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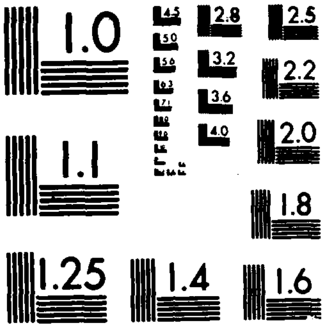
MASSACHUSETTS UNIV AMHERST DEPT OF POLYMER SCIENCE AND
ENGINEERING F E KARASZ 30 APR 87 AFOSR-TR-88-0067
UNCLASSIFIED   F49620-85-C-0127   F/G 11/9   NL



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AFOSR-TR- 88-0067

FINAL REPORT

IMPROVED STRUCTURAL POLYMER ALLOYS AND COMPOSITES

DARPA/AFOSR F49620-85-C-0127

1 May 1985 - 30 April 1987

Frank E. Karasz
Polymer Science and Engineering
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UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

ADA192092

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
Approved for Public release;
Distribution Unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)
AFOSR-TR- 88-0067

6a. NAME OF PERFORMING ORGANIZATION
University of Massachusetts

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
AFOSR/NC

6c. ADDRESS *(City, State, and ZIP Code)*
Amherst, MA 01003

7b. ADDRESS *(City, State, and ZIP Code)*
Bldg 410
Bolling AFB DC 20332-6448

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
AFOSR

8b. OFFICE SYMBOL *(If applicable)*
NC

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
F49620-85-C-0127

8c. ADDRESS *(City, State, and ZIP Code)*
Bldg 410
Bolling AFB DC 20332-6448

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
61102F	2303	A3	

11. TITLE *(Include Security Classification)*
Improved Structural Polymer Alloys and Composites

12. PERSONAL AUTHOR(S)
Frank E Karasz

13a. TYPE OF REPORT
FINAL

13b. TIME COVERED
FROM ________ TO ________

14. DATE OF REPORT *(Year, Month, Day)*

15. PAGE COUNT
36

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

Considerable success was achieved relative to the goals of this project. Most importantly, a new generic class of high performance polymer blends was discovered. It is believed that polybenzimidazoles and polymides are miscible over a wide range of compositions, structural variations and temperature regimes. This assertion is based on work with the blends described in this report, utilizing commercially available materials. Evidence for their miscibility was displayed in their glass transition behavior, as elucidated by DSC and DMA, and in their IR spectral properties. Their phase behavior was also examined. Several blend combinations have been scaled up for evaluation to delineate technologically useful systems.

The systhesis and properties of two high performance ionomers were also investigated: sodium sulfonate (Udel) polysulfone (Na-SPSF) and sodium sulfonate poly(ether ether ketone) (Na-SPEEK). Improved and novel syythetic techniques were developed so that random, homogeneous copolymers could be prepared. Their glass transition behavior and

(over)

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
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22b. TELEPHONE *(Include Area Code)*
(202) 767-4963

22c. OFFICE SYMBOL
NC

DD Form 1473, JUN 86

Previous editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

thermal stabilities were assessed. Their blend properties were also assessed and analyzed theoretically in terms of a mean-field treatment. Interaction parameters were calculated.

Also studied were blends of aryl homopolymers and aryl copolymers containing ether ketone (EK), either ether ketone (EEK) and ether ether sulfone (EES) repeat units. Their transition and phase behaviors were examined. UCST type behavior was generally observed. Interaction parameters were calculated using a mean-field formalism.

Another important area of blend study was that of liquid crystal copolyester blends. Important property synergies were observed and delineated. Their morphology and phase behavior were defined. Improved processing was observed, wherein molding could be accomplished as much as 60C lower than with the neat resins.

Some important theoretical problems were addressed. These included: the theory of microphase separation of graft and staf copolymers and the effect of sequence distribution on miscibility in copolymer/copolymer blends. sans and TJLS were used to describe the phase decomposition kinetics of PS/PVME blends.

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CONTENTS

Acknowledgement

The Principal Investigators would like to express their sincere thanks to Dr. Donald L. Ball, Director of Chemical Sciences, Air Force Office of Scientific Research, to Dr. Donald R. Ulrich, Program Manager, Directorate of Chemical Sciences and to Dr. Phillip Parrish and Major Steven Wax, Defense Advanced Research Projects Agency for their unfailing cooperation, help and courtesy extended to them during the period of this grant.

I. TITLE: Improved Structural Polymer Alloys and Composites

II. PRINCIPAL INVESTIGATORS: Dr. Frank E. Karasz
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III. INCLUSIVE DATES: 3 May 1985 - 2 May 1987

IV. CONTRACT/GRANT NUMBER: F49620-85-C-0127

V. COSTS AND FISCAL YEAR SOURCE: $888,511 FY '85
$1,048,272 FY '86

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VII. ABSTRACT

Considerable success was achieved relative to the goals of this project. Most importantly, a new generic class of high performance polymer blends was discovered. It is believed that polybenzimidazoles and polyimides are miscible over a wide range of compositions, structural variations and temperature regimes. This assertion is based on work with the blends described in this report, utilizing commercially available materials. Evidence for their miscibility was displayed in their glass transition behavior, as elucidated by DSC and DMA, and in their IR spectral properties. Their phase behavior was also examined. Several blend combinations have been scaled up for evaluation to delineate technologically useful systems.

The synthesis and properties of two high performance ionomers were also investigated: sodium sulfonate (Udel) polysulfone (Na-SPSF) and sodium sulfonate poly(ether ether ketone) (Na-SPEEK). Improved and novel synthetic techniques were developed so that random, homogeneous copolymers could be prepared. Their glass transition behavior and thermal stabilities were assessed. Their blend properties were also assessed and analyzed theoretically in terms of a mean-field treatment. Interaction parameters were calculated.

Also studied were blends of aryl homopolymers and aryl copolymers containing ether ketone (EK), ether ether ketone (EEK) and ether ether sulfone (EES) repeat units. Their transition and phase behaviors were examined. UCST type behavior was generally observed. Interaction parameters were calculated using a mean-field formalism.

Another important area of blend study was that of liquid crystal copolyester blends. Important property synergies were observed and delineated. Their

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Some important theoretical problems were addressed. These included: the theory of microphase separation of graft and star copolymers and the effect of sequence distribution on miscibility in copolymer/copolymer blends. SANS and TJLS were used to describe the phase decomposition kinetics of PS/PVME blends.

VIII. UNIVERSITY OF MASSACHUSETTS ACCOMPLISHMENTS

(1) Sodium Sulfonate (Udel) Polysulfone (Na-SPSF):

An improved synthesis procedure was developed to produce Na-SPSF copolymers with random, homogeneous structures for less than 30 mole % sulfonation. Previous methods produced ill-defined, heterogeneous copolymers. Na-SPSF copolymers are not sufficiently stable for use as high-temperature, high-performance ionomers, but they are more soluble and tractable than their sulfonated PEEK counterparts to be described below. Thus, they are useful as model systems in studies of solution behavior and membrane performance. In contrast to earlier work, T_g was found to increase non-linearly with sodium sulfonate content. A SAXS study provided no evidence of ionic clustering in these polymers. Binary blends of Na-SPSFs differing only in composition were prepared by casting films from solution, and their phase behavior was studied by dynamic mechanical analysis after annealing at 250°C. It was found that the blends were miscible up to a composition difference of about 9 to 10 mole % sodium sulfonate. Using this fact, it was possible to calculate a value for $\chi_{AB}n$ of 200 to 250, where χ_{AB} represents the segmental interaction parameter between modified and unmodified repeat units, and n is the degree of polymerization. Uncertainty in the degree of ionic association places a degree of uncertainty on the effective value of n and therefore on χ_{AB}. The product, however, is independent of any assumptions regarding molecular associations.

(2) Sodium Sulfonate Polyaryletheretherketone (Na-SPEEK):

Earlier published methods for preparing SPEEK produced ill-defined, heterogeneous copolymers, with sulfonation levels generally greater than 20 to 30 mole %. The latter are higher than one normally employs in membrane and ionomer applications. Two synthesis procedures were developed to produce random, homogeneous copolymers over the entire accessible composition range of zero to 100 mole % sulfonation. One method is applicable to the lower sulfonation levels (0 to 40 mole %) and thereby allows the production of an entirely new series of ionomers. It is believed that the ionomers produced by this method are the most solvent and heat resistant ionomers yet produced. The other method is applicable to higher sulfonation levels (30 to 100 mole %), and it represents an improved version of earlier methods.

Sodium SPEEK copolymers appear to be sufficiently stable, both thermally and chemically, to merit consideration as high performance ionomers, ionomeric interpenetrating polymer networks (IIPNs) and membranes - perhaps to temperatures as high as 300°C. Sodium SPEEK copolymers, covering the 5 to 100 mole % sulfonation range, were prepared and examined by DSC, TGA, SAXS and moisture absorption techniques to elucidate their structure. The behavior of T_g, ΔT_g and ΔC_p at the glass transition as a function of composition suggested the onset of ionic clustering below 25 to 30 mole % sodium sulfonate - an observation confirmed by SAXS studies. In particular, T_g increased sigmoidally from about 150°C for 5 mole % Na-SPEEK to 415°C for 100 mole % Na-SPEEK. No evidence of crystallinity was observed by DSC in thermally annealed and quenched samples above 9 mole % sodium sulfonate. The equilibrium water content at room temperature and 58% relative humidity was four molecules of water per sodium sulfonate group for all compositions. For immersed films, this value increased from 9 molecules of water per sodium sulfonate group for 38 mole % Na-SPEEK to an undeterminably large number for 100 mole % Na-SPEEK, which slowly dissolved. Upon re-equilibration at 58 mole % relative humidity, the water content of the films decreased to about 5.5 molecules per sodium sulfonate group. A low temperature (-80 to -60°C) mechanical relaxation peak was present in the films conditioned at 58% relative humidity.

(3) Polybenzimidazole/Polyimide (PBI/PI) Miscible Blends:

A new family of miscible polymer blends, based on aromatic polybenzimidazoles (PBIs) and aromatic polyimides (PIs) has been discovered. Polymers of these generic types are believed to be miscible over a comparatively wide range of compositions and structural variations. This assertion stems from work carried out with the polymers listed in Table I. Since this initial discovery, the UMass research team has focused its efforts on several fundamental objectives, using PBI/PI blend combinations based on the polymers listed in Table I: (a) to study the thermal parameters associated with the glass transition, (b) to delineate the limits of miscibility in terms of composition and temperature and (c) to obtain evidence for the existence of specific interactions and to elucidate the nature of these interactions.

(a) Glass Transition Behavior. The parameters of interest were the value (T_g), the width ($\Delta T_g = T_g$ - Tonset) and the magnitude (ΔC_p). In all cases single composition dependent T_g's were obtained over the entire composition range. For blends of PBI with Ultem 1000, XU 218 and PI 2080 all three thermal parameters were obtained. Figures 1 and 2 show the relevant data for a representative system, PBI/XU 218. In this case, the T_g-composition line lies above the values expected from linear interpolation, ΔT_g displays a maximum and ΔC_p displays a minimum. In all cases, T_g lies close to the weight average line displaying deviations that are small compared to the values measured, and ΔT_g displays maxima with deviations that are also small compared to the T_g values. All the PBI/PI systems display ΔC_p maxima, and the deviations are of the same order as the values measured (0.08 to 0.20). The latter behavior may be attributed to strong intermolecular bonding.

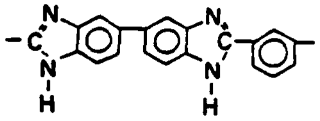
(b) Phase Behavior. Three of the blend compositions based on the materials listed in Table 1 were shown to exhibit lower critical solubility temperature (LCST) phase behavior. The miscibility/immiscibility phase boundary was reasonably well defined for the PBI/XU 218 system using DSC techniques. The LCST occurred between 420 and 430°C at 50 wt % PBI.

Because of the thermal instability of PI 2080, DSC techniques could not be used to establish the phase boundary; rather, IR was used to follow the loss of the shift in the N-H stretching band as a function of annealing temperature (T_a) and annealing time (t_a). LCST type behavior was indicated, but it was not possible to locate the phase boundary. The PBI/Ultem 1000 system displays a LCST below the T_g-composition line between 30 and 80 wt % PBI. No evidence for phase separation was observed for the PBI/LaRC TPI systems for T_a up to and including 450°C by using either the DSC or IR techniques.

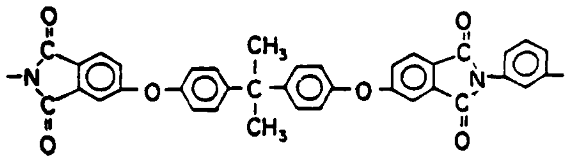
Table 1 Polymers Studied in PBI/PI Blend Program

Chemical Name/Source: Common Name (T_g) Structure

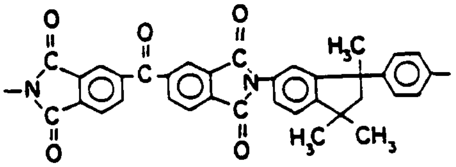
(a) Poly(2,2'(m-phenylene)-5,5'-bibenzimidazole)
[Celanese Corporation: PBI (T_g = 420°C)]



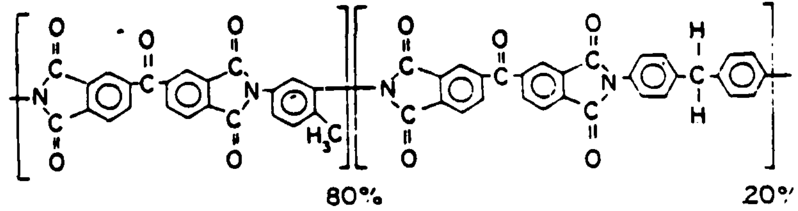
(b) Poly[2,2'-bis(3,4-dicarboxyphenoxy)phenylpropane]-2-phenylene bisimide]
[General Electric Company: Ultem 1000 (T_g = 220°C)]



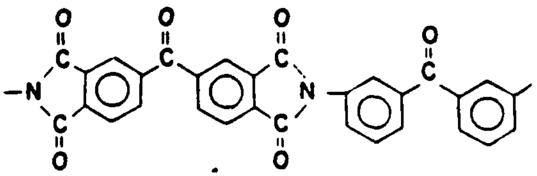
(c) Condensation product of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 5(6)-amino-1-(4'aminophenyl)-1,3,3-trimethylindane
[Ciba-Geigy Corporation: XU 218 (T_g = 320°C)]



(d) Condensation product of BTDA and a 4/1 molar mixture of 2,4-toluene diisocyanate and 4,4'-diphenylmethane diisocyanate
[Dow Chemical Co.: PI 2080 (T_g = 310°C)]



(e) Condensation product of BTDA and 3,3'-diaminobenzophenone (DABP)
[Mitsui Toatsu Chemicals, Inc.: LaRC TPI (T_g = 267°C)]



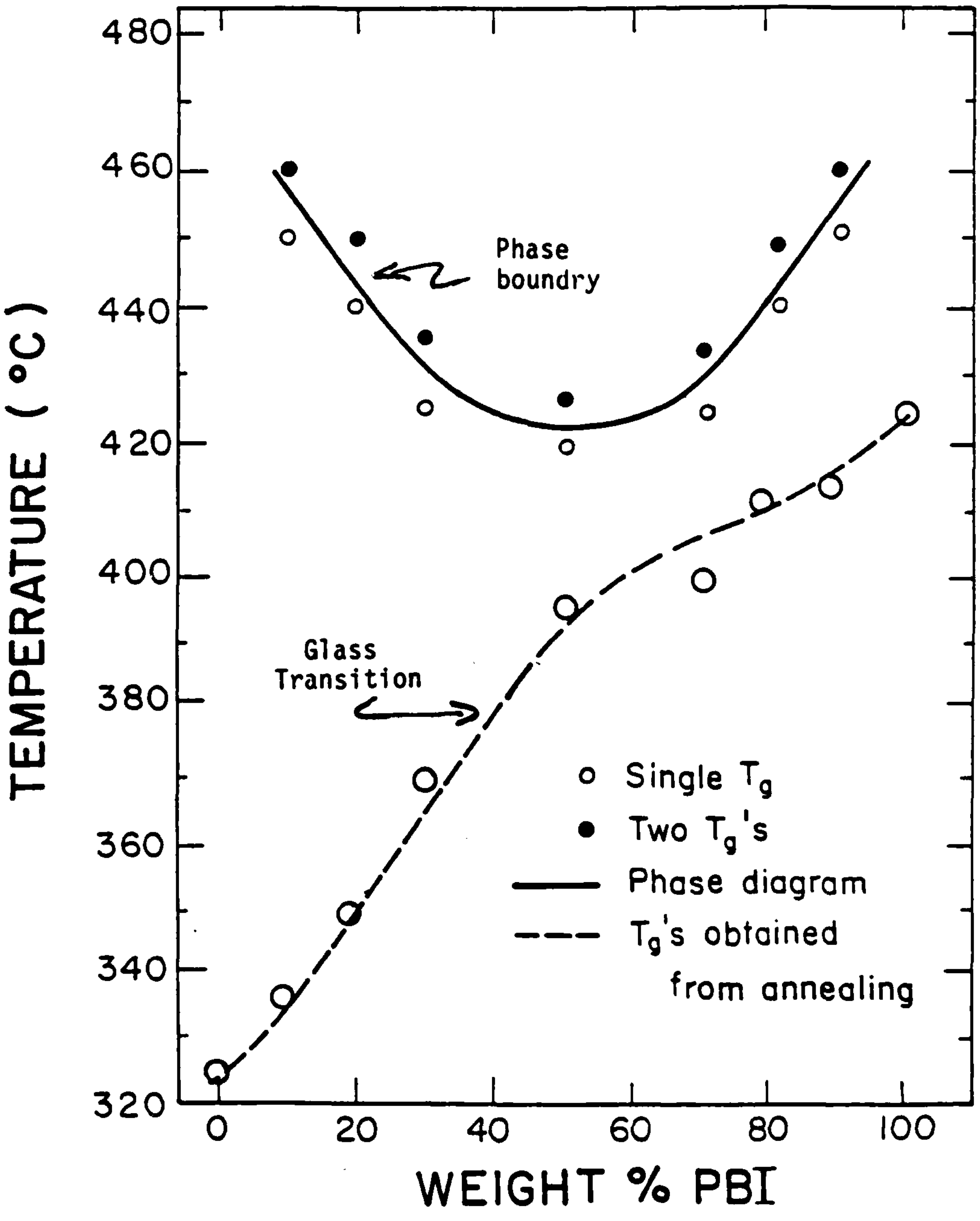


Fig. 1. Phase diagram of PBI/ XU 218 blend.

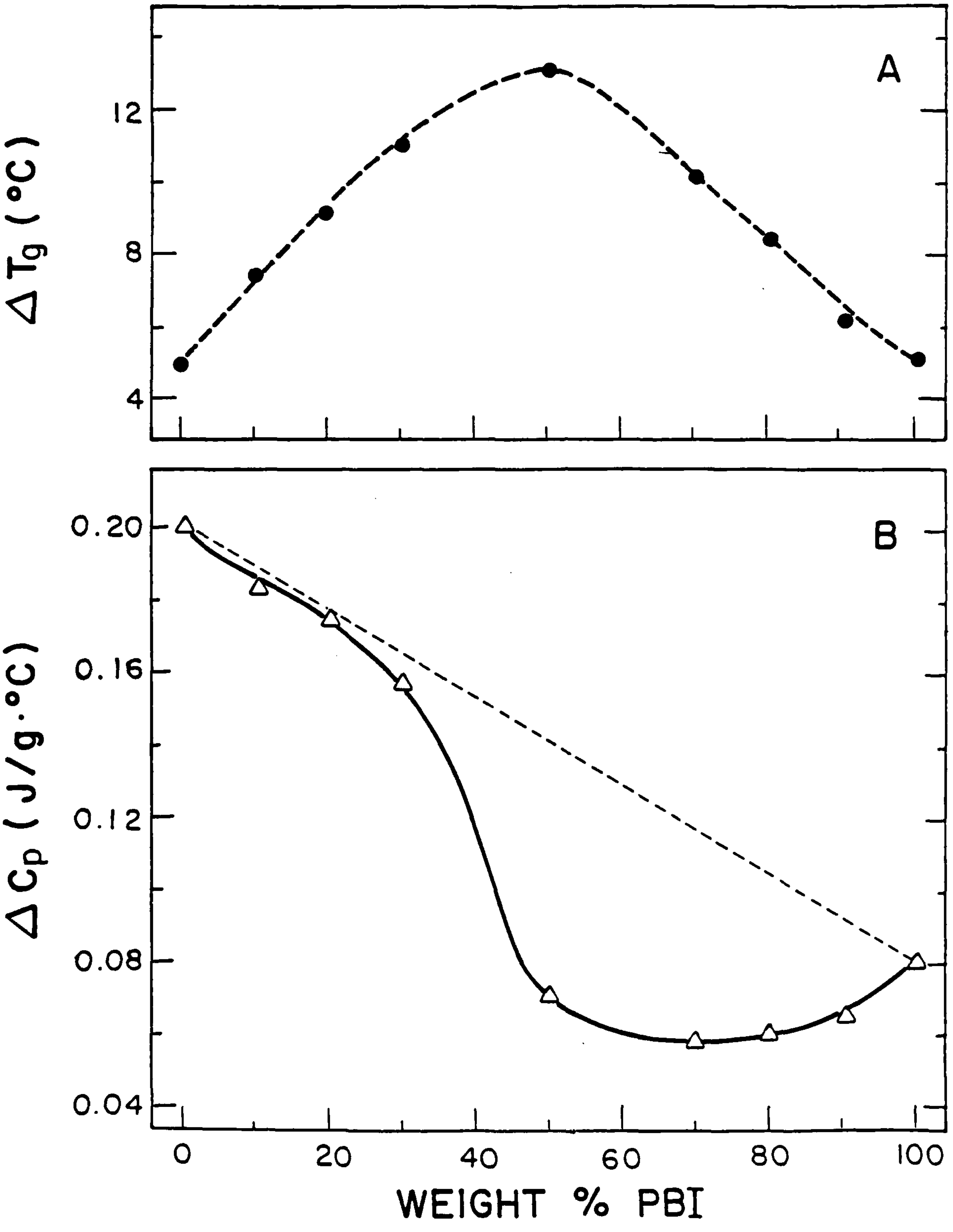


Fig. 2. ΔT_g (A) and Δc_p (B) vs. composition in PBI/ XU 218 blend.

(c) IR Spectroscopy. The IR spectra of all the PBI/PI blends displayed composition dependent frequency shifts of up to 55 cm^{-1} in the N-H stretching band of PBI and up to 6 cm^{-1} in the carbonyl stretching band of the PIs. These shifts could be removed by thermally-induced phase separation. These results suggest that the miscibility of these blends derives from specific intermolecular interactions involving the >NH and carbonyl groups.

(d) Catalytic Activity of Benzimidazole in the Immidization of Polyamic Acids. The catalytic effect of benzimidazole on the rate of immidization of several polyamic acids is described. With benzimidazole, equivalent levels of immidization could be attained at up to 100°C below the temperature required in its absence. The effect is not solvent dependent. Much lower catalytic activity was displayed by imidazole.

(4) Phase Behavior of Homopolymers and Copolymers Containing Ether Ether Ketone and Ether Ether Sulfone Repeat Units.

(a) PEES/COPEEKS Blends. Upper Critical Solubility Temperature (UCST) behavior was found in blends of the homopolymer poly(ether ether sulfone)(PEES) with the copolymer poly(ether ether ketone-*co*-ether ether sulfone)(COPEEKS) for copolymer compositions ranging from 43 to 56 mole % EEK units. Blend compositions studied ranged from 25 to 75 wt % PEES. The consulate temperature occurred at a 50/50 PEES/COPEEKS ratio and increased with the EEK content of the copolymer. This miscibility behavior was interpreted using a mean-field theoretical approach, and a segmental interaction parameter ranging from 0.054 to 0.032 was calculated.

(b) PEEK/COPEEKS Blends. The transitional and miscibility behavior of PEEK/ /COPEEKS blends was studied, over the copolymer composition range of 50 to 73 mole % EEK units. UCST behavior was observed for blends miscible in the melt state with EEK contents ≥ 73 mole %. COPEEKS/COPEEKS blends were miscible for composition differences of less than about 50 mole % and the segmental interaction parameter was found to be between 0.040 and 0.045 in agreement with the value cited above.

(5) PEK/PEEK Blends.

The miscibility of the amorphous and crystalline phases of poly(ether ketone)(PEK) and poly(ether ether ketone)(PEEK) blend was studied using DSC and WAXS. These polymers co-crystallize only upon quenching from the melt. A comparison of DSC scans of physical mixtures and melt blends indicates that conclusions about miscibility in the amorphous phase cannot be drawn on the basis of the appearance of a single glass transition. Results relative to the crystalline phase of the blend suggests miscibility in the amorphous state.

IX. CELANESE RESEARCH CO. ACCOMPLISHMENTS

IMPROVED STRUCTURAL POLYMER ALLOYS AND COMPOSITES

FINAL REPORT - SUMMARY

M. JAFFE, E. CHENEVEY, W. COOPER, M. DEMEUSE

PBI Containing Polymer Blends

PBI is a high molecular weight thermally stable thermoplastic polymer produced by Hoechst-Celanese. As such, it offers a very high glass transition temperature coupled with excellent chemical resistance and thermal stability, thereby providing a commercial base for new high temperature resistant polymeric blends.

Initial systems investigated were blends of PBI with polyacrylonitrile, polysulfone, and poly-m-phenylene isophthalamide (PPI). The first two systems seemed incompatible and were dropped. Although initial cast film samples showed phase separation, the PBI/PPI system was continued since copolymers of PBI/PPI could be made and studied to verify theoretical predictions.

Blending was done with solutions in dimethyl acetamide (DMAc) containing lithium chloride (LiCl). From these dopes, films were cast on glass plates, the bulk of the solvent removed in an oven, and the remainder washed out with water. Phase separation was evident; the size and amount varying with the composition and the solvent removal rate.

Compositions containing 75, 85 and 95% PBI with the remainder PPI were spun into fiber utilizing standard PBI spinning procedures and equipment. Properties similar to 100% PBI were obtained. Upon drawing, the plasticization afforded by the PPI evidenced itself as lower optimum draw temperatures. At 450°C, the 85/15 and 75/25 blends were so plasticized that they could be stretched without increasing either strength or modulus. Microscopic examination of the undrawn fibers showed them to be homogeneous down to the micron level.

Copolymers of PBI/PPI were made and preliminary characterization was done at U Mass. The conclusions reached were: (a) the copolymers were not thermally stable, increasing in T_g upon heating, (b) the T_g's fell on a reasonable compositional straight line between the homopolymers, and (c) the copolymers containing 35 and 50% PPI were immiscible with PBI as determined by DSC. At that time, efforts shifted to studying blends of PBI with ULTEM polyetherimide which had been shown to be miscible in all proportions with PBI at U. Mass.

PBI/ULTEM compositional screening was done with hand cast films by blending DMAc polymer solutions and casting on glass plates. Physical properties and moisture regain fell on a straight line between the two parent polymers. Compositions containing mostly ULTEM tended to turn cloudy during casting due to moisture. These films were found to be very brittle. Later machine cast films were no better.

Compositional screening at U. Mass had determined that about 30% PBI added to ULTEM produced a blend with resistance to methylene chloride and chloroform, an effect which we confirmed. Additional work was done by the PBI Business Group to define the features of the 30/70 PBI/ULTEM blend. They found that contrary to experience with PBI, the DMAc solvent was not removed by water washing but could be removed thermally. Lithium chloride was not needed for dope stability as is the case for PBI, and in fact adding LiCl to the dope produced brittle film while without it, tough films were obtained. Later it was found that LiCl caused phase separation of the sample and this was the source of the brittleness. Fibers were also prepared from this composition. Lithium chloride in the fiber produced a "dull" fiber which proved to be phase separated whereas without LiCl, a "bright" homogeneous fiber resulted.

Thermal phase separation was observed at 300°C for this blend composition, again in agreement with U. Mass results. ULTEM was observed exuding to the surface in the hot stage microscope and its presence was confirmed by FTIR. Methylene chloride removed it while subsequent heating caused it to reappear.

Two other thermoplastic polyimides were found to be miscible with PBI; Ciba-Geigy XU 218 and Dow 2080. These materials were screened with hand cast films in the same manner as done with ULTEM and behaved similarly. Moisture sensitivity did not seem to pose a problem with these materials; clear films were obtained. U Mass also showed that the NASA-LANGLEY developed LARC-TPI was miscible with PBI. Since the fully cyclized polymer is insoluble, the precursor polyamic acid form was blended with PBI. In attempting this with viscous high solids solutions, the LARC gelled in the PBI; it being an acid and acids gell PBI. Although some cyclization of the polyamic acid can occur and still leave a soluble polymer, these complexities caused work with this system to be deferred.

Half pound sized quantities of fiber were spun using PBI like conditions from compositions of 75% PBI with 25% ULTEM, XU 218, and 2080. To obtain sufficient viscosity for spinning, the solids levels had to be raised significantly above that necessary for PBI itself. All of these polyimides had lower solution viscosities than PBI. Blending with PBI generally produced a blend viscosity lower than either parent.

After spinning, the fibers were hot drawn. Consistent with their lower glass transition temperature, the blends showed optimum draw at somewhat lower temperatures than did PBI. These drawn variants were screened for their thermal resistance by exposure in a circulating air oven for an hour at temperatures up to 400°C. Subsequent testing at room temperature showed that strength had decreased about one half although modulus had decreased only slightly. All compositions gave similar results as did PBI itself. Aging was also done for one and 15 minutes directly in the Instron oven with the fibers broken at temperature. Strength and modulus levels of one third to one half of their original room temperature properties were obtained. Temperatures to 450°C were tested. The blend containing ULTEM was the poorest as expected but only at the highest temperature. Typical properties at 400°C after 15 minutes aging were: 30ksi tensile strength with 0.5Msi modulus.

Molding studies were initially done with fibrids prepared by precipitating a blend dope in a blender with water. After washing out the solvent and drying, the resulting fluffy polymer was molded into disks. Molding below the T_g of the composition produced low density opaque disks, while above T_g, shiny somewhat translucent disks with high density were obtained. All compositions were found to be brittle, probably because there was no real melt and thus no mechanism to connect and orient the individual particles. Thermal phase separation in the PBI/ULTEM system was observed in these moldings but was not studied.

Since the ultimate use objective of these blends is as a high temperature matrix material and one method for preparing prepreg is by use of a woven matrix resin fiber, molded bars were prepared directly by winding fiber into a mold and then pressing at temperatures above T_g. Bars were made at 20 and 50°C above the respective T_g's with 300 psi pressure. Typical flex strengths were 30-40ksi with 0.5-0.9Msi modulus. Properties were not better with higher molding temperatures. Void content was in fact greater, probably due to small amounts of residual solvent. Generally, complete solvent removal has been a persistent and seious problem, it being tenaciously held by the polymer. Tensile strengths measured on several samples were found to be comparable to the flex values.

Trials to prepare blends via melt processes were unsuccessful. ULTEM formed a stable melt at 350°C; however, even small amounts of PBI did not dissolve in it. Both XU 218 and 2080 did not melt although softness was evident, while cyclized LARC-TPI melted but then gelled after a few minutes.

Based on the above screening and all the characterization at U. Mass, two compositions were selected for further evaluation in composites. The first, 85/15 PBI/ULTEM should have about a 20-30°C "processing window" between its T_g and the temperature of thermally induced phase separation. Higher PBI contents would provide larger windows but at the expense of less blend plasticization of the PBI. The second candidate is 75/25 PBI/XU 218, chosen as generally having the best level of properties. Work to characterize these systems along with PBI itself and to prepare composite samples for process and property evaluation is continuing under the new program.

LCP CONTAINING BLENDS

The work that has been performed has centered on defining the structure-property relationships of blends in which both of the component materials are capable of forming liquid crystalline phases. It had previously been determined by a number of workers that such blends often displayed mechanical property synergisms. In this context, synergism refers to properties given by more than a weighted average of the component material values. These original observations were confirmed in the present study. Characterization of both the mesophase and solid state structure which is present in these blends has provided insight into the occurrence of these synergisms.

Work has concentrated primarily on three systems:

(1) CO/CO

(2) CO/COTH blends and

(3) CO/HNATH blends

The second and third systems were used as model systems for the evaluation of injection molded performance. The CO/CO blend system has been used as a test of traditional blend theory as it applies to liquid crystal polymer systems.

The rheological response which is observed on a small scale in LCP/LCP blends was characterized as falling into two categories. Either the power-law response was given by a rule of mixtures (CO 73/27 + HNATH 50/25/25) or the response deviated from rule of mixtures behavior (CO 73/27 + COTH 57-41/1/1). Using these two systems as models, scale-up to extruder level production occurred. After extrusion of the blends, injection molding followed. Evaluation of the physical properties and characterization of the solid state structure which is responsible for those properties completed the protocol.

The CO/COTH system has demonstrated that it is possible to modify the rheology of one LCP by blending with another LCP. Use of this concept has allowed a blend which is predominantly CO to be processed as much as sixty degrees lower than the neat CO is typically processed. This results in an increase in mechanical properties, particularly notched Izod values, where values as high as 30 ft.-lbs./in. notch have been observed.

The CO/HNATH system yielded property synergisms in tensile, flex and HDT properties. The maxima in properties have been observed at the 75 percent HNATH level. By sectioning molded flex bars, this composition blend has also been shown to have two directional orientation in the core of the bar. This result could have implications toward solving the transverse property problem which is normally associated with LCP's. It has also been shown, by careful thermo-optical work, that the flow behavior of the CO/HNATH blend systems can change, depending on the particular temperature. Most interestingly, blends which contain 25 percent HNATH have been shown to display flow characteristics at elevated temperatures which are similar to the HNATH component. This result has implications for using low levels of a more orientable LCP in a blend with CO in order to achieve higher mechanical property profiles.

Solid state characterization techniques, particularly DSC and DMTA, have been used to define the solid state structure which is present in the blend samples. Careful DSC experiments have shown that all of the blend compositions display a single endotherm in the as-produced samples. Annealing has been shown to change the structure of these samples. In some blend compositions, the structure which is obtained displays two melting endotherms. It is also these compositions which display the lowest mechanical properties. Conversely, samples which display a homogeneous structure, as judged by DSC measurements, display the highest mechanical properties in molded pieces. DMTA work has further confirmed that the blend compositions which display the highest mechanical properties have a more homogeneous solid state structure than the other compositions.

Along with studying the structure-property relationships of LCP blends, a good deal of work has also been devoted to understanding the science of LCP/LCP blends. What has been sought is a framework for understanding the experimental observations. With this in mind, CO/CO blends were studied as a model system.

The formalism of Karasz and MacKnight for treating blends containing copolymers makes definite predictions about such systems. The CO/CO system was a natural test of such ideas for blends containing liquid crystal polymers.

It was found that blends consisting of CO 75/25 with CO 58/42 display viscosity values intermediate to those of the component materials, behavior often associated with compatible blends. On the other hand, blends of CO 75/25 with CO 30/70 display viscosities which are governed by the lower viscosity component, behavior which is generally ascribed to incompatible systems. This observation would be in agreement with the predictions of Karasz and MacKnight's ideas, which suggest that as the difference in copolymer composition increases, the likelihood of immiscibility occurring increases.

The solid state properties of these blends were investigated mainly by X-ray diffraction and DSC techniques. Careful X-ray diffraction work eliminated the possibility of chemical reaction as being a dominant mechanism in the blend samples. DSC studies of these same samples always indicated a single endotherm regardless of blend composition. Both of the blend systems also had a composition at which the melting transition temperature was lower than for either of the component materials.

These DSC observations were interpreted in terms of Alan Windle's sequence matching arguments to explain the solid state order present in these random copolymer samples. Windle has been able to show that the primary match length correlates very well with the observed transition temperature for the neat copolymers. It has been possible to apply similar ideas to the CO/CO blend systems. Using this formalism, it has been shown that the transition temperature bahavior described previously can be explained by establishing a correlation with the average primary match length of the blend. This formalism should be useful for making progress in designing blend systems with a particular transition temperature behavior.

In summary, it has been shown that it is possible to control and modify both the mechanical properties and the rheological response of LCP's through blending techniques. This has the potential utility of being able to meet particular property requirements by blending. It has also been shown that the highest mechanical property level is achieved in homogeneous blends. A formalism for treating the solid state structure of LCP blends has been developed. Ultimately, these same ideas will be useful for describing the neat LCP's themselves and being able to correlate structures with desirable properties.

X. NATIONAL BUREAU OF STANDARDS CONTRIBUTION

Theoretical and Experimental Studies of Polymer Blends

Charles Han

Abstract

Theoretical and experimental work supported by this contract have been carried out at the Polymers Division, NBS. Our accomplishments can be summarized in four subjects listed as follows:

I. Theory of Microphase Separation in Graft and Star Polymers

II. Copolymer/copolymer Blends: Effect of Sequence Distribution on Miscibility

III. *SANS and TJLS Study of the Phase Decomposition Kinetics of PS/PVME*

IV. Morphological Studies of PBI/PEI Blends

I. THEORY OF MICROPHASE SEPARATION IN GRAFT AND STAR COPOLYMERS

Phase stability criteria and static structure factors have been calculated for simple AB graft copolymers, for star copolymers with equal number of A and B arms, and for n arm star diblock copolymers. The A-B interactions are characterized by the usual χ parameter. The fraction of A monomer in the graft copolymer is denoted as f and the fractional position along the A chain backbone at which the B graft is chemically linked is denoted as τ. When $\tau = 0$ or 1 the graft copolymer degenerates to a simple diblock copolymer. Leibler previously calculated that the critical value, $(\chi N)_c$, at which an AB diblock copolymer containing N monomer units undergoes microphase separation is 10.5. This critical value occurs at $f = 0.5$ and is the only composition for which the transition is second order. According to the present theory, a graft copolymer ($0<\tau<1$) does not have a critical point for any f; i.e. all transitions are first order. For a given τ, the spinodal values, $(\chi N)_s$, always reach a minimum value at $f = 0.5$; for $\tau = f = 0.5$, $(\chi N)_s = 13.5$. However, star copolymers with equal number (n) of A and B arms each containing N/2 monomers ($f - 0.5$) have a cricial point at $(\chi N)_c = 10.5$ for all values of n. Like the graft copolymers, the n arm star diblock copolymers (each arm is a diblock copolymer of composition f containing N monomer units) do not have a critical point. At $f = 0.5$ $(\chi N)_s$ equals 8.86, 7.07, 5.32 and 4.33, for n = 2, 4, 10, and 30, respectively. At a spinodal point the static structure factor S(q) diverges at a finite wave vector q^*. Near a critical point $q^*/2\pi$ determines the periodicity of the lowest symmetry ordered structure (mesophase) and is expressed in units of the copolymer's radius of gyration R.

II. COPOLYMER/COPOLYMER BLENDS

In a previous paper, we have discussed the effect of the sequence distribution of monomer units in a copolymer on the phase behavior of copolymer/homopolymer blends. Our model yielded an improvement to Flory-Huggins type theories for mixtures involving copolymers in that it was possible to make a distinction between the copolymer types (random, block, etc.) participating in the mixture. This was accomplished by introducing a parameter, θ, which described the binary sequence distribution of the monomers in the copolymer. By varying θ, a block, random or alternating copolymer could be described. Further, we assumed that the interaction energy between a monomer of homopolymer C and the monomer A (or B) in the copolymer AB is mediated by the nearest neighbors chemically bonded to the A (or B) structural unit. We showed that for a fixed composition, there is an optimal range of θ values (or sequence distributions) for which the AB/C system may be miscible.

We apply the above model to the mixture of two copolymers that differ only in composition, one containing f_A units of A comonomer and f_B units of B comonomer ($f_A + f_B = 1$) and the other g_A units of A and g_B units of B ($g_A + g_B = 1$). A special case of interest is where both copolymers have the same composition ($f_A = g_A$) and differ only in the sequence distribution of their monomers. An interesting question is: are there circumstances under which these polymers are immiscible? Experimentally it is known that blends of PVC and chlorinated polyethylene (CPE) are immiscible even when the CPE has the same Cl content as PVC. In this context, CPE may be considered as a random copolymer of CH_2(≡A) and CHCl(≡B), while PVC is the alternating copolymer composed of these units.

The theoretical formulations have been calculated and compared to experimental observations of the phase behavior of blends of CPE. Various interaction parameters required by the theory have been determined.

III. SANS AND TJLS STUDIES OF THE PHASE DECOMPOSITION KINETICS OF PS/PVME:

Phase decomposition kinetics of polymer blends has become an increasingly interested subject in recent years because of its fundamental and practical importance. deGennes and Pincus (D-P) presented calculations on the subject of spinodal decomposition in polymer blend systems by adapting the original Cahn-Hilliard (C-H) theory which was developed for low molecular weight systems. Later on, Binder and Strobl (B-S) extended the C-H development to include thermal fluctuations which was originally introduced by Cook in 1970. Although these two theories (D-P and B-S) have introduced different viewpoints to describe the fluctuations which have wave lengths smaller than that of a polymer coil; but for length scales larger than the polymer coil, their results lead to expressions different only by a thermal fluctuation (or thermal noise) term. They both used Flory-Huggins description for free energy and interaction parameter, χ. They also adapted Helfand's model for the interfacial free energy density of the square gradient term.

We have studied both static and dynamic behaviors of phase decomposition of polystyrene/poly(vinylmethylether) blends system by small angle neutron scattering (SANS) and time resolved temperature jump light scattering (TJLS) techniques. We have obtained the phase diagram, critical exponents, ν and γ and the spinodal temperatures. We have also obtained the temperature and composition dependence of the binary interaction parameter, χ and the second derivative of free energy versus composition, $\partial^2 f/\partial^2\phi$, which is the thermodynamic driving force for phase decomposition. From the TJLS experiments, we have obtained the growth rate (decomposition rate) at various composition, and quench depth.

We have been able to compare the early stage results with the Cahn-Hilliard-

Cook calculation. The mean-field nature of polymer system has been examined. The linearized theory has been verified quantitatively. The thermal noise contribution introduced in Cook's calculation has been extracted for the first time and compared with the "virtual structure factor" calculated from experimental data measured in the one phase region. The interfacial free energy density has been measured and compared quantitatively with the static structure factor, S(q). Mutual diffusion coefficients have been measured in both one phase and two phase regions. By containing static results with kinetic measurement, the Onsager mobility, M has been obtained as a function of temperature.

Last stage coursing has been evaluated according to scaling analysis. Percolation behavior has been observed.

IV. MORPHOLOGICAL STUDIES OF PBI/PEI BLENDS

Solution cast films of blends of poly(benzimidazole)(PBI) and poly(etherimide) PEI have been examined by small angle x-ray scattering (SAXS), transmission electric microscopy (TEM) and nuclear magnetic resonance (NMR). Films were cast from a 0.5% (w/v) solutions of PBI and PEI in dimethylacetamide (DMAc) from coworkers at the University of Massachusetts. The morphology studies have concentrated on one composition, 25-75 PBI/PEI (by weight) because the glass transition of the blend is relatively low (270°C).

SAXS and TEM Studies

The unannealed solution cast films showed essentially no small angle x-ray scattering indicating that the blend was homogeneous with no measurable electron density fluctuations over a size scale of 50-500 Å. After annealing above T_g (300°C, 350°C and 450°C) the SAXS intensity increased dramatically. This was evidence for phase separation of the blend above T_g. The scattering profile could be modeled by a random, two phase system with an exponential correlation function. The correlation length obtained from such an analysis was in the range of 50-150 Å and increased with increasing annealing temperature. Transmission electron microscopy complemented the SAXS results with unannealed films exhibiting no observable inhomogeneous structure. After annealing above T_g evidence for phase separation was also observed by TEM. Composition fluctuations on the scale of a few hundred angstroms were observable with the higher annealing temperatures leading to more pronounced composition differences.

NMR Studies

Measurements of the spin diffusion relaxation times T_1 and $T_{1\rho}$ by NMR indicate that the unannealed 25/75 PBI/PEI blend is homogeneous on a size scale of 60 Å and larger. After annealing at above T_g (400°C) the spin diffusion measurements clearly show phase separated regions between 200 Å and 1000 Å in size.

Conclusions

The PBI/PEI blends are homogeneous as cast from solution. The system phase separates upon heating above T_g (of the homogeneous blend) with the resulting morphology consisting of PBI rich and PEI rich domains a few hundred angstroms in size.

The phase separation may be self limiting in a sense because, at a fixed annealing temperature above T_g, the PBI rich domains will increase in PBI content until their T_g equals the annealing temperature whereupon the phase separation will stop. Pure PBI has a T_g of about 420°C (PEI T_g~220°C) and phase separation will halt at an early stage at annealing temperature less than 420°C.

XI. Publications

1. "Effect of Sequence Distribution on the Miscibility of Polymer/Copolymer Blends", A.C. Balazs, I.C. Sanchez, I.R. Epstein, F.E. Karasz, W.J. MacKnight, Macromolecules, 18, 2188-2191 (1985).
2. "Copolymer/Copolymer Blends: Effect of Sequence Distribution on Miscibility", A.C. Balazs, F.E. Karasz, W.J. MacKnight, H. Ueda, I.C. Sanchez, Macromolecules, 18, 2784-2786 (1985).
3. "Solubility and Properties of a Poly(aryl ether ketone) in strong Acids", M. Bishop, F.E. Karasz, P. Russo and K. Langley, Macromolecules, 18, 2786 (1985).
4. "Compatibility in Blends of Two Random Copolymers Having a Common Monomer Segment", T. Shiomi, F.E. Karasz and W.J. MacKnight, Macromolecules, 19, 2274-2280 (1986).
5. "Miscible Blends of Aromatic Polybenzimidazoles and Aromatic Polyimides", L. Leung, D. Williams, F.E. Karasz and W.J. MacKnight, Polymer Bulletin, 16, 457-464 (1986).
6. "A Small Angle X-ray Scattering Study of Sodium Sulfonate Poly(ether ether ketone)", L. Leung, C. Bailly, J. O'Gara, D. Williams, F.E. Karasz and W.J. MacKnight, Polymer Communications, 28, 20-21 (1987).
7. "The Effect of Chain Microstructure on Polymer-Polymer Miscibility", A.C. Balazs, F.E. Karasz and W.J. MacKnight, Croatica Chem. Act., 60, 147-154 (1987).
8. "Random Homogeneous Sodium Sulfonate Polysulfone Ionomers: Preparation, Characterization, and Blend Studies", J.F. O'Gara, D.J. Williams, W.J. MacKnight and F.E. Karasz, J. Polymer Sci., Part B: Polymer Physics, 25, 1519-1536 (1987).
9. "The Sodium Salts of Sulphonated poly(aryl-ether-ether-ketone)(PEEK): Preparation and Characterization", C. Bailly, D.J. Williams, F.E. Karasz and W.J. MacKnight, Polymer, 28, 1009-1016 (1987).
10. "Fourier Transform Infrared Spectroscopy of Some Miscible, Polybenzimidazole/Polyimide Blends", G. Guerra, S. Choe, D.J. Williams, F.E. Karasz and W.J. MacKnight, Macromolecules, submitted.
11. "Miscible Polybenzimidazole Blends with a Benzophone Based Polyimide", G. Guerra, D.J. Williams, F.E. Karasz and W.J. MacKnight, J. Polym. Sci., Polym. Phys. Ed., submitted.
12. "Upper Critical Solution Temperature Behavior in Poly(ether ether sulfone)/Poly(ether ether ketone-co-ether sulfone) Blends", C.K. Sham, C.H. Lau, D.J. Williams, F.E. Karasz and W.J. MacKnight, British Polymer J., submitted.
13. "Catalytic Activity of Benzimidazole in the Imidization of Polyamic Acids", A. Nelson, G. Guerra, D.J. Williams, F.E. Karasz and W.J. MacKnight, J. Appl. Polym. Sci., submitted.

14. "On Blends of Two Poly(Aryl Ether Ketones)", C.K. Sham, G. Guerra, F.E. Karasz and W.J. MacKnight, Polymer, submitted.

15. "Miscible Blends of Polybenzimidazole and a Diisocyanate-based Polyimide", S. Stankovic, G. Guerra, D.J. Williams, F.E. Karasz and W.J. MacKnight, Polymer, submitted.

16. "Fourier Transform Infrared Temperature Studies of Miscible Polybenzimidazole/Polyimide Blends", S. Choe, W.J. MacKnight and F.E. Karasz, in preparation.

17. "Thermal Studies of Polybenzimidazole/Polyimide Blends", S. Choe, F.E. Karasz and W.J. MacKnight, in preparation.

18. "Polybenzimidazole/Polyimide Miscible Blends", S. Choe, W.J. MacKnight, and F.E. Karasz, in preparation.

19. "Phase Decomposition Phenomena of Polystyrene/Poly(vinylmethylether)", C.C. Han, M. Okada, Y. Muroga, B.J. Bauer, and Q. Trang-Cong; Plastics 85, Proc. of the SPE 43rd Annual Technical Conference and Exhibition, p. 306.

20. "A Universal Coexistence Curve for Polymer Solutions", I.C. Sanchez; J. Appl. Phys. <u>58(8)</u>, 2871 (1985).

21. "Static and Kinetic Studies of Polystyrene/Poly(vinylmethylether) Blends", C.C. Han, M. Okada, Y. Muroga, F.L. McCrakin, B.J. Bauer and Q. Trang-Cong, Polym. Eng. Sci., <u>26(1)</u>, 3 (1986).

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23. "Experimental Study of Thermal Fluctuation in Spinodal Decomposition of a Binary Polymer Mixture", M. Okada and C.C. Han, J. Chem. Phys. <u>85(9)</u>, 5317 (1986).

24. "Theory of Microphase Separation in Graft and Star Copolymers", M. Olvera de la Cruz, I.C. Sanchez, Macromolecules, <u>19</u>, 250 (1986).

25. "Microphase Separation in Block Copolymer/Homopolymer Blends", M. Olvera de la Cruz, I.C. Sanchez, Macromolecules, <u>20</u>, 440 (1987).

26. "Model System for Liquid Crystal Polymer Blends", M. De Meuse and M. Jaffe, Presented at International Symposium on Liquid Crystals and Ordered Fluids at New Orleans, LA, 1987, Mol. Cryst. and Liquid Cryst., to be submitted.

27. "Thermal Studies of the Structure of Blends Containing Two Liquid Crystal Polymers", M. De Meuse, M. Jaffe and L. Sawyer, in preparation.

28. "Blends of a Copolymer of p-Hydroxybenzoic Acid and 2-Hydroxy-6-Naphthoic Acid with Another Liquid Crystal Polymer", M. De Meuse and M. Jaffe, in preparation.

29. "Formalism for Treating Blends of Liquid Crystal Polymers", M. De Meuse, M. Jaffe, F.E. Karasz and W.J. MacKnight, in preparation.

30. "Structure-Property Relationships of Blends of Liquid Crystal Polymers", M. De Meuse, M. Jaffe and L. Sawyer, in preparation.

XII. Patent Applications

(1) "Compositions of Aromatic Polybenzimidazoles and Aromatic Polyimides," U.S. Patent Application Serial No. 831, 389, Filed 2/19/86, D.J. Williams, L. Leung, F.E. Karasz, W.J. MacKnight and M. Jaffe.

(2) "Compositions of Aromatic Polybenzimidazoles and Aromatic Polyetherimides," U.S. Patent Application Serial No. 831, 385, Filed 2/19/86, L. Leung, D.J. Williams, F.E. Karasz, W.J. MacKnight and M. Jaffe.

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