REACTIVE POLYMER BLENDING

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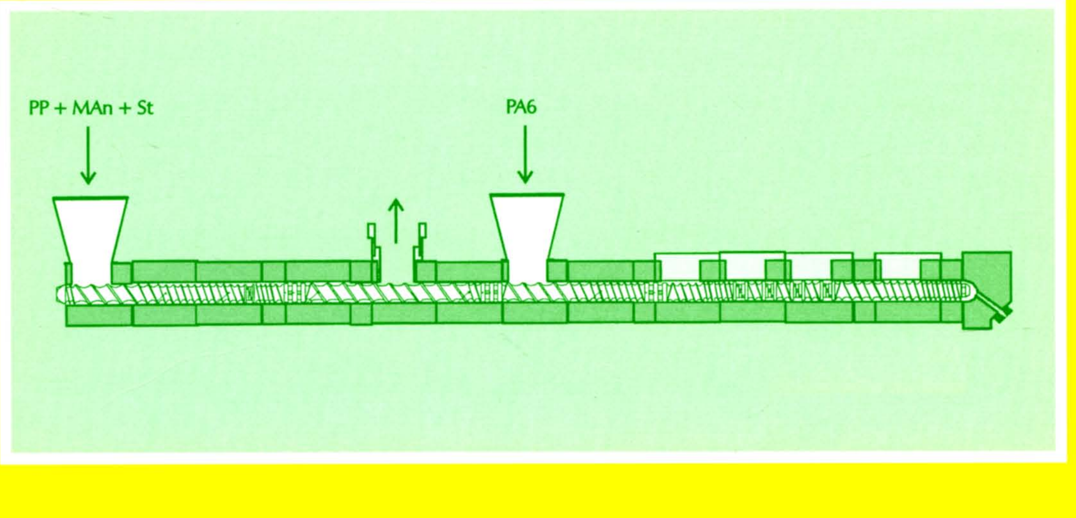

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Reactive Polymer Blending

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PROGRESS IN POLYMER PROCESSING SERIES

Kun Sup Hyun, *Series Editor*

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Foreword

Since World War II, the industry based on polymeric materials has developed rapidly and spread widely. The polymerization of new polymeric species advanced rapidly during the sixties and the seventies, providing a wide range of properties. A plethora of specialty polymers have followed as well, many with particularly unique characteristics. This evolution has been invigorated by the implementation of metallocene catalyst technology. The end-use of these materials has depended on the development of new techniques and methods for forming, depositing, or locating these materials in advantageous ways, which are usually quite different from those used by the metal or glass fabricating industries. The importance of this activity, ''Polymer Processing'', is frequently underestimated when reflecting on the growth and success of the industry.

Polymer processes such as extrusion, injection molding, thermoforming, and casting provide parts and products with specific shapes and sizes. Furthermore, they must control, beneficially, many of the unusual and complex properties of these unique materials. Because of their high molecular weights and, in many cases, tendency to crystallize, polymer processes are called upon to control the nature and extent of orientation and crystallization, which in turn have a substantial influence on the final performance of the products made. In some cases, these processes involve synthesizing polymers within a classical polymer processing operation, such as reactive extrusion. Pultrusion and reaction injection molding both synthesize the polymer and form a finished product or part all in one step, evidence of the maturing of the industry. A new family of polymer blends is prepared by reactive polymer blending processes. For these reasons, successful polymer process researchers and engineers must have a broad knowledge of fundamental principles and engineering solutions.

Some polymer processes have flourished in large industrial units, synthetic fiber spinning for example. However, the bulk of the processes are rooted in small- and medium sized entrepreneurial enterprises in both developed and new developing countries. Their energy and ingenuity have sustained growth to this point, but clearly the future will belong to those who progressively adapt new scientific knowledge and engineering principles, which can be applied to the industry. Mathematical modeling, online process control and product monitoring, and characterization based on the latest scientific techniques will be important tools in keeping these organizations competitive in the future.

The Polymer Processing Society was founded in Akron, Ohio, in 1985 with the aim of providing a focus, on an international scale, for the development, discussion, and dissemination of new and improved polymer processing technology. The Society facilitates this by sponsoring several conferences annually and by publishing the journal International Polymer Processing, and the volume series Progress in Polymer Processing. This series of texts is dedicated to the goal of bringing together the expertise of accomplished academic and industrial professionals. The volumes have a multi-authored format, which provides a broad picture of the volume topic viewed from the perspective of contributors from around the world. To accomplish these goals, we need the thoughtful insight and effort of our authors and volume editors, the critical overview of our Editorial Board, and the efficient production of our Publisher.

This volume deals with the reactive polymer blending in the development of new polymer materials, which attain the specific mechanical properties due to unique combination of their component polymers. These processes have developed into what is arguably the best route to prepare new materials by combining different, existing polymers while most monomers cannot be easily copolymerized to gain intermediate properties. Many excellent polymer blends have been developed economically for the major applications in the transportation, electronic, appliances and packaging area with properties important in each application. Therefore, most important in this volume are the extensive discussions on the unique aspects of reactive blending in the developments of polymer blends, and morphology changes and how these lead to improvements in properties especially mechanical properties. Therefore this volume covers all aspects, from fundamentals of interfacial reactions and morphology developments, compatibilizer chemistry and design, reactive blending process fundamentals, to the process equipment and present major classes of commercially significant blends. This volume includes numerous contributions, industrial and academic, from Europe as well as Asia and North America and, as such, forms a very useful contribution to the plastics industries. This volume was initiated by Dr. Warren Baker, my predecessor and one of the volume editors, and became the third volume in this series with which I had the pleasure to be associated.

Midland, Michigan
U.S.A.

Kun Sup Hyun
Series Editor

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Preface

This volume was written to support an area of very significant technical and industrial interest in the field of polymer development. Over the last 30 years polymer blends of many types have become the dominant material class of polymers in commercial practice. From infant beginnings in the 1970s, the use of carefully designed chemistry has grown to augment physical blending strategies and several good volumes have been written which cover ''Polymer Blends'' in general. However, none have focussed specifically on reactive blending and the material and process issues involved. This is an attempt to do just that.

Polymer blends have grown to take on a very significant role in the major application areas for polymers. A plethora of applications in the packaging, electronics/electrical, transportation, and construction industries have been instrumental in allowing polymeric materials to expand against other, more traditional materials. Many of these blends are phase separated, which leads to the need to control morphology and hence properties. Cleverly designed di-block and tri-block copolymers, which had no chemical functionality, were developed which aided in improving the performance of blends. However, their complexity of design and difficulty of use led to the innovations starting in the 1970s to use selective chemistry to enhance performance by controlling and stabilizing preferred morphologies and influencing interfacial adhesion. Some of the first applications and developments related to polyamide blends, but now reactive blending and compatibilization extends to essentially all polymeric material classes.

This volume covers a wide range of the issues important in reactive blending. It starts in Chapter 1 with an overview of some of the basic fundamental issues in polymer blending in general and feeds into a brief overview of the historical developments in reactive blending. Chapter 2 is a comprehensive review and bibliography of the many classes of chemistry, which have been reported in reactive blending. Chapter 3 deals with the dynamics and interfacial issues, which are at play and Chapter 4 discusses the design and function of reactive compatibilizers. Chapter 5 focuses in on the topic of morphology development and the rheological factors that are so influential in reactive blending. Chapters 6 and 7 deal with the processing issues and process equipment involved. Chapter 8 takes the most extensively investigated reactive blend material, polyamide, and follows it through the many developments as an example of a particular class. Chapter 9 makes a departure and deals with a new, possibly emerging approach to blending, using low molecular weight reactive additives. While we have not covered all aspect of reactive blending, we trust that this will be a useful contribution to the field for both fundamental researchers and industrial practicioners.

In keeping with the philosophy and membership of the Polymer Processing Society this volume is the collaboration of authors from Europe, the Americas, and Asia. We believe this diversity of views and inputs is important in disseminating the latest of technical developments. Many authors have assisted in this project but we are particularly indebted to N. C. Liu, G. Groeninckx, R. Jerome, T. Sakai, and K. Akkapeddi for co-ordinating their chapters. Several individuals provided helpful reviews of the chapters including C. Tzoganakis, C. K. Shih, J. Curry, L. Geottler and S. Balke. We hope this volume will further contribute to the field of polymer blending.

Brampton, Canada	*Warren Baker*
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1 Introduction

Warren E. Baker and Guo-Hua Hu

During the last three decades polymer blends have become a very important part of the commercialization of polymers. By combining two or more different polymers one can tailor compositions to meet specific end use requirements. Some of the general principles involved in successful blending are discussed followed by an introduction to the elements of reactive blending. Pioneering work on several key issues including copolymer formation, interface development and morphology are mentioned. Toughening of polyamide systems dominates the early patent literature and signalled a plethora of oncoming commercial developments. The importance of processing is also introduced.

1.1 Background

The practice of blending polymers is as old as the polymer industry itself with early examples involving natural rubber. However, through the first half of the 1900s the greatest progress in the industry was in the development of a wide range of different polymers. This was based on the new understandings of polymer synthesis and the development and commercialization of economical manufacturing methods for a range of monomers. With a few exceptions most of the major commodity and engineering polymers in current use were being manufactured in the 1950s. By the 1970s however most of the economical monomeric starting points had already been exploited and while elegant chemistry continues to lead to exciting new polymer developments and applications, these are generally reserved for quite specialized, low volume applications.

Over the last forty years two additional directions have evolved in the polymer industry. First is the development of significant new polymerization processes to manufacture both homopolymers and copolymers based on the monomers used much earlier. The invention of the Unipol process by Union Carbide Corp., to make ethylene homopolymers and copolymers in the latter 1970s, has revolutionized polyethylene to the extent that this process and its unique polymers have taken on a dominant position in that industry. This was followed closely thereafter by the development of the Spheripol process to make propylene polymers with a near similar impact. Meanwhile, during approximately the same period, a separate development has flourished, namely polymer blending. It was gradually recognized that new, economical monomers were less likely but rather a range of new materials could be developed by combining different, existing polymers. While most monomers cannot be easily copolymerized to gain intermediate properties, their polymers could be melt blended economically, using the diverse and improving processing technologies of the day. Out of this has come a near explosion of new materials, to the extent that polymer blends, in one form or another, dominate much of polymer practice. Who could think of the major applications in the transportation, electronics, appliances and packaging without encountering blends? The rational for this rapid development is captured in one or more of the following points:

- the opportunity to develop new properties or improve on properties to meet specific customer needs,
- the capability to reduce material costs with little sacrifice in properties,

- the ability to improve the processability of materials which are otherwise limited in their ability to be transformed into finished products,
- permit the much more rapid development of modified polymeric materials to meet emerging needs by by-passing the polymerization step.

The history of polymer blend discoveries and developments has been well documented very recently by Utracki [1].

1.2 Important Blending Principles

Some of the major issues involved with polymer blending need to be introduced. With a few exceptions, simply adding a polymer to another one brings both good and bad properties to the latter. The adverse effects are often so important that the resulting material is most likely unusable. The main reason is that most polymer pairs are immiscible. Blending two immiscible polymers necessarily leads to a phase-separated material. The latter often has three inherent problems if the morphology and the interfaces of the blend are not well controlled:

1. Poor dispersion of one polymer phase in the other. For most polymer pairs, the interfacial tension, Γ_{12}, is high ($\Gamma_{12} = 1.5 \times 10^{-3}$ to $1.5 \times 10^{-2}\,\mathrm{J \cdot m^{-2}}$). This makes it difficult to disperse one phase in the other by melt blending. When the inclusions of the dispersed phase are large, the interfacial contacts between the two phases are small. When the material is subjected to a mechanical load, the two phases are unable to show their best features in a ''concerted'' manner in order to respond efficiently.
2. Weak interfacial adhesion between the two phases. For most polymer pairs, the Flory parameter, χ, is large ($\chi = 0.05$–0.5) and the interfacial width, h, is narrow (1–5 nm). This latter corresponds only to a fraction of the radius of gyration of a typical Gaussian polymer chain (10–50 nm). This means that there is little penetration of polymer chains from one phase into the other and vice versa, and consequently few entanglements are formed across the interfaces [2]. In this case, failure of the interface between two glassy polymers thus requires only the breaking of weak Van der Waals bonds, as in the fracture of a low-molecular-weight polymer. The fracture energy or fracture toughness of such an interface can be approximated as the ideal work of adhesion, $W = \Gamma_1 + \Gamma_2 - \Gamma_{12}$, where Γ_1 and Γ_2 are the surface energies of polymers 1 and 2, respectively. For most polymer pairs $W \approx 0.1\,\mathrm{J \cdot m^{-2}}$, much weaker than the fracture toughness of even ''brittle'' high-molecular weight homopolymers such as PS and poly(methyl methacrylate) (PMMA). Even for these two very brittle polymers, the values of fracture toughness are about $500\,\mathrm{J \cdot m^{-2}}$. This implies that for most uncompatibilized polymer blends, the interfaces are probably the most vulnerable locations (mechanical flaws). When they are subjected to an external stress, the interfaces will most likely fail well before the base polymer components.
3. Instability of immiscible polymer blends. An immiscible polymer blend is thermodynamically unstable. The state of dispersion of one phase in another is governed by both thermodynamics (interfacial tension) and thermo-mechanics (agitation). It is a

result of the competition between the interfacial energy of the system which encourages maximum separation of the components, and the external mechanical agitation imposed on it, which is designed to induce mixing. Agitation produces flow stresses which tend to deform and break-up domains. Interfacial tension opposes the deformation and break-up of domains and encourages coalescence of the dispersed phase domains when they come in close proximity. The dispersion can be quantified by a number of means. For example, the extent of contact between the two phases can be quantified by the total interfacial area A. For a blend of given composition, which consists of dispersed spheres in a matrix, the interfacial area per unit volume is inversely proportional to the radius of the spheres.

When agitation ceases, the interfacial tension becomes the unique driving force for the system to evolve. Each phase seeks to ''get together'' by coalescence by minimizing the total interfacial area and thus the total interfacial energy ($\Gamma_{12}A$) of the system. Coalescence proceeds very rapidly in a water-oil system because the viscosity is low and drops can move easily with little hydrodynamic resistance. It is much slower in an immiscible polymer blend owing to a much higher viscosity. Nevertheless, it may still be too fast for most practical applications. A major problem caused by the instability of such a phase-separated blend is that its morphology evolves when conditions to which it is subjected vary. For example, the morphology of an immiscible polymer blend obtained from a screw extruder may not be the same as that which is later injection molded.

The above discussion does not mean that immiscible polymer blends are of little use and that the only solution is to search for miscible ones. In fact, immiscible polymer blends are much more interesting for commercial development. This is because immiscibility allows one to preserve the good features of each of the base polymer components of the blend. Some properties can be achieved only through immiscible blends. For example, the impact strength of a polymer can not be improved significantly by adding an elastomer miscible to it. It is thus fortunate that most polymer pairs are immiscible. The challenge is to develop processes or techniques that allow control of both the morphology and interfaces of phase-separated blends. Such processes or techniques are called compatibilization. Polymer blends with intentionally modified morphology and interfaces are called compatibilized blends.

Strategies developed for compatibilizing immiscible polymer blends are largely inspired from colloidal sciences and technologies. For example, adding a molecule (surfactant or emulsifier) possessing both hydrophilic and hydrophobic entities to a water-oil system helps the dispersion of one phase in the other and improves the stability of the system. Addition of a suitable block or graft copolymer to an immiscible polymer blend plays virtually the same roles as the small molecule does in a water-oil system. However, it has an additional role, which consists of enhancing the interfacial adhesion between the two phases. Such a copolymer is known under various names such as ''compatibilizer'', ''interfacial agent'', ''emulsifier'', and ''adhesion promoter''. Basically, there are three distinct strategies for compatibilizing immiscible polymers:

1. Non-reactive compatibilization: adding non-reactive block or graft copolymers;
2. Specific compatibilization: attaching to polymer chains groups having non-bonding specific interactions;
3. Reactive compatibilization: introducing reactive molecules capable of forming the desired copolymers in-situ, directly during blending.

Non-reactive compatibilization is the classical approach to compatibilizing immiscible polymer blends. When introduced to an immiscible polymer blend, a well-selected copolymer bearing two distinct segments, typically a block or a graft copolymer, will be located preferentially at the interfaces. Each segment will penetrate to the phase with which it has specific affinity. This will reduce the interfacial tension, enhance the interfacial adhesion, promote dispersion of the dispersed phase in the matrix, and stabilize the morphology of the blend. The effectiveness of this approach has been largely proven. Additionally, influences of the molecular architecture of block copolymers and, to a lesser extent, graft copolymers have been extensively documented. Among the many substantial contributions to these understandings, the work of Fayt, Jerôme and Teyssié deserves mention [3, 4]. However, this approach inherently bears two major limitations:

1. Compatibilization of each immiscible polymer blend needs a specific block or graft copolymer. Consequently, a particular synthetic procedure is required to obtain the copolymer. This is often tedious and costly. For some immiscible polymer pairs, synthetic procedures are presently unavailable for preparing the corresponding block or graft copolymers.
2. The amount of the block or graft copolymer to be added may have to be significantly higher than that required to saturate the interfaces. This is because for thermodynamic and thermomechanical reasons, a portion of the copolymer introduced may never reach the interfaces. In order for the copolymer to reach the interfaces during melt blending, it has to undergo successively, melting/plastification, dispersion, solubilization and molecular diffusion, respectively. In other words, it has to be dispersed first in sufficiently small domains so as to be "solubilized" by chain disentanglement and distributed as single macromolecular chains and/or micelles in the base polymer components. These solubilized macromolecular chains will ultimately reach the interfaces by molecular diffusion. Although little is known about each of these steps under melt blending environments, it is speculated that the time scales of these steps may be relatively long with respect to the residence time of a typical melt blending process in a screw extruder (a few seconds to a few minutes). Furthermore the steps may depend, among other things, on the molecular architecture of the copolymer and mixing. The role of mixing is twofold: to disperse the copolymer in the blend and to shorten the diffusion distance necessary for the copolymer to reach the interfaces. Thus, how to get the compatibilizer to the interfaces is a major problem facing non-reactive compatibilization [5]. The amount of the copolymer that is not present in the interfaces is useless for compatibilization. It can be quite significant.

Nevertheless, the proven effectiveness of using block or graft copolymers to control both the interfaces and the morphology of immiscible polymer blends has triggered tremendous efforts to devise new approaches to produce block and graft copolymers as compatibilizers. The most important one is reactive compatibilization, as it allows one to generate the desired compatibilizers *in situ* during melt blending, using reactive polymers. Conceptually, there are three main scenarios for reactive compatibilization of two immiscible polymers:

1. The base polymer components are mutually reactive. In this case, reactive compatibilization is straightforward. The reaction between them at the interfaces will lead to

the formation of a copolymer. Most polycondensates inherently bear functional groups. For example, polyamide 6,6 (PA 6,6) is expected to possess a terminal amine group and a terminal carboxylic group.

2. One polymer (A) bears potentially reactive groups and the other (B) is chemically inert with respect to them. Reactively compatibilizing them requires that the non-reactive polymer be functionalized with functional groups that can react with the reactive one. A typical example is blends based on polypropylene (PP) and polyamide 6 (PA6), two highly immiscible polymers. Reactive compatibilization can be achieved by functionalizing PP with maleic anhydride. The corresponding succinic anhydride moieties attach onto the PP backbones and react readily with the terminal amine group of the PA6 leading to an *in situ* formed graft copolymer. An alternative is to introduce a reactive polymer (C) that is miscible with the non-reactive polymer and can react with the reactive one. The situation then becomes similar to (1). The compatibilizer formed will be of type A-C, of which segment A is identical to A polymer and segment C miscible with B polymer.
3. Neither of the two base polymers (A and B) contain reactive groups. Most hydrocarbon polymers, such as polyethylene PE, PP, PS and copolymers thereof, are in this situation. In such cases, different compatibilization methods can be envisioned. The first one is to add two reactive polymers (C and D) which are mutually reactive and are miscible with A and B, respectively. The resulting copolymer will be of type C-D. The second one is to functionalize polymers A and B with different functional groups, which are mutually reactive. Take PE/PS blends as an example. When PE is functionalized with a carboxylic group and PS with an oxazoline group, they will be able to react with each other and form a desired compatibilizer [6].

The basic principles are the same for non-reactive compatibilization and reactive compatibilization, except that in reactive compatibilization, chemical reactions (functionalization and interfacial reaction) are involved in the blending process. This makes reactive compatibilization very attractive and cost-effective because:

1. It offers the possibility of generating compatibilizers during melt blending directly at the interfaces between the base polymer components without separate synthetic and purification steps, which are otherwise involved in non-reactive compatibilization.
2. Since the copolymer is formed directly at the interfaces, there is no problem getting it to the interfaces where it is most needed. Thus, reactive compatibilization is also known under the term "*in situ* compatibilization" or "reactive blending".
3. Sometimes desired compatibilizers cannot be synthesized separately by existing synthetic procedures. Reactive compatibilization then becomes the method of choice. In fact, functionalization of existing polymers in the melt can now be "readily" done in a polymer processing machine. Free radical grafting of functional monomers is one example [7].
4. Understanding reactive compatibilization from the standpoint of the ultimate compatibilizer structure has been difficult in that it is formed *in situ* and is very difficult to extract and characterize unambiguously. One of the unforeseen advantages of the reactive blending technique to some commercial organizations is that the process can be conducted in different ways with different property outcomes. Thus, the product

cannot be de-engineered easily by analysis, which provides an element of secrecy to the manufacture.

The study of reactive polymer blending has attracted researchers from many different classical disciplines because it involves many aspects. Polymer chemistry and organic reaction chemistry are vital, as the thermodynamics and kinetics of the interfacial reactions need to be understood. Equally important is an understanding of the flow regimes in the various processing devices used. The melting and mixing processes control the generation of new surface between the two polymers at which the graft copolymer is formed, and they also control the resulting morphology.

Reactive compatibilization dominates, in some fashion or another, commercial blending practices today, and is the main theme of this volume. The chapters that follow look at the fundamentals that enable this approach to material design, and will cover the important practical examples of implementation.

1.3 A Historical Perspective on Reactive Blending

Very rarely does one research report, patent or publication, clearly mark the starting point for any new technological development; this is the case for reactive polymer blending. However there are usually some early highlights and the paper by Ide and Hasegawa of Mitsubishi Rayon, published in 1974, was certainly one [8]. In this work, the authors prepared two different reactive compatibilizers, PP grafted with maleic anhydride (PP-g-MA) and PS grafted with methacrylic acid (PS-g MAA). These were then combined into Polyamide 6 (PA6)/PP and PA6/PS blends of varying proportions and injection molded into test specimens. Though limited to the mixing occurring in the extrusion section of the molder, useful samples were obtained. Many of what are now understood to be the basic aspects of reactive blending were examined and explained. There was evidence for the *in situ* formation of a compatibilizer. New copolymers of the polyamide combined with either the PP copolymer or PS copolymer were isolated by solvent extraction and indirectly identified using DSC. The reaction of the terminal amine groups with the anhydride was confirmed by monitoring the continuous decrease in free amine groups with the addition of more anhydride copolymer. Finer morphology was observed in micrographs of PP rich blends, which contained the PP-g-MA, compared to those with no copolymer. Using tensile, Izod impact, and dynamic mechanical testing, the mechanical properties of the PP/PA6 system, at least, were observed to improve. Illustrated with two different copolymers potentially reactive with polyamide, this work must have been a useful starting point for many others.

The blends of polyamides (PA) with various modified elastomers and polyolefins became the most common research platform for studying the fundamentals of reactive polymer blending. The favorable reactivity between the primary amine of the PA and anhydride in the second phase enabled researchers to examine many of the fundamental issues of reactive blending including, kinetics, characteristics of newly formed interfaces, morphology effect, and mechanics of failure to mention only a few. As will be seen later, this system has become one of the most significant commercial examples of reactive blending as well. Among these many studies the work of Borggreve and Gaymans deserves mention [9–14]. Their work centered on the system of PA6 blended with 0–20% EPDM rubber, grafted with maleic anhydride. They looked at the amount and nature of the maleic anhydride grafted additive, the average dispersed phase elastomer particle size and inter-particle spacing, the impact behavior of the blends as a function of temperature and the interplay between the interface character and the morphology, and the failure mechanism. Increasing the elastomer concentration and decreasing its domain size generally lowered the brittle–tough transition to a lower temperature. The resulting interfacial layer was examined using IR spectroscopy and elemental analysis. The issue of whether mechanical properties were enhanced by interfacial adhesion between the PA and elastomer was considered. It was generally felt that the benefit of the compatibilizer was more in helping to achieve the appropriate morphology, and that adhesion during impact was less important. Rather, the importance of the inter-particle spacing and cavitation within the elastomer phase to the failure mechanism were described. It was also found that there was an optimum particle size, below or above which the impact behavior worsened [15].

The issue of the role of interfacial adhesion on the impact performance of reactively compatibilized blends has attracted considerable effort. In the system that Borggreve and Gaymans studied they found that neither the MA content of the EPDM-g-MA, nor the amount of PA coupled at the interface after melt blending, have an influence on the impact toughness of PA/EPDM blends if the morphology is not changed. For the rubber toughened PA case Inoue [15] found that matrix yielding and large energy dissipation was favored by a strong interface preserved from de-bonding. In a different system of PS/NBR [16], it was found that increasing interfacial adhesion, while retaining the same morphology, was important to increase impact properties. In yet another system, PET toughened with reactive and non-reactive EPR [17], the link was made among finer dispersion, thicker interface and higher impact strength for the reactive case. The issue of the importance of interfacial adhesion on mechanical property enhancement remains open and is surely dependent on the nature of the impact event.

The whole topic of how interface evolves during the preparation of a blend involving reaction demands careful experimentation. A series of fundamental studies from Prof. Inoue's laboratory have developed useful insights. In a mini-mixer, they followed, with time, the increase in specific interfacial area using light scattering and the increase in interfacial thickness using time resolved ellipsometry. The amounts of block copolymer reactively formed at the interface were determined by GPC. For a system hydroxy-terminated caprolactone/carboxylic acid terminated liquid rubber, with and without a reactive coupling agent, the kinetics of new block copolymer formation and the interface thickness development were monitored [18]. In a different system of amorphous PA/SMA, the same techniques monitored both the blend evolution and subsequent annealing. The interface thickness attained constant values in the range of 10–50 nm. As the thickest interfaces were several times the coil size of the component polymers this suggested that the whole graft copolymer chain would likely exist in a graduated, interface region [19]. The interface thickness observed using non-reactive block copolymer compatibilization is closer to the 5–10 nm range. The formation of such thick interfaces seems to be characteristic of blends involving *in situ* copolymer formation and provides preliminary understanding of the *in situ* reactive compatibilization of polymer blends.

1.4 The Evolution of Commercial Practice

1.4.1 Patents and Products

A complete review of the patent literature related to reactive blending is beyond the scope of this volume. The reader is referred to the excellent volume by Utracki [1] where, in Appendix IV, one can find a chronological summary of ''Polymer Blend Discoveries and Development''.

Over time the nature of both the blend patent literature and commercial practice has moved in the direction of reactive compatibilization. A few patents appeared in the 1970s where reference was made to chemical interactions enhancing blend performance. In 1972 a British patent [20] referred to a PA/PP with 0.5% maleated PP having improved elongation at break and notched impact strength. However, the patent, which was the most significant in influencing the early practice of reactive blending, was the one to DuPont [21] which included a wide range of chemistry for toughening PA polymers using ethylene based copolymers. It was accompanied by another patent [22] that related similarly to PET and to polycarbonate. Using a vented, intermeshing, co-rotating twin screw extruder, ethylene-based polymers with carboxylic acid, anhydride or epoxide groups were melt blended with PA, leading to impact toughening. Epstein claimed that additional improvements were seen if carboxylic acid groups were neutralized with zinc salts. The ethylene copolymers ranged widely from ethylene/methyl acrylate to EPDM and the polyamides included PA6, PA66 as well as some amorphous grades. Many more DuPont patents as well as those from other companies followed, but this was the springboard for DuPont's very successful Zytel-ST^{TM} product line. The available chemistry and polymer backbones were sufficiently broad that many other companies quickly had toughened polyamide grades on the market.

Another example of commercially important blends, which relies on reaction during blending, is the polycarbonate/polyester family. Either PET or PBT is added to polycarbonate to enhance the stiffness and solvent resistance to an otherwise tough polymer. Owing to the transesterification reaction that occurs fairly easily between these polymers in the melt, compatibilization chemistry is readily available. However, an appropriate balance is necessary so that adequate compatibilization occurs, but without excessive interphase reaction. When the transesterification goes too far the polyester is less able to crystallize and stiffness, and solvent resistance is reduced. The challenge in this system was not to develop new chemistry as much as to control the existing opportunity. More recently, combined impact modifier/reactive compatibilizers have been introduced based on acrylate, acid or anhydride functionality. This class of blends, made by several producers, was first developed in the late 1970s and now enjoys wide sales.

Yet another example of reactive blending practice is ''dynamic vulcanization'', first disclosed and patented in the late 1970s. The term refers to a process pioneered by Coran and Patel [23, 24] in which an elastomer and a semi-crystalline thermoplastic are melt blended together during which the elastomer phase crosslinks, but not the continuous thermoplastic phase. By crosslinking the elastomer phase, which usually makes up more than 50% of the system, the dispersed elastomer morphology is stabilized, preventing coalescence later. These phase-separated blends have the properties of thermoplastic elastomers, with excellent toughness, elongation and dimensional stability over a wide range of Shore hardnesses and, also, the processability of a thermoplastic. A typical composition would consist of 40% PP and 60% EPDM to which is added small amounts of zinc oxide, stearic acid, tetramethylthiuram disulfide and sulfur. The selection and addition of the additives is carefully sequenced to ensure that the crosslinking is localized into the elastomer phase during blending. Some interfacial compatibilizer is reported to form during the process. While the early patents refer to the PP/EPDM combination, subsequent disclosures include natural rubber, NBR or polybutadiene combined with polyamide, PBT, polycarbonate and several others. The crosslinking additives are also varied. This technology led to the commercialisation of Santoprene^{TM} by Monsanto Chemical.

In the early 1980s, a quite different, reactively compatibilized blend was introduced by DuPont, which not only controlled the dispersed phase size, but also enabled the dispersed phase domains to take on a preferred shape in later processing [25–27]. The addition of a PE-g-MA compatibilizer to a 80/20 PE/PA6 blend sufficiently strengthened the interfacial layer that melt drawing of the blend in film or bottle forming processes results in overlapping lamellae of the PA. The lamellar structure provides an excellent barrier to the diffusion of molecules soluble in the polyolefin but insoluble in PA6. This concept was commercialized by DuPont in 1982 as Selar^{TM}. Other Selar grades were introduced later, in which the PA6 was replaced by amorphous PA and PET.

1.4.2 Processing

The importance of processing to effective reactive blending cannot be overestimated. The principles of reactor engineering need to be applied to complex environments, which involve staged reactions, high viscosity reactants that influence mixing and heat transfer and multiple phases through the process. In the commercial examples given above, considerable process development has been carried out to understand and control many factors. They include the residence time in various parts of the processing equipment, the temperature profile and thermal history, the shear rates and stresses throughout, the specific energy input, and the injection points and withdrawal points for reactants and by-products.

A wide range of commercial processing equipment is used for reactive blending. This range includes various types of twin screw extruders, Farrel continuous mixers, Buss kneaders and single screw extruders. These must be configured to give adequate residence time so that both the requisite mixing and reaction can occur. Each blend system has a unique set of processing requirements; therefore, it is very difficult to make generalizations on equipment preferences. For an immiscible blend and one compatibilized with a non-reactive block copolymer, Plochocki organized a systematic comparison of three different twin screw extruders, a diskpack, a continuous mixer and a Buss kneader [28–31]. The fact that no similar comparison has been done for a reactive blend may be a reflection on the complexity of these systems. The reader may find the Plochocki study useful. Both patent literature and industrial practice shows that screw extruders play a dominant role in the preparation of reactively compatibilized blends, and these devices will be the focus of Chapters 6 and 7.

While the range of reactive polymer blends found in practice are indeed varied, something can be learned from the specific cases that have been published. White [32] has conducted studies in which the development of morphology has been monitored down the length of various types of equipment. Curry [33] examined the evolution down a ZSK twin screw extruder with a well characterized, reactive blend system. In fundamental studies of the influence of the melting process, the interactive effects of several factors have been shown on the development of blend morphology, including the melting point of the polymers as well as volume fraction and melt viscosity of the components [34–38].

One example of how processes for reactive blending are evolving comes out of the laboratory of the late Prof. Lambla [39–41]. In a tandem process, two different reactions were carried out in one pass through a 40 : 1 L/D ZSK twin screw extruder. In the first stage, glycidyl methacrylate was grafted onto PP in a peroxide initiated step. After a midpoint vent, PBT was added to the extruder and reactively blended with the grafted PP to form a blend of improved properties. While chemical kinetics may not allow this in all cases, it illustrates the potential to use innovative process technology to prepare reactively compatibilized blends.

1.5 Summary

Reactive polymer blending has become a very important contributor in the development of new polymer materials. While many volumes deal with blends in general, this is the first volume to focus specifically on the unique aspects of reactive blending. Chapters 3 and 5 will address some of the fundamentals of interfacial reactions and morphology development. Compatibilizer chemistry and design are discussed in Chapters 2 and 4. The important issue of applying the reactive blending fundamentals in processes is covered in Chapter 6 while the process equipment is covered in Chapter 7. The most widely studied family of blends based on polyamides will be the focus of Chapter 8. Low molecular weight compatibilizing systems are discussed in Chapter 9. It is hoped that this combination of fundamentals and practice will be useful, both to new students and practitioners in the field.

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2 Types of Reactive Polymers Used in Blending

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Blending of immiscible polymers offers attractive opportunities for developing new materials with useful combinations of properties. However, simple blends often have poor mechanical properties and unstable morphologies. Compatibilization of such blends is necessary. Preformed graft or block copolymers have been traditionally added to act as compatibilizers. Another route, however, is to generate these copolymer compatibilizers "in-situ" *during melt blending using functionalized polymers. In this review, a variety of reactive polymers that have been utilized in the reactive compatibilization of polymer blends is examined. They are classified into eight major categories according to the types of reactive functionality and the characteristics of blending reactions, namely, maleic anhydride, carboxylic acids, groups capable of interchange reactions, primary and secondary amines, hydroxyl groups, heterocyclic groups, groups capable of ionic bonding, and others. Their preparation methods and applications, and the chemical reactions they undergo during melt blending are presented.*

2.1 Introduction

There is intense commercial interest in multiphase polymer blends or alloys because of the potential opportunities for combining the attractive features of several materials into one, or to improve deficient characteristics of a particular material including recycled plastics [1–9]. However, most blends are immiscible and have poor physical properties compared to their components. This problem is rooted in the lack of favorable interaction between blend phases. This leads to a large interfacial tension between the components in the blend melt which makes it difficult to deform the dispersed phase of a blend during mixing and to resist phase coalescence during subsequent processing. It also leads to poor interfacial adhesion in the solid state which frequently causes premature mechanical failure, depending on the nature of the applied stress and the failure mechanism.

Morphology and interfacial adhesion can be improved by the addition of suitable block or graft copolymers that act as interfacial agents. These block or graft copolymers can, in principle, be made separately and then added to polymer blends. However, due to the lack of economically viable routes for the synthesis of suitable copolymers for important systems, compatibilization by preformed copolymers has not been used as extensively as the potential utility might suggest. A more proactive alternative is to generate these copolymers *in situ* during the blend preparation through polymer-polymer grafting reactions using functionalized polymers.

In this chapter general strategies for the compatibilization of polymer blends and the functionalization of polymers are briefly reviewed, which is followed by a detailed summary of a variety of reactive polymers, the chemical reactions they undergo, and their applications.