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13. ABSTRACT (Maximum 200 words) The principal focus of this research has been on improving adhesion at the polymer-polymer interface in order to achieve useful polymer blends and certain composites. Adhesion measurements were made on several systems to demonstrate that favorable enthalpic interactions between the segments of a block copolymer and a homopolymer substrate can improve their adhesion and that appropriate chemical reactions at the polymer-polymer interface also promote adhesion. These principles were used for developing polymer blends that are tough. The matrix materials of the systems examined include polyamides, styrene/acrylonitrile copolymers, styrene/maleic anhydride copolymers, etc. Composites based on liquid crystalline polymers were examined briefly. Gas transport properties in selective systems are also included. A useful way for introducing chemical functionality for in situ reactions at the polymer-polymer interface is to add a polymer having this functionality which is miscible with one of the components. Several examples of such miscible systems were discovered and are reported here.					
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Polymer-Polymer Interfaces in Blends and Composites

Final Report

D. R. Paul and J. W. Barlow
November 11, 1991

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The views, 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

Multiphase polymer blends or composites often have poor physical properties because of low adhesion at the polymer-polymer interface. This fact seriously limits the use of this attractive approach for solving important materials problems. The interfacial bond can be greatly improved by addition of appropriate block or graft copolymers which locate at these interfaces. One thesis of this research is that favorable enthalpic interactions between segments of the block copolymer and the adjacent phases will enhance adhesion by virtue of greater interpenetration of the copolymer segments into that phase. Thus, for compatibilization, it may be advantageous to select block copolymers whose segments are not identical with the adjacent phase but are chemically different while having a favorable interaction that promotes miscibility based on enthalpic considerations rather than entropic ones alone. Nevertheless, the availability of such preformed copolymers is severely limited and other strategies for compatibilization are desirable. A potentially important alternative is to form these copolymers in situ by reactive processing during blending, coextrusion, or thermal lamination using functionalized polymers. A major goal of this research has been to examine the fundamental principles of this idea and to demonstrate its potentially broad applicability. The functionally reactive groups can be attached directly to the two immiscible polymers of interest or attached to other polymers which form miscible mixtures with these phases. The latter approach is especially attractive but has not been widely considered by others. Thus, it is a main feature of the current program. It requires discovering or designing functionalized polymers that are miscible with the phases of interest. This strategy includes many facets about which more fundamental knowledge is required.

These include selection of the chemistry to be used (types of functional groups), synthesis to incorporate functional groups, processing, rheology, blend analysis (chemical and morphological), interfacial adhesion, mechanical properties and fracture characteristics, to mention only the most obvious. While the main focus has been on the polymer-polymer interface, appropriate considerations have been given to all of these issues since the concept cannot be adequately demonstrated in blends without doing so.

The polymer-polymer interface is also important in more structured polymer-polymer composites such as multilayer laminates. This area was briefly considered where one of the components was a thermotropic liquid crystalline polymer. These rigid chain materials have high stiffness and strength and are exceptionally good barriers to the permeation of small molecules. However, their transverse mechanical characteristics are very poor, but that problem could be mitigated through cross-plying in the laminate. If the interfacial adhesion problem can be solved, then combinations with conventional polymers as alternating layers could lead to novel and useful materials.

Some of the major conclusions from this research are summarized in the following sections. Details of the research leading to these conclusions can be found in twenty-seven papers published during this grant period and in six papers submitted for publication, which have not yet appeared in print.

II. Summary of Important Results

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

A. Reviews of Polymer Blends

During the course of this research, we had occasion to write three review papers related to this research (10, 11, 26). These have been published in various places which should provide considerable help in dissemination of the findings of our research.

B. New Miscible Polymer-Polymer Pairs

As outlined previously, one strategy for interfacial coupling of two immiscible polymers in a blend or composite is to introduce different functional groups into each phase that can meet at the interface and react. This forms block or graft copolymers that can "compatibilize" the system by reducing the interfacial tension in the melt and enhancing the adhesion in the solid state. An interesting but relatively unexplored approach for functionalization is to incorporate functional groups into a polymer that is added to the appropriate phase. Of course, it must be miscible with that phase. Therefore, knowledge about miscible polymer pairs including techniques for prediction that will allow design of miscible, functionalized, addition polymers is an essential fundamental skill required to implement this approach. Research initiated under prior ARO support in this area came to fruition during the period covered by this report. A series of papers (3, 7, 12) from the Ph.D. work of C. H. Lai describes a novel group contribution method for predicting miscibility of polymer-polymer pairs. The technique is based on predicting the heat of mixing which is the principal quantity needed to determine blend phase behavior. This work divided the polymer repeat unit into various smaller molecular units and assigned both enthalpic and entropic interaction parameters to each pair of groups. The enthalpic data required to evaluate these parameters was obtained

from heat of mixing data for low molecular weight liquids. The entropic information stems from a fitting of the data to a modification of the Guggenheim quasi-chemical approach to mixtures. This scheme can be used as a guide in designing copolymers to be miscible with other materials.

Two papers (14, 22) from the Ph.D. work of G. R. Brannock describe the discovery that styrene/acrylic acid copolymers and styrene/maleic anhydride copolymers are miscible with poly(methyl methacrylate) and certain other polymethacrylates. The anhydride and acid functions are, of course, reactive with amine and amino functions in polyamides. These observations are currently being employed as part of a strategy for toughening polyamides with shell-core impact modifiers where the shell is based on PMMA. The styrene-based copolymers are miscible with the PMMA shell but can react with the polyamide matrix. These strategies are being pursued as part of current ARO research.

A paper by Kim (8) describes the interactions between styrene/acrylonitrile copolymers, SAN, and styrene/maleic anhydride copolymers, SMA. Another paper (6) describes the observations that certain imidized acrylic polymers are miscible with SAN materials over a useful range of AN content. Some of these imidized materials also have reactive anhydride functionality. Thus, both systems provide a mechanism for introducing anhydride functionality into SAN or ABS materials. This was used effectively for reactive blending of nylon 6 and ABS materials (23) as described later. These observations are also being used in the current ARO research.

Another paper (20) describes the miscibility of PMMA with phenoxy (the polymer based on bisphenol A and epichlorohydrin). Since phenoxy has a hydroxyl group that can react, this system also has the potential for use in reactive processing; however, this has not been pursued yet.

C. Interfacial Adhesion Measurements

The adhesion of a triblock copolymer, with short styrene end-blocks and a hydrogenated mid-block, to a polystyrene-containing substrate was studied using both lap shear and peel test methods (19). The two approaches gave very similar results. Within the limits examined, the adhesive bond strength did not significantly depend on bonding temperature or time. However, the adhesive strength did increase substantially as a phenylene ether copolymer or PEC, essentially poly(phenylene oxide), was added to the substrate. This effect is believed to be the result of exothermic mixing of PEC with polystyrene that causes an additional driving force, other than combinatorial entropy, for interpenetration of segments of the substrate and the styrenic phase of the block copolymer at the interface. Attempts to use a block copolymer having longer styrenic segments resulted in adhesive bond strength so large that cohesive failure occurred first. We believe that the enthalpic hypothesis is also the basis for the greater solubilization of PPO than PS in SEBS microdomains and why SEBS is a more efficient compatibilizer of blends of polyolefin with materials containing PEC than PS. The fact that the adhesion level does not significantly depend on bonding temperature or time implies that the adhesion is the result of a relatively fast diffusional process and more nearly reflects issues relating to the equilibrium nature of the system. These observations led to an investigation of toughening polystyrene and PEC containing matrices using styrene-based block copolymers (31) described later.

Lap shear adhesion measurements were also made on laminates of nylon 6 with SAN (23) and polyolefin (9) phases. To the former, miscible functionalized polymers including an SMA were added. This caused a dramatic increase

in adhesion resulting from the reaction of the anhydride units with the polyamide to form graft copolymers at the interface. Similarly, glycidyl methacrylate units in a polyolefin phase allowed development of strong adhesion to nylon 6. In all cases, it proved impossible to follow the kinetics of this adhesion development since apparently the reactions of anhydrides and glycidyl methacrylate units with polyamides are so rapid. Thus, attempts to gain fundamental information by following time changes in adhesion were abandoned.

D. Polymer Blends Compatibilized by In Situ Reaction

The first phases of this research involved blending an ethylene glycidyl methacrylate copolymer with nylon 6 (9). As indicated above, the glycidyl methacrylate units react readily with nylon 6. Because this olefin polymer is relatively soft it acts as an impact modifier for the polyamide and produces quite high levels of toughness.

A major component of this research involved blends of nylon 6 with various ABS materials including its SAN matrix component. These mixtures have very poor mechanical properties unless properly compatibilized. This was done here by adding to the SAN phase a polymer that is miscible with it but which contains functional groups that can react with the nylon 6 to form in situ, graft copolymers at the polymer-polymer interfaces. These compatibilizer molecules contained either anhydride or oxazoline units for reactivity. Evidence of reactions in the blends was seen in the rheological behavior of the melt and in the morphology and mechanical behavior of the solid. Some blends exhibited outstanding toughness. A more quantitative assessment of the extent of reaction was provided by selective solvent extraction technique. As mentioned above, lap shear adhesion measurements

for laminates of nylon 6 with materials containing reactive polymers provided a direct way to assess the effectiveness of the interfacial reaction.

Polystyrene chains with terminal anhydride groups were synthesized by direct chain transfer reaction between poly(styryl) lithium and trimellitic anhydride chloride (TMAC) and by the alkoxy-dehalogenation reaction between TMAC and hydroxy terminated polystyrene (25). For the direct reaction a poly(styryl) lithium with a molecular weight of approximately 1000 (a low molecular weight was used for characterization purposes) was prepared and then reacted with TMAC. Higher molecular weight hydroxy terminated polystyrenes were used for the indirect addition of terminal anhydride groups. These materials were characterized by NMR, gel permeation chromatography, and FTIR. A maximum yield of 61% for the direct functionalization route and 85% for the indirect functionalization route using hydroxyl terminated polystyrene were achieved. Nylon 6/polystyrene blends were reactively compatibilized by addition of these various anhydride functionalized polystyrenes (32). The morphology of the blends was examined using a scanning electron microscopy technique. The particle size of the dispersed styrenic phase was about 3.2 μm for the uncompatibilized 8/2 nylon 6/PS blend while those of the compatibilized blends were decreased by as much as two orders of magnitude depending on the amount and type of the functionalized polystyrene, FPS, added. The effective molecular weight on particle size reduction depended on the basis of comparison, mass of additive, or moles of anhydride units. A high molecular weight random copolymer of styrene and maleic anhydride was most effective when compared on a mass basis. The increase in adhesion between the nylon 6 and the styrenic phases caused by the in situ reaction were evaluated by lap shear adhesion techniques. The free polystyrene, nylon 6, and nylon-FPS copolymer form were separated by solvent

extraction techniques using formic acid and toluene. The extent of coupling between the functionalized polystyrene and nylon 6 ranged from 25% to 43%.

The toughening of nylon 6 using triblock copolymers of the type SEBS and a maleic anhydride functionalized version SEBS-g-MA was examined and compared with a conventional maleated ethylene/propylene elastomer (28). The changes in rheology, adhesion, crystallinity, morphology, and mechanical behavior associated with the reaction of the anhydride with the nylon 6 were documented. Combinations of the SEBS and SEBS-g-MA elastomer blends with nylon 6 gave higher levels of toughening than is achieved with the functionalized elastomer alone. The particles of pure SEBS were about 5 μm in diameter (too large for toughening nylon 6); whereas, SEBS-g-MA alone yielded particles of about 0.05 μm (apparently too small for optimal toughening). Combination of the two types of elastomers gave a continuously varying particle size between these extreme limits. This suggests the two rubbers form essentially a single population of mixed rubber particles. That is, the functionalized triblock copolymer compatibilizes the unfunctionalized copolymer in the nylon matrix. The order of mixing did not significantly affect the mechanical properties of these ternary blends. The evidence for maximum and minimum rubber particle sizes that can be effective for toughening nylon 6 is convincing. Similar studies were made on toughening of nylon 6,6 (29). A main difference is that nylon 6,6 can be made super-tough by blending with SEBS-g-MA alone while addition of SEBS merely reduces toughness. The reason for this is that blends of nylon 6,6 with SEBS-g-MA give rubber particles that are within the optimal size range (just less than 1 μm); however, these particles have a very complex structure. For blends containing both SEBS and SEBS-g-MA, there seemed to be two distributions of shape but not size. Evidence has shown that the extent of

grafting to nylon 6,6 is less than in nylon 6 for similar conditions. It was proposed that the large difference in morphology found for nylon 6,6 versus that for nylon 6 stems from basic chemical differences between the two polyamides rather than rheological or processing factors. Nylon 6 is monofunctional while nylon 6,6 is difunctional in their reactions with anhydrides. This startling result is being pursued with current ARO funding.

Melt blends of poly(m-xylene adipamide), MXD6, and nylon 6 prepared by extrusion at 260°C have two glass transitions and are opaque; whereas, similar preparation at 290°C yields transparent melts and materials with a single glass transition. This phase homogenization was shown by thermal, dynamic mechanical, and NMR analyses to be the result of interchange reactions. A single phase develops after as few as five interchange reactions per molecule. This segmented block structure explains the high level of crystallinity that is retained after phase homogenization. Such behavior is possible when the unreacted components have an unfavorable but small interaction energy density, i.e., near miscibility, as argued using thermodynamic theories. Retention of crystallinity is useful for certain property considerations. These phase homogenized mixtures became super-tough when blended with SEBS-g-MA (33). Pure nylon 6, pure MXD6, or mixtures of the two prepared under low temperature extrusion conditions that do not lead to phase homogenization are not similarly super-toughened by blending with SEBS-g-MA. The reasons appear to relate to differences in elastomer particle morphology and inherent ductility for the various matrices. SEBS-g-MA blends with nylon 6 are not super-tough because the rubber particles are too small. Addition of MXD6 causes the particles to become larger and of optimum size for toughening, but it is postulated that MXD6 is difficult to toughen because of low inherent ductility. The polyamide mixtures that

were not phase homogenized are also inherently incompatible. The differences in rubber particle geometry apparently stem from the functionality of the two polyamides towards reactions with anhydride groups as mentioned above.

E. Rubber Toughening

The work described above involved toughening of polyamide matrices where in situ chemical reactions were required. Here, the discussion is about systems where no reaction is needed. Interfacial adhesion is accomplished through physical interactions.

One paper (1) describes the synergistic toughening of an SAN matrix using two different types of elastomers while a second paper (5) describes the distribution of a shell-core impact modifier between two immiscible matrix phases. The latter phenomenon has since been explained in terms of interfacial tension arguments.

Beginning from observations described above, the effects of the molecular architecture of elastomeric styrene-based block copolymers on efficiency of toughening a brittle (polystyrene) and a ductile (a miscible blend of 80% PEC and 20% polystyrene or 80PEC) polymer were explored (31). Toughening appears to be mainly controlled by the blend morphology which is determined by the rheological characteristics of the block copolymer relative to that of the matrix. The formation of dispersed particles during melt blending in a Brabender Plasticorder is strongly influenced by the ratio of the viscosities of the matrix and block copolymers. To a first approximation the effect of block copolymer architecture on toughening efficiency is related to how this structure affects the rheological behavior of the copolymer. Excellent toughness of polystyrene was achieved when the particle size was larger than 1 to 2 μm . The 80% PEC material is best toughened

by block copolymers that form a co-continuous phase morphology. The extent of toughening of this matrix appears to be a strong function of the styrene block molecular weight; whereas, this structural feature seems to have no significant effect in toughening polystyrene.

Styrene/maleic anhydride copolymers were toughened by blending with an SAN grafted rubber (16). The AN content of the SAN graft was fixed at about 22.5% and the MA content of the SMA matrix was varied from 8% to 25%. The maximum impact strength was observed for blends based on SMA copolymers containing 14% to 17% MA depending on the rubber content. These compositions are near the boundary of miscibility between the SMA matrix and SAN graft since miscibility of SMA and SAN occurs when the MA and AN contents are about the same in each copolymer. Dilational processes were shown to be the major mechanism of deformation for these blends. Scanning electron microscopy showed fracture surfaces that changed as the miscibility between SMA and SAN changed. Toughening of miscible SMA/SAN matrices by this modifier was also examined. The results demonstrate the benefits of coupling of the rubber to the matrix via miscibility of the latter with the SAN graft chains.

SAN copolymers were toughened by the addition of several SAN emulsion grafted rubbers (24). The main variables of this study included the AN content of the SAN graft and the AN content of the SAN matrix. The aim was to develop general principles underlying the properties of rubber toughened SAN or ABS materials. Rubber-matrix adhesion, state of rubber particle dispersion, and the inherent ductility of the matrix polymer were evaluated. The trends found in mechanical behavior of the blends were reasonably explained in terms of these three factors. The concept of inherent ductility, in particular, was effectively utilized and its importance

in the ultimate properties of rubber toughened SAN was demonstrated.

The plain strain fracture toughness, K_{IC} , of a series of styrene copolymers with acrylonitrile, maleic anhydride, and acrylic acid were investigated (27) in order to further examine the issue of inherent ductility on rubber toughening of brittle matrices. Relative to polystyrene, the values of K_{IC} for the copolymers increase with acrylonitrile content but decrease with maleic anhydride or acrylic acid content. The values of K_{IC} for SAN copolymers are lowered by addition of PMMA but are maximum in the AN range where SAN is miscible with PMMA. The toughness of rubber modified blends of these materials correlate with the K_{IC} of the matrix.

Since PMMA is miscible with SAN, it is possible to couple an SAN matrix to a rubber phase that has been grafted with MMA. Monodisperse methyl methacrylate grafted latex rubber (MMA-g) particles (approximately 0.12 μm in diameter) were, thus, used for the impact toughening of a series of SAN copolymers of varying AN content (18). It was found that the MMA-g particles are most effective in toughening SAN copolymers containing about 25% to 34% AN. Mechanical properties, interphase adhesion, mechanical dilatometry, and phase morphology by transmission electron microscopy were determined on blends containing 20% to 30% rubber. The range over which SAN copolymers are miscible with the PMMA graft is a factor that determines the relationship between the mechanical properties and the characteristic features of the blends. Issues relating the impact strength and deformation mechanisms, interphase adhesion, and particle morphology are also factors. It appears that the high impact strength of some of the blends is caused by particle clustering. Craze initiation, shear yielding, and significant matrix deformation all contribute to the overall ductility of the blend.

F. Gas Permeation

Research on gas permeation initiated under previous ARO funding was completed during the period covered by this report. One paper describes the permeation of gases in dry Nafion films (4) while another (2) describes the effect of tacticity of PMMA on gas permeation. Two papers (13, 21) describe gas permeation behavior of liquid crystalline polymers.

G. LCP Composites

A visiting scholar who was associated with this program for one year synthesized some novel liquid crystalline polymers that are described in two papers (15, 17). Two undergraduate students, who received no support from this contract, were used to explore laminated composites based on liquid crystalline polymers. It was found that the liquid crystalline materials produced by the Eastman Kodak Company, which are based on ethylene terephthalate and p-oxybenzoate units, adhere strongly to poly(ethylene terephthalate), PET. Three layer, coextruded films were prepared where the two outer layers were PET and the inner layer was the liquid crystalline polymer, LCP. Next, multiple sheets of these layered composites were bonded together in a compression molding step. Of course, the chains of the LCP are preferentially oriented in the direction of extrusion. This direction was varied from layer to layer in the laminate that was bonded by compression molding. Two problems were encountered. The first was that during the slow cooling from the compression molding step the PET crystallized into a large spherulitic form that embrittled this component. That problem was resolved by switching to a polyester copolymer that did not crystallize but did adhere to the LCP. However, a second problem could not be resolved. As it turned out, during the compression molding step the LCP material lost its continuity

by evidently an instability driven by interfacial tension. In the melt, the LCP has a relatively low viscosity and experienced drop breakup driven by interfacial tension. This problem could be solved by continuous extrusion processes; however, we did not have the equipment necessary to effect this approach. Consequently, this promising avenue of investigation could not be pursued further.

III. Publications Completed to Date

A. Theses and Dissertations

<u>Name</u>	<u>Title</u>
G. P. Shaver (M.S.)	"Compatibilization of Immiscible Blends through Chemical Reaction"
I. Park (Ph.D.)	"Interfacial Adhesion between Polymer Phases in Multicomponent Polymer Systems"
V. Triacca (Ph.D.)	"Reactive Compatibilization of Nylon-ABS Blends"
J. H. Kim (Ph.D.)	"Phase Behavior of Polymer Blends Based on Random Copolymers"
H. Kim (Ph.D.)	"Toughening of Styrene-Acrylonitrile Copolymers by Emulsion Grafted Submicron Rubber Particles"
A. J. Oshinski (M.S.)	"Rubber Toughening of Polyamides Using Functionalized Block Copolymers"
D. H. Weinkauff (Ph.D.)	"Gas Transport Properties of Liquid Crystalline Polymers"
C. H. Lai (Ph.D.)	"Predicting Polymer-Polymer Miscibility with a Group Contribution Method"

B. Papers in Print

1. M. E. Fowler, H. Keskkula and D. R. Paul, "Mechanical Behavior of Dual-Rubber-Modified SAN", J. Appl. Polym. Sci., 35, 1563 (1988).
2. K. E. Min and D. R. Paul, "Effect of Tacticity on Permeation Properties of Poly(methyl methacrylate)", J. Polym. Sci.: Part B: Polym. Phys., 26, 1021 (1988).
3. C. H. Lai, D. R. Paul and J. W. Barlow, "Group Contribution Methods for Predicting Polymer-Polymer Miscibility from Heats of Mixing of Liquids. 1. Comparison of the Modified Guggenheim Quasi-Chemical (MGQ) and UNIQUAC Models", Macromolecules, 21, 2492 (1988).
4. J. S. Chiou and D. R. Paul, "Gas Permeation in a Dry Nafion Membrane", Ind. Eng. Chem. Res., 27, 2161 (1988).
5. M. E. Fowler, H. Keskkula and D. R. Paul, "Distribution of MBS Emulsion Particles in Immiscible Polystyrene/SAN Blends", J. Appl. Polym. Sci., 37, 225 (1989).
6. M. E. Fowler and D. R. Paul, "Blends of Imidized Acrylic Polymers with SAN Copolymers and with PVC", J. Appl. Polym. Sci., 37, 513 (1989).

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9. G. Shaver, O. R. Paul and J. W. Barlow, "Polymer Blends Compatibilization through Chemical Reaction", *Proceedings of the First International Congress on Compatibilizers and Reactive Polymer Alloying (COMPALLOY '89)*, p. 221 (1989).
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12. J. W. Barlow, C. H. Lai and O. R. Paul, "Prediction of Polymer-Polymer Miscibility with a Group Contribution Method", *Contemporary Topics in Polymer Science: Vol. 6: Multiphase Macromolecular Systems*, B. M. Culbertson, Ed., Plenum Press, New York, p. 505 (1989).
13. D. H. Weinkauff and D. R. Paul, "Effects of Structural Order on Barrier Properties", *ACS Symp. Ser. on "Barrier Polymers and Barrier Structures"*, 423, 60 (1990).
14. G. R. Brannock, J. W. Barlow and O. R. Paul, "Blends of Styrene/Acrylic Acid Copolymers and Acrylic Polymers", *J. Polym. Sci.: Part B: Polym. Phys.*, 28, 871 (1990).
15. H. D. Kim and D. R. Paul, "Preparation and Properties of a Series of Thermotropic Liquid Crystalline Copolyesters", *J. Appl. Polym. Sci.*, 40, 155 (1990).
16. J. H. Kim, H. Keskkula and D. R. Paul, "Toughening of SMA Copolymers with an SAN-Grafted Rubber", *J. Appl. Polym. Sci.*, 40, 1B3 (1990).
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25. I. Park, J. W. Barlow and D. R. Paul, "Terminal Anhydride Functionalization of Polystyrene", J. Polym. Sci.: Part A: Polym. Chem., 29, 1329 (1991).
26. D. R. Paul, "Strategies for Compatibilization of Polymer Blends", Proceedings of the Sixth International Conference on Mechanical Behavior of Materials, M. Jono and T. Inoue, Eds., Pergamon Press, Oxford, Vol. 3, p. 287 (1991).
27. H. Kim, H. Keskkula and D. R. Paul, "The Role of Inherent Ductility in Rubber Toughening of Brittle Polymers", Polymer, 32, 2372 (1991).

C. Papers Submitted or Accepted for Publication

28. A. J. Dshinski, H. Keskkula and D. R. Paul, "Rubber Toughening of Polyamides with Functionalized Block Copolymers: Part I: Nylon 6", Polymer.
29. A. J. Dshinski, H. Keskkula and D. R. Paul, "Rubber Toughening of Polyamides with Functionalized Block Copolymers: Part II: Nylon 6,6", Polymer.
30. Y. Takeda and D. R. Paul, "Phase Homogenization of Mixtures of Poly(m-xylene adipamide) and Nylon 6 by Interchange Reactions", Polymer.
31. I. Park, H. Keskkula and D. R. Paul, "Toughening of Polystyrene and Poly(phenylene oxide) Matrices with Elastomeric Styrene-Based Block Copolymers: The Role of Molecular Architecture", J. Appl. Polym. Sci.
32. I. Park, J. W. Barlow and D. R. Paul, "The in situ Reactive Compatibilization of Nylon 6/Polystyrene Blends Using Anhydride Functionalized Polystyrenes", J. Polym. Sci.: Part B: Polym. Phys.
33. Y. Takeda, H. Keskkula and D. R. Paul, "Toughening of Phase Homogenized Mixtures of Nylon 6 and Poly(m-xylene adipamide) with a Functionalized Block Copolymer", Polymer.

IV. Participating Scientific Personnel

The following individuals received some financial support from this contract:

<u>Name</u>	<u>Status</u>	<u>Comments</u>
D. R. Paul	Faculty	summer support
J. W. Barlow	Faculty	summer support
H. D. Kim	Visiting Scholar	partial support
G. P. Shaver	M.S. student	M.S. granted
I. Park	Ph.D. student	Ph.D. granted
V. Triacca	M.S. student	M.S. granted
H. Keskkula	Research Fellow	one month support/year
J. H. Kim*	Ph.D. student	Ph.D. granted
E. Baude	Exchange student	no degree sought
S. Ziaco	Ph.D. student	temporary help
A. J. Oshinski	M.S. student	M.S. granted
H. Kim*	Ph.D. student	Ph.D. granted
D. H. Weinkauff*	Ph.D. student	Ph.D. granted
A. Gonzalez	Ph.D. student	continuing
B. Majumdar	Ph.D. student	continuing
M. Lu*	Ph.D. student	continuing
G. R. Brannock*	Ph.D. student	Ph.D. granted
C. H. Lai*	Ph.D. student	Ph.D. granted
S. Kemmerer*	Undergraduate student	B.S. received
D. Vernino*	Undergraduate student	B.S. received

*No salary support provided from this contract.

REPORT OF INVENTIONS AND SUBCONTRACTS

(Pursuant to "Patent Rights" Contract Clause) (See Instructions on Reverse Side.)

Form Approved
OMB No. 0704-0297
Expires Jun 30, 1992

Public reporting burden for this collection of information is estimated to average 5 minutes per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0297), Washington, DC 20503.

1a. NAME OF CONTRACTOR/SUBCONTRACTOR	c. CONTRACT NUMBER	2a. NAME OF GOVERNMENT PRIME CONTRACTOR	c. CONTRACT NUMBER	3. TYPE OF REPORT (X one)
b. ADDRESS (Include ZIP Code)	d. AWARD DATE (YYMMDD)	The University of Texas at Austin	DAAL03-88-K-0004	a. INTERIM ☒ b. FINAL ☐
		Dept. of Chem. Engineering Austin, TX 78712	March 15, 1988	4. REPORTING PERIOD (YYMMDD)
				a. FROM 88/3/15
				b. TO 91/9/14

SECTION I - SUBJECT INVENTIONS

5. "SUBJECT INVENTIONS" REQUIRED TO BE REPORTED BY CONTRACTOR/SUBCONTRACTOR (If "None," so state) No inventions reported.

a. NAME(S) OF INVENTOR(S) (Last, First, MI)	b. TITLE OF INVENTION(S)	c. DISCLOSURE NO., PATENT APPLICATION SERIAL NO. OR PATENT NO.	d. ELECTION TO FILE PATENT APPLICATIONS		e. CONFIRMATORY INSTRUMENT OR ASSIGNMENT FORWARDED TO CONTRACTING OFFICER
			(1) United States (a) Yes (b) No	(2) Foreign (a) Yes (b) No	

f. EMPLOYER OF INVENTOR(S) NOT EMPLOYED BY CONTRACTOR/SUBCONTRACTOR		9. ELECTED FOREIGN COUNTRIES IN WHICH A PATENT APPLICATION WILL BE FILED	
(1) (a) Name of Inventor (Last, First, MI)	(2) (a) Name of Inventor (Last, First, MI)	(1) Title of Invention	(2) Foreign Countries of Patent Application
(b) Name of Employer	(b) Name of Employer		
(c) Address of Employer (Include ZIP Code)	(c) Address of Employer (Include ZIP Code)		

SECTION II - SUBCONTRACTS (Containing a "Patent Rights" clause)

6. SUBCONTRACTS AWARDED BY CONTRACTOR/SUBCONTRACTOR (If "None," so state) No subcontractors.

a. NAME OF SUBCONTRACTOR(S)	b. ADDRESS (Include ZIP Code)	c. SUBCONTRACT NO.(S)	d. DFAR "PATENT RIGHTS"		e. DESCRIPTION OF WORK TO BE PERFORMED UNDER SUBCONTRACT(S)	f. SUBCONTRACT DATES (YYMMDD)	
			(1) Clause Number	(2) Date (YYMM)		(1) Award	(2) Estimated Completion

SECTION III - CERTIFICATION

7. CERTIFICATION OF REPORT BY CONTRACTOR/SUBCONTRACTOR		(Not required if Small Business or Non-Profit organization.) (X appropriate box)	
a. NAME OF AUTHORIZED CONTRACTOR/SUBCONTRACTOR OFFICIAL (Last, First, MI)	c. I certify that the reporting party has procedures for prompt identification and timely disclosure of "Subject Inventions," that such procedures have been followed and that all "Subject Inventions" have been reported.		
b. TITLE	d. SIGNATURE	e. DATE SIGNED	
		11/11/91	
		Donald R. Paul	