manifested by the volume change on mixing. The results found follow closely, but not exactly, a simple free volume theory developed for this purpose. Crystallization of one component of the blend reduces gas permeability, decreases gas and liquid sorption and improves solvent resistance. It was found that high pressure CO₂ can effectively plasticize polymers. A liquid crystal polymer was found to have extremely good gas barrier properties.

It was found that a styrene/acrylonitrile copolymer could be toughened more when two types of rubber particles were introduced than when either were present alone. This synergism apparently relates to the combined crazing and shearing modes of deformation involved.
Interactions in Miscible Polymer Blends

Final Report

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The view, opinions and/or findings contained in this report are those of the authors and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.
I. Statement of the Problem Studied

The general objective of this research has been to examine interactions in polymer blends to determine their effect on thermodynamic phase behavior and various physical properties. Interactions in this sense involve those at the polymer segmental level and at the more macroscopic level of interfaces. This has been a three component research plan to bring fundamental understanding of the thermodynamics governing polymer blend phase behavior, to quantify the relationships which exist between the interaction energies of the blend components and the resulting blend physical properties, and to investigate aspects of the mechanisms of rubber toughening of glassy polymers. Specific accomplishments have included discovery of some new important miscible polymer blends, demonstration of how copolymer composition can affect lower critical solution temperature behavior beneficially, quantification of blend thermodynamics using heats of mixing data for low molecular weight compounds, determination of the effects of segmental interactions on gas transport properties of polymer blends, environmental effects on polymers, and identification of a synergistic toughening mechanism for glassy polymers. Some of the major conclusions are summarized in the following section. Details of the research leading to these conclusions can be found in thirty-one papers published during this grant period and in five papers submitted for publication, which have not yet appeared in print.

II. Summary of Important Results

In the following discussions the numbers in parentheses refer to the papers in print or in press listed in Section III.B and III.C.

A. New Miscible Blend Systems

Based on our qualitative intuition and quantitative knowledge about
interactions in polymer blend systems, we have been able to identify numerous new miscible blends during the course of this research (3, 9, 15, 18-23, 31). Some of the most important ones will be mentioned specifically. Blends of polycarbonate and poly(methyl methacrylate) were found to be miscible (23) despite previous reports in the literature that this pair was not miscible. This discovery resulted from a carefully designed solution preparation method that avoided phase separation on casting. This blend, however, separates into two phases upon heating at rather low temperatures which makes it impossible to melt process this material and obtain a one phase mixture. However, as pointed out later, there is considerable hope that suitable copolymerization techniques can be developed to circumvent this problem. Doing so will lead to an important transparent material having properties intermediate between those of the low cost acrylic and the high performance (but high cost) polycarbonate. We have also discovered that polycarbonate is miscible with copolymers of vinylidene chloride such as the commercial materials known as "Saran". Owing to the excellent barrier characteristics of the latter, these blends might be useful where the superior properties of polycarbonate and good barrier characteristics are simultaneously needed. This research has also shown that copolymers of styrene/acrylonitrile and poly(vinyl chloride) are miscible with a series of new polymers called imidized acrylics. The latter are made by reacting poly(methyl methacrylate) with methylamine. These blends offer some interesting and perhaps useful property combinations.

B. Effect of Copolymerization on Lower Critical Solution Temperature Behavior

As part of this research, it has been shown that copolymerization
can be a useful way of modifying polymer blend phase behavior (21, 24, 31). These effects stem from intramolecular interactions of the various monomer units in the copolymer as well as intermolecular interactions with other polymers. A simple binary interaction model has been constructed to formally represent these notions. This approach has proved very useful both qualitatively and quantitatively. Two important consequences of copolymerization that have been found are described.

First, it has been realized in the last few years that a polymer may form miscible blends with a random copolymer when it will not form miscible blends with the homopolymers made from the monomers comprising the copolymer. An example of this is poly(methyl methacrylate) blends with styrene/acrylonitrile or SAN blends (24). Copolymers containing between 10% and about 30% acrylonitrile are miscible with poly(methyl methacrylate) whereas those outside this miscibility window are not. We have shown that poly(ethyl methacrylate) and poly(propyl methacrylate) have similar miscibility windows with SAN copolymers (24). Each of these systems exhibits phase separation on heating, i.e., lower critical solution temperature behavior. In some instances, these phase boundaries are at such low temperatures that melt processing to form a homogeneous mixture is not practical. We have shown that by manipulation of the copolymer composition by small amounts that this problem can often be circumvented. The temperature at which phase separation occurs, for these systems, goes through a maximum at copolymer compositions in the mid-region of the miscibility window. Therefore, by knowing these boundaries and the interactions involved, one can optimize systems for preferred phase behavior.

Second, as mentioned above, many polymer blends phase separate at temperatures that are too low for convenient processing. The blend polycarbonate/poly(methyl methacrylate) mentioned above is an example. A less extreme
example is tetramethyl bisphenol-A polycarbonate/polystyrene blends whose phase boundary has a minimum at about 240°C. We have shown that by incorporating relatively small amounts of acrylonitrile or maleic anhydride into the styrenic polymer will elevate this temperature very dramatically (21). This effect can be understood in terms of the intramolecular repulsion that exists between the two comonomers. We believe this is a very important and powerful concept for manipulation of polymer blend phase behavior.

C. Quantitative Blend Thermodynamics by Analog Calorimetry

One of the premises of this research has been that useful information about interactions in polymer blends can be obtained from direct measurements of heats of mixing of low molecular weight liquids having molecular structures analogous to those of the polymer segments. Of course, direct calorimetry is not possible for polymer-polymer blends. This point of view has been explored in depth. We have found many cases (10, 34, 35) where this is indeed true, but some important exceptions have been noted. The use of FTIR has proved to be a valuable complimentary tool for these studies.

We have successfully shown that the concept of intramolecular repulsion in copolymers can indeed be simulated using mixtures of low molecular weight liquids having structures similar to those of the comonomers (10, 35). This was shown vividly for a system analogous to PMMA-SAN. Related work on blends of SAN with styrene/maleic anhydride or SMA copolymers have verified that these copolymers are miscible when the content of acrylonitrile or maleic anhydride in each is not too different. It has also been shown that the miscibility stems from an exothermic interaction between the acrylonitrile and maleic anhydride units. We have successfully mapped the region of miscibility by use of interaction information obtained from analog calorimetry.
(35). To do this, it was necessary to employ theories which allow for the effects of volume changes on mixing.

An alternate approach has been developed using a group contribution method (34). Here, a modified Guggenheim Quasichemical theory has been developed and fitted to the heats of mixing of a variety of ester, alkane, and chloronated hydrocarbon systems. The group interaction parameters obtained by this method have been used to predict the heat of mixing and miscibility of poly(vinyl chloride) with a series of aliphatic polyesters with good success. Application of this approach to other systems will be pursued.

D. Gas Permeation in Miscible Blends

Segmental interactions in polymer blends should have some influence on various physical properties of these materials. One direct result of the interaction can be a volume change on mixing, usually densification, which influences free volume. Properties like permeability should be rather sensitively influenced by changes in free volume. We have developed a simple theory to predict this effect, and as a part of this research a systematic examination of these effects has been made (2, 14, 17, 25, 27). We find that volume contraction on mixing in polymer blends causes these materials to have lower gas permeation coefficients than would have been anticipated in the absence of such interactions. These trends are explained rather well, but not completely, by this simple model. The effects seem to be reasonably well understood at the present time such that reasonable predictions about these properties can be made. We have shown that systems that interact very weakly behave nearly ideally, i.e.

\[ \ln P = \Phi_1 \ln P_1 + \Phi_2 \ln P_2 \]

Elastomeric blends of poly(methyl acrylate) and poly(epichlorohydrin) conform
quantitatively to this picture (2). However, systems which interact more strongly, like tetramethyl bisphenol-A polycarbonate and SAN blends (27), show lower permeability coefficients than given by this equation.

The system poly(vinylidene fluoride)/poly(methyl methacrylate) or PVF$_2$/PMMA forms semicrystalline mixtures. Gas transport properties in these systems have been examined to illustrate the effects that crystallinity can have on this behavior (14, 17). The results found can be rationalized based on the above approach when allowance is made for the presence of a crystalline, impermeable phase.

E. Environmental Effects on Blends

For the system PVF$_2$/PMMA we have examined several interesting environmental effects (4, 6, 7, 12, 16). The chemical resistance of this mixture is greatly improved as the amount of the semicrystalline PVF$_2$ is increased. This is reflected in a higher level of stress required for environmental stress cracking or crazing (12). We have also examined the equilibrium and kinetic uptake of liquids in this system (16). These results show conclusively that introduction of a semicrystalline component into a blend can endow the material with much better chemical or solvent resistance.

In addition, these studies have shown some very novel effects associated with contact of polymers by gaseous CO$_2$. Normally, one thinks of gases as being rather inert and not changing the properties of polymers. However, CO$_2$ is rather soluble in polymers, and we have shown conclusively that it can plasticize glassy polymers, i.e., the glass transition is lowered as carbon dioxide is sorbed (4). We have also shown that sorption of carbon dioxide can induce crystallization for glassy materials not fully crystallized (6). For polymers just below their glass transition temperature, we
have shown that sorption isotherms for carbon dioxide can be very complex owing to the plasticization phenomenon (7).

F. Rubber Toughening of Glassy Polymers

Glassy polymers are often rather brittle, and incorporation of rubber has proved to be a useful means of toughening these materials. It is generally believed that the rubber must adhere to the glassy matrix for this mechanism to operate. In polystyrene, this is accomplished by grafting during the polymerization step. For emulsion made rubber modifiers, an outer shell of a hard polymer is grafted to the rubber core. In some cases the outer shell is made of a material identical with the matrix; however, in other cases it is not. It is our thesis that the stronger the interaction between the outer shell and the matrix the greater the adhesion and the better the toughening. Demonstration of this point of view has proved difficult because suitable materials for testing this hypothesis are not readily available. However, we have made several important investigations related to this area.

We examined the adhesion between poly(methyl methacrylate) and SAN copolymers as a function of the acrylonitrile content of the latter (30). Adhesion develops in these systems as a result of interpenetration of chains at the interface owing to the miscibility of PMMA and SAN. We have shown that the rate of interpenetration, or diffusion, is related to the degree of interaction between the two polymers and is maximum at the same point where the LCST shows a maximum. This suggests that for a PMMA matrix, that one would want to use a rubber modifier having an SAN shell containing about 15% acrylonitrile or that for a rubber modifier with a PMMA shell, maximum adhesion would occur to an SAN matrix containing this amount of acrylonitrile.

In related studies, we have discovered that using two different types
of rubber particles can lead to a synergistic toughening \((28, 32)\). In this work a commercial shell-core emulsion-made impact modifier and a commercial SBS triblock copolymer were used as the sources of rubber particles. The former particles are about 0.2 microns in diameter while the latter are of the order of 5 microns. This wide discrepancy in size seems to be related to the mechanism leading to this synergism. It is believed that the small particles are involved in the shear yielding process while the larger particles may be responsible for craze formation. Some justification for this explanation has been developed using stress dilatometry to learn the relative proportions of shear and craze deformation mechanisms \((33)\).

We have also shown that the emulsion-made rubber modifier particles will preferentially locate either in one phase of an immiscible blend or at the interface depending on interactions between the shell material and the matrix material and the method of processing \((32)\). This is an important lead that needs additional investigation since there is growing interest in rubber toughening of multiphase polymer blend systems.

G. Gas Permeation in Liquid Crystalline Polymers

During this research program, we briefly investigated the gas transport properties of a thermotropic liquid crystalline polymer since such measurements had not been previously reported in the literature. We found that this particular polyester has outstanding barrier properties \((26)\). This material has gas permeability coefficients which are lower than that of polyacrylonitrile which is, of course, well known for its barrier characteristics. However, polyacrylonitrile cannot be used as a homopolymer owing to its intractability. This is an important discovery that may find considerable application. We are continuing this investigation.
H. Reviews of Polymer Blends

On several occasions during the course of this research, we had occasion to write reviews on the subject of polymer blends (5, 11, 13, 29, 31). These have been published in various places which should provide considerable help in dissemination of the findings of our research.
III. Publications Completed to Date

A. Theses and Dissertations

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<tr>
<th>Name</th>
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<tr>
<td>J. L. Pfennig</td>
<td>&quot;Thermodynamics and Physical Properties of Blends Containing SAN Copolymers&quot;</td>
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<td>(M.S.)</td>
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<td>J. S. Chiou</td>
<td>&quot;Sorption and Transport Behavior of Miscible Polymer Blends&quot;</td>
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<td>(Ph.D.)</td>
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<td>A. C. Fernandes</td>
<td>&quot;Structure-Miscibility Relationships for Selected Polymer Blends&quot;</td>
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<tr>
<td>(Ph.D.)</td>
<td></td>
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<tr>
<td>M. E. Fowler</td>
<td>&quot;Multicomponent Polymer Blends: Miscibility, Rubber Toughening and Kinetics of Diffusion&quot;</td>
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B. Papers in Print


C. Papers Submitted or Accepted for Publication


IV. Participating Scientific Personnel

The following individuals received some financial support from this contract:
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<tr>
<td>D. R. Paul</td>
<td>Faculty</td>
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<tr>
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<td>one month/year</td>
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<tr>
<td>J. S. Chiou</td>
<td>Ph.D. student/Postdoctoral Fellow</td>
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<tr>
<td>D. H. Weinkauf</td>
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