This research has examined the use of functionalized polymers that react at the interfaces in polymer blends to form block or graft copolymers during melt processing. These grafts act as "compatibilizers" that strengthen the interface and provide a powerful means of controlling blend phase morphology. Consequently, this approach provides an effective means of controlling the properties of multiphase polymeric materials. Most of the work involved the use of various polyamides as one component in the blend. The other component was a reactive elastomer, an ABS material, a core-shell impact modifier, or polypropylene. The end group configuration of the polyamide was shown to be an important consideration in morphology development. Functionalized additives are most efficient when both physical and chemical interactions are optimized. A variety of approaches for producing super-tough polyamide blends with low ductile-brittle transition temperatures are described. Cavitation of the rubber phase was shown to be an important part of the toughening mechanism in certain cases.
Reactive Compatibilization of Polymer Blends

Final Report

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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

There is intense practical interest in multiphase polymer blends, or alloys, because of the potential opportunities for combining the attractive features of each material into one or for improving deficient characteristics of a particular material. However, quite often immiscible blends have poor mechanical properties relative to their components and their phase morphology is strongly dependent on details of the processing history. The reason for this is the unfavorable interaction between molecular segments of the components, responsible for their immiscibility in the first place, that leads to (a) a large interfacial tension in the melt which makes it difficult to homogeneously disperse the components during mixing and drives phase rearrangements during low stress or quiescent conditions and (b) poor interfacial adhesion in the solid state which causes premature mechanical failure via these weak defects between phases. Remediation of these problems, or compatibilization, can be effected by the addition of appropriate block or graft copolymers that act as interfacial agents as demonstrated repeatedly over the last two decades. Grafting has been widely used with considerable success to incorporate a rubber phase into brittle polymers to effect toughening. With this exception, compatibilization by *preformed* block or graft copolymers has not been used as extensively as the potential utility might suggest. A primary reason for this is the lack of practical routes for synthesis of such additives, for systems of interest, that would be economically viable.

An attractive alternative is to form the block or graft copolymer in situ during blend preparation via interfacial reaction of added functionalized polymeric components. This approach has already been implemented in a number of commercial products and appears in many instances to be the method of choice for compatibilization. There are many important fundamental questions about how to most effectively design and implement a reactive compatibilization scheme that cannot be answered with available experience or theory. This report describes results from a broad-based fundamental program designed to address these questions and by necessity it includes many facets: 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. Of course, the only route to this general knowledge is investigation of specific systems such as those described later. The central theme revolves about the interface between the phases since this is believed to be the most critical issue in controlling morphology and achieving the desired properties; however, the approach encompasses other factors that influence mechanical behavior of multiphase blends.

A key element of this work has been to understand more about how the phase morphology evolves during blend processing and how it can be controlled by in situ chemical reactions that form block or graft copolymers at the interface between phases. We have developed the necessary skills for characterizing the morphology of such blends using transmission electron microscopy (TEM) as will become apparent in what follows.

II. Summary of Important Results

Section III lists all of the publications which have resulted from this project. This section summarizes the most important findings. The numbers which appear in parentheses refer to the papers which are already in print (Section III.B) or in press (Section III.C).

A. Review Papers

During the course of this project, two review papers (16, 21) and a book chapter (20) were written. One of the review papers (21) summarizes our strategy for the control of morphology and interfacial strengthening in polymer blends using reactive compatibilization. The other review paper (16) summarizes characterization of polymer-polymer interfaces using a thermodynamic approach. The interfacial tension and thickness have been estimated from basic thermodynamic information. The results show good
agreement with experimental results for the polycarbonate/styrene-acrylonitrile copolymer (SAN) pair. It was also demonstrated that the extent of chemical reactions at interfaces is influenced by the thermodynamic interaction between the polymer pairs forming the interface. The book chapter (20) summarizes information from the literature and for our own work on toughening of polyamides.

B. Effect of Physical Interactions on Reactions at Interfaces

The modern literature has demonstrated that the interface between two polymers is not sharp but has a definite thickness that is governed by the interaction between these two materials. Thus, it was proposed that the extent of chemical reaction at a polymer-polymer interface should be affected by the thickness of the interface (thus, by the polymer-polymer interaction energy) since this determines the volume of mass in which the reactive groups have access to each other. During the course of this project, two independent bodies of evidence to support this proposal were established. In one, the progress of interchange reactions between two polyamides was followed using NMR and thermal analyses (1, 9). As the thermodynamic interaction energy between the two polyamides became more unfavorable and the interface became more sharp, the reaction progressed much more slowly. The reaction time to achieve phase homogenization between poly(m-xylene adipamide) and nylon x,y increased systematically by two orders of magnitude in going from nylon 6,6 to nylon 12,12.

The other example involved a chemical analysis of the blend series (nylon x,y/SEBS-g-MA). (This system will be described in more detail in the next section.) The extent of reaction of polyamide amine end groups with the maleic anhydride grafted to the SEBS elastomeric triblock copolymer were determined by a sensitive end group titration technique (16, 17). The fraction of unreacted amine groups steadily declines with the polyamide CH2/NHCO ratio. From the rubber/nylon x,y interaction energy calculated from copolymer theory, the interfacial thickness was estimated. A distinct correlation
between the interfacial thickness and extent of amine end group reaction was established. Thus, the thermodynamic interaction between the two polymers affects the nature of their interface, which in turn determines the extent of grafting possible in a fixed processing protocol. Both the physical and chemical aspects are reflected in the rubber particle size (17) and ultimately the mechanical properties of the blends (18).

C. Toughening of Polyamides with Reactive Elastomers

One of the most well-developed examples of reactive coupling of phases in polymer blends is the rubber toughening of polyamides. The most common route is the use of an ethylene/propylene type elastomer to which maleic anhydride has been grafted (at the level of 1% to 2% by weight) using well-known techniques. This material is melt blended with nylon where the reaction of the anhydride unit with nylon amine end groups occurs at the rubber-nylon interface to give graft copolymer at the interface. This reaction can dramatically change the size of the dispersed rubber particles and the properties of the mixture. For nylon 6 and nylon 6,6 it is well established that the rubber particles must be smaller than some critical level (<1 μm) for generating super-tough materials.

Much of our research in this area has used a newly available styrene-based triblock copolymer that has maleic anhydride grafted to its ethylene/butene-like midblock. This material is designated as SEBS-g-MA while the unmaleated version is designated as SEBS. Blends of SEBS with either nylon 6 or nylon 6,6 lead to large rubber particles (~ 5 μm in diameter) that do not adhere well to the polyamide matrix and there is no toughening (2, 3, 6, 7, 10, 17, 18). However, when SEBS-g-MA containing about 2% MA is blended in a single screw extruder with nylon 6, very small rubber particles of about 0.05 μm in diameter are produced. These particles are so small that they do not toughen some polyamides. However, similar blends with nylon 6,6 yield much larger particles with a complex shape. These particles are on the border of being too large for toughening; however, by use of the more intensive shearing in a fully intermeshing, co-rotating, twin
screw extruder, these particles can be broken down to an optimal size for effective toughening (24).

The compelling question was why nylon 6 and nylon 6,6 of very similar rheological characteristics should yield such different morphologies when processed identically. We have found that the different reactive end group configurations of these materials is the cause. Nylon 6, as usually prepared, has only one amine end group per chain that can react with rubber particles, and this is a very efficient graft structure for drop breakup and preventing coalescence. However, approximately one-third of the nylon 6,6 chains as usually prepared have amine groups on both ends of the chain. This difunctionality can lead to loops and bridges of grafted chains on the rubber particles. We have shown that this type of grafting makes it very difficult to break the grafted rubber particles into smaller ones during processing (17, 18). However, by the use of intensive mixing devices (24) the proper particle dispersion can be achieved. However, this is not necessary in the case of monofunctional polyamides like nylon 6, nylon 11, and nylon 12.

This differentiation between morphology development in reactive blends involving monofunctional versus difunctional polyamides is an extremely important principle established by this work. Its generality for polyamides was established in several ways. It is possible to make nylon 6 using end capping techniques that have on average more than one amine group per molecule. These materials when blended with maleated elastomers lead to large particles like those described above for nylon 6,6. Polyamides of the type nylon x,y where x and y are other than 6 also show enlarged particles. However, the extent of the enlargement diminishes as the hydrocarbon content of these materials increases owing to the physical issue described earlier (17, 18). All nylon x type materials show small particles (6, 7, 17, 18). Blends based on a matrix of a phase homogenized mixture of a mono and difunctional polyamide show morphology generation characteristic of the difunctional material (7) even at relatively low proportions of the difunctional component. We have demonstrated a number of powerful means through chemistry of
controlling particle morphology. These principles are expected to apply to other polymer systems as well.

As might be expected, the rubber particle size observed in blends of nylon 6 depend strongly on the amount of maleic anhydride grafted to the rubber phase. This has been demonstrated by two different routes. In one, the maleic anhydride level actually grafted to SEBS was changed while in the other, SEBS-g-MA containing about 2% MA was diluted with SEBS. Both series gave essentially identical particle diameters when the maleic anhydride content of the rubber phase was equal. Evidently blends of SEBS and SEBS-g-MA form a single phase which is equivalent to uniformly grafted SEBS-g-MA of lower MA content. This is a very useful way of controlling morphology, but it will most likely only be possible if the MA graft does not destroy the miscibility between the two rubbers.

We have generated rubber particle sizes that traverse approximately two orders of magnitude (0.05 to 5μm). The particles on the high end of this scale are too large while those on the low end are too small for toughening nylon 6. There is an optimum range in between these limits where very tough materials can be produced (2, 6, 7, 18). This entire range can be achieved with a single screw extruder for nylon 6; however, such a range cannot be achieved for nylon 6,6 without the more intensive shear during blending (24).

Our work in this area will continue under current ARO funding. Mr. A. J. Oshinski will finish his Ph.D. in early 1995. His work is concerned primarily with the effect of polyamide molecular weight (or melt viscosity) on morphology generation in reactive elastomer systems and subsequent toughening of these blends. Mr. Y. Kayano will focus over the next year on the deformation mechanisms involved in toughening these materials.

D. Reactive Compatibilization of Nylon/ABS Blends

There are numerous reasons to be interested in materials that combine the properties of nylon and ABS, and we have adopted this as a useful model system for exploring
fundamental issues related to reactive compatibilization. We have explored the use of a variety of polyamide and ABS type materials. However, the vast majority of this work has been done using one nylon 6 and an ABS material having a high rubber content (50% by weight). This ABS material consists of a styrene/acrylonitrile copolymer (SAN) grafted to a butadiene-based latex rubber having a broad distribution of particles sizes with typical ones in the range of 0.2 μm in diameter. The SAN contains about 24% AN by weight of which 40% is chemically grafted to the rubber. This graft rubber concentrate has been blended with additional SAN copolymer to obtain rubber levels typical of most commercial ABS materials.

Our strategy for this system has been to incorporate into the ABS a polymer that is miscible with its SAN phase and that can react with the nylon when the two meet at the nylon-SAN interface. The compatibilizer precursor must contain a certain number of functional groups. This work is focused primarily on selection of compatibilizers that contain either anhydride or acid type functionality which can readily react with the end groups on the polyamide. Initial work focused on the reactive compatibilization using a styrene/maleic anhydride copolymer containing 25% MA, i.e., SMA 25. The SMA 25 is miscible with the SAN matrix of the ABS, and, of course, can react with the nylon. We have shown that these materials can be made tough at room temperature, but they become brittle just below room temperature (23). We are confident that the cause for this is that SMA 25 has too many functional groups per chain. However, the results of this are not demonstrably evident in the morphology of the blends. Evidently, some other issue than morphology is the cause.

During the course of this project, we abandoned SMA 25 in favor of examination of a unique series of imidized acrylic polymers formed by reacting poly(methyl methacrylate) with methyl amine (13, 14, 22-24, 26-28). These polymers contain small amounts of anhydride and acid units in addition to the glutarimide structure and residual methyl methacrylate units. A well characterized series of these for materials were provided to us
through a cooperative agreement with Rohm and Haas Company. Some of these materials were found to be miscible with SAN copolymers, and, of course, their anhydride (or free acid) groups can react with polyamides. We have fully characterized the miscibility characteristic of the entire series of imidized acrylates, IA, polymers with SAN copolymers of varying AN content to gain an understanding of the thermodynamic interactions as a function of the composition of each polymer (13, 22). In turn, we evaluated the effectiveness of these materials to alter the morphology of nylon 6/SAN blends (no rubber phase present in order to simplify the problem). The diameter of the dispersed phase of SAN particles, mixed into a nylon 6 matrix by extrusion, decreased with the AN content of the SAN. This is the result of a decrease in the nylon 6-SAN interfacial tension (8); the SAN viscosity was constant over this AN range. At a fixed content of the imidized acrylic material, it was shown that optimum morphology control was achieved when the imidized acrylic and the SAN were miscible. Within this range, particle size decreased the higher the functionality level of the imidized acrylic. As the amount of an optimal imidized acrylic material was varied in the blend, the particle size of the dispersed phase decreased dramatically.

From the studies described above, an optimum imidized acrylic material was identified and used in subsequent work. This material was found to be a very effective compatibilizing agent for nylon 6/ABS blends (13, 14, 23-27). A key element in the fundamental studies done on this system involved developing effective transmission electron microscopy techniques for characterizing blend morphology. Stains were identified that could darken either the polyamide or the ABS phase. This dual capability led to an unambiguous definition of blend morphology.

When no compatibilizer is added to a nylon 6/ABS blend, the ABS domains are quite large and tend to be co-continuous with the nylon 6. The presence of the rubber particles greatly altered the morphology from what would be seen in a comparable nylon 6/SAN blend partly because of rheological issues. The addition of the imidized acrylic
causes the ABS phase to be much better dispersed as was found in the case of nylon 6/SAN blends. By judicious control of morphology, blends containing the imidized acrylic can become super-tough for certain nylon 6/ABS ratios and are much tougher at room temperature than either the pure nylon or the pure ABS. Blends without this additive are less tough than either individual component. These compatibilized blends have very low ductile-brittle transition temperatures relative to those compatibilized using SMA 25. Of course, the stiffness and strength depend on the proportions of nylon 6/ABS in the blend. The rubber content of the ABS phase is a critical factor affecting toughness at a given temperature. The total content of rubber in these blends has been varied in two ways while holding all other factors constant. In one, the high rubber content ABS material was diluted by adding additional SAN copolymer. Comparable results were obtained using a series of commercial ABS materials having different rubber contents (not all have the same rubber particle size or morphology). These two series indicate a critical rubber content for toughness that is about the same despite significant differences among the various ABS materials. Approximately 17% rubber is required to achieve super-toughness at room temperature. The choice of the nylon 6 has a significant effect on the ductile-brittle temperature that can be achieved in these blends (28). Interestingly, blends based on nylon 6,6 could not be made super-tough even when prepared in a twin screw extruder. No doubt this stems from some of the chemical issues mentioned in Section II.C.

The mechanism of the deformations that occur during fracture of a nylon 6/ABS blend compatibilized with the imidized acrylic polymer were compared to those of an uncompatibilized blend. A postmortem examination of deformed zones in samples loaded to failure in a double-notch four-point-bend geometry was made using transmission electron microscopy techniques. For the compatibilized blend, cavitation of the rubber particles followed by massive shear yielding of the polyamide matrix was concluded to be the sequence of events leading to toughness; while, for the brittle uncompatibilized blend, the evidence indicated that a lack of adhesion at the nylon/ABS interface prevented the
rubber particles from cavitation and the subsequent plastic deformation of the polyamide matrix.

E. Dispersion of Core-Shell Impact Modifiers in Engineering Thermoplastics

Emulsion polymerization can be used to make core-shell type impact modifiers for toughening rigid but brittle or notch-sensitive polymers. Such modifiers are especially convenient because particle size can be precisely set independently of processing and rheological parameters. The core of the particle contains the elastomer while the shell functions to aid dispersion in the matrix and to couple the particle to the matrix among other things. Usually the shell-matrix interaction is physical, i.e., the grafted chains are identical with the matrix or is miscible with it, e.g., PMMA or SAN grafts for PVC toughening. Such compatibility or miscibility usually does not exist between matrices consisting of engineering polymers like nylons, polyesters, polyacrylates, etc. and the types of polymers that can be used as the shell material. We have explored two routes for solving this problem; one physical and one chemical.

Commercial core-shell impact modifiers where the shell is comprised of poly(methyl methacrylate), PMMA, chains grafted to a rubber core, either acrylate or butadiene based, cannot be adequately dispersed in a matrix of poly(butyl terephthalate), PBT, to achieve useful toughening (25). However, it is known that tough materials can be achieved when these blends also contain polycarbonate, PC. It was demonstrated during the course of this project that 10% by weight or less of PC greatly facilitates the dispersal of such core-shell impact modifiers in a PBT matrix and leads to tough blends even at low temperatures. It is known that PC wets PBT and PMMA better than the latter two wet each other, which allows the PC to act as a dispersing agent for these impact modifier particles in the PBT matrix. The morphology and mechanical properties of ternary blends where PC is a major matrix component rather than simply a dispersing agent were also determined (25).
There does not appear to be a comparable physical approach for solving the dispersal problem of such modifiers into polyamide matrices. One chemical route is to incorporate functional units into the shell material by copolymerization which then can subsequently react with the polyamide chain ends to effect good dispersion and toughening. This project has demonstrated a viable alternative. Through previous ARO research, we found that SMA copolymers, over a certain range of MA comonomer content, are miscible with PMMA. Of course, the anhydride groups can react with polyamides. The proposal is then to use SMA as a dispersant for conventional impact modifiers (with PMMA grafted shells) in polyamides. Thus, we envisioned that addition of a small amount of an SMA copolymer should greatly improve the dispersion of the core-shell impact modifier in a nylon 6 matrix. The SMA copolymer is anticipated to reside in the PMMA shell via physical miscibility while also reacting with the nylon 6 amine end groups to form graft copolymers. We have shown using transmission electron microscopy that this concept does work and produces super-tough blends with low ductile-brittle transition temperatures (12).

Styrene/acrylic acid copolymers, SAA, are also miscible with PMMA. In principle, the acid functionality should also react with the polyamide. We examined SAA materials as potential compatibilizers for nylon 6/core-shell impact modifier blends (15). The SAA materials do work but not nearly as effectively as the SMA materials. The reason for this is that the reaction of amine groups with anhydride units is much more efficient and rapid than with acid groups. Thus, very effective chemistry is needed for reactive compatibilization.

Research in this area will continue under current ARO funding. Mr. A. J. Brady will receive his M.S. Degree in late 1994 while Mr. M. Lu will receive his Ph.D. Degree in early 1995.

F. Rubber Toughening of Polyamide/Polypropylene Blends
There has been considerable interest in blends of polyamides with polyolefins driven by the need to reduce the water sensitivity of nylon and the cost of these materials. To achieve compatibilization, various polyolefins have been functionalized, primarily by grafting with maleic anhydride, for reaction with the nylon component. Our work has employed polypropylene, PP, as the polyolefin and nylon 6 as the polyamide. We are using polypropylene grafted with maleic anhydride, PP-g-MA, as the compatibilizer. Various reactive elastomers are also being added to effect toughening (19). A series of papers will be written on this subject during late 1994 as Mr. A. Gonzalez completes his Ph.D. program. However, two important conclusions can be described already.

First, by the appropriate use of reactive compatibilization, tough blends can be produced which contain significant amounts of polypropylene. However, toughness is significantly sacrificed when polypropylene becomes the matrix phase in these materials.

Second, we have found that PP and PP-g-MA become immiscible or phase separated at relatively low levels of MA content. These mixtures when blended with nylon 6 produce a bimodal particle distribution when the PP and PP-g-MA are phase separated. This bimodality is not observed below the MA limit where the PP and PP-g-MA do not phase separate. This has major ramifications for developing polyamide/polyolefin blends. As noted above, such bimodality did not occur in SEBS/SEBS-g-MA mixtures blended with nylon 6 when the MA content was as high as 2%. However, for the PP/PP-g-MA system the upper limit of MA content without bimodality is below 1%.

III. Publications Completed to Date

A. Theses and Dissertations

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<tr>
<td>B. S. Lombardo</td>
<td>&quot;The Influence of ABS Type on the Morphology and the Mechanical</td>
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<tr>
<td>(M.S.)</td>
<td>Properties of PC/ABS Blends&quot;</td>
</tr>
<tr>
<td>B. Majumdar</td>
<td>&quot;Control of Morphology and Mechanical Properties in Polyamide Based</td>
</tr>
<tr>
<td>(Ph.D.)</td>
<td>Blends through Reactive Compatibilization&quot;</td>
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B. Papers in Print


C. Papers Submitted or Accepted for Publication


25. A. J. Brady, H. Keskkula, and D. R. Paul, "Toughening of Poly(butylene terephthalate) with Core-Shell Impact Modifiers Dispersed with the Aid of Polycarbonate", Polymer.


### IV. Participating Scientific Personnel

The following individuals received some financial support from this contract:

<table>
<thead>
<tr>
<th>Name</th>
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<tr>
<td>D. R. Paul</td>
<td>Faculty</td>
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</tr>
<tr>
<td>H. Keskkula</td>
<td>Research Fellow</td>
<td>Partial support</td>
</tr>
<tr>
<td>B. Majumdar</td>
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<td>M. Lu</td>
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<td>G. S. Wildes</td>
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<td>W. R. Hale</td>
<td>Ph.D. student</td>
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<tr>
<td>A. J. Oshinski*</td>
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</tr>
<tr>
<td>Y. Kayano*</td>
<td>Visiting Scholar</td>
<td>Continuing</td>
</tr>
<tr>
<td>A. Gonzales-Montiel*</td>
<td>Ph.D. student</td>
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*No salary support provided by this contract.*