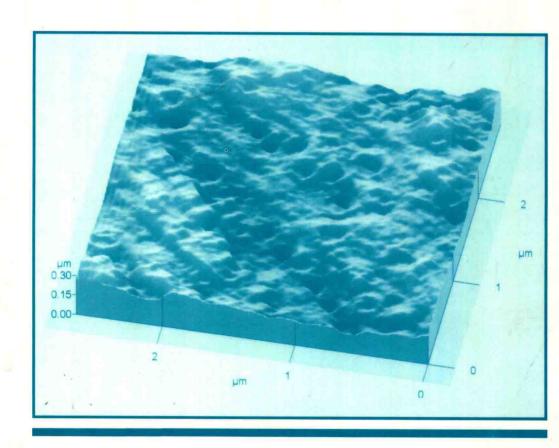
INTERFACIAL ASPECTS OF MULTICOMPONENT POLYMER MATERIALS



Edited by
David J. Lohse, Thomas P. Russell,
and L. H. Sperling

Interfacial Aspects of Multicomponent Polymer Materials

Edited by

David J. Lohse

Exxon Research and Engineering Co. Annandale, New Jersey

Thomas P. Russell

University of Massachusetts Amherst, Massachusetts

and

L. H. Sperling

Lehigh University Bethlehem, Pennsylvania

Library of Congress Cataloging-in-Publication Data

Interfacial aspects of multicomponent polymer materials / edited by David J. Lohse, Thomas P. Russell, and L.H. Sperling.
p. cm.
Includes bibliographical references and index.
ISBN 0-306-45718-0
1. Polymers--Surfaces. 2. Interfaces (Physical sciences)
3. Copolymers--Surfaces. I. Lohse, David J. II. Russell, Thomas P., 1952 - . III. Sperling, L. H. (Leslie Howard), 1932TA455, P58154 1998
547'.70453--dc21 97-35366
CIP

Cover illustration: Atomic force microscopy scan, L. H. Sperling, Figure 6, Chapter 1, ©1995 John Wiley & Sons, Inc.

ISBN 0-306-45718-0

© 1997 Plenum Press, New York A Division of Plenum Publishing Corporation 233 Spring Street, New York, N.Y. 10013

http://www.plenum.com

10987654321

All rights reserved

No part of this book may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, microfilming, recording, or otherwise, without written permission from the Publisher

Printed in the United States of America

Interfacial Aspects of Multicomponent Polymer Materials

PREFACE

In August, 1996, the ACS Division of Polymeric Materials: Science and Engineering hosted a symposium on Interfacial Aspects of Multicomponent Polymer Materials at the Orlando, Florida, American Chemical Society meeting. Over 50 papers and posters were presented. The symposium proper was preceded by a one-day workshop, where the basics of this relatively new field were developed. This edited book is a direct outcome of the symposium and workshop.

Every object in the universe has surfaces and interfaces. A surface is defined as that part of a material in contact with either a gas or a vacuum. An interface is defined as that part of a material in contact with a condensed phase, be it liquid or solid. Surfaces of any substance are different from their interior. The appearance of surface or interfacial tension is one simple manifestation.

Polymer blends and composites usually contain very finely divided phases, which are literally full of interfaces. Because interfaces are frequently weak mechanically, they pose special problems in the manufacture of strong, tough plastics, adhesives, elastomers, coatings, and fibers. This book provides a series of papers addressing this issue. Some papers delineate the nature of the interface both chemically and physically. The use of newer instrumental methods and new theories are described. Concepts of interdiffusion and entanglement are developed. Other papers describe state-of-the-art approaches to improving the interface, via graft and block copolymers, direct covalent bonding, hydrogen bonding, and more.

While some papers and patents in the field of polymer blend and composite interfaces appeared very early, the modern field of research and engineering started around 1989. In that year, a number of theoretical papers appeared, together with novel experimental results, often using new instruments. Since that date, the field has literally exploded, with great attention now being devoted to polymer interfacial research.

The entire field of polymer science and engineering is interdisciplinary, and this is especially true for any and all studies of polymer interfaces. Scientists and engineers working in chemistry, chemical engineering, materials science and engineering, physics, and mechanical engineering as well as polymer science and engineering will all find this book useful.

There are many organizations and people to thank. First of all, financial support for the symposium was provided by the U.S. Department of Energy, Office of Basic Energy Sciences, the ACS Petroleum Research Fund, Rohm and Haas, Exxon, Kodak, Dow Corning, and the ACS Division of Polymeric Materials: Science and Engineering. The Lehigh University Fairchild–Martindale Library provided Dr. Sperling with a carrel where much of the preparation and editing of this work was carried out. Plenum Publishing, especially Ms. Patricia M. Vann, provided much support and encouragement for the preparation and publication of this book.

D. J. Lohse Exxon Research and Engineering

T. P. Russell University of Massachusetts

L. H. Sperling Lehigh University

CONTENTS

Introduction to Interfacial Aspects of Multicomponent Polymer Materials	1
L. H. Sperling	
Improved Compatibilization of Immiscible Homopolymer Blends Using Copolymer Mixtures Yulia Lyatskaya and Anna C. Balazs	17
Brownian Motion Simulation of Chain Pullout: Modeling Fracture in Polymer Blends Galen T. Pickett, David Jasnow, and Anna C. Balazs	33
Polyelectrolytes at Interfaces: Pattern Recognition	41
Real-Space Studies on Interface in a Phase-Separated Polymer Blend by Laser Scanning Confocal Microscopy Hiroshi Jinnai, Yukihiro Nishikawa, Tsuyoshi Koga, and Takeji Hashimoto	53
Interfacial Characteristics of Amorphous Polystyrene and Binary Polymer Blend Thin Films Based on Scanning Force Microscopy	63
Solid State NMR Studies of Polymer Interfaces	73
Adsorption and Wetting from Tunable Polyolefin Mixtures	81
Strength of the PC-SAN Interface as Determined by Delamination of Polymer Microlayers A. Hiltner, T. Ebeling, A. Shah, C. Mueller, and E. Baer	95
The Formation of Polymer Monolayers: From Adsorption to Surface Initiated Polymerizations	07
Changes of Interfacial Adhesion by the Addition of Reactive Polymers	23

Pulsed NMR Studies on the Interfacial Structure of the Block Copolymers of Styrene and Isoprene with Variable Interface
Compatibilization of HDPE/PS Blends by Tapered Diblock PE-PS Copolymers14: Michel F. Champagne and Michel M. Dumoulin
Compatibilizer-Phase Morphology-Mechanical Property Relationships of Multicomponent Heterophase Polymer Blends
Wettabilities and Adhesive-Autohesive Properties of Poly(Tetrafluoroethylene) Surfaces Photografted with Hydrophilic Monomers
Siloxane Terpolymers as Compatibilizers for Polymer Blends
Interfacial Strengthening with Random Copolymers
Molecular Design of Reactive Compatibilizers for Polypropylene–Nitrile Butadiene Rubber Blends
Transition-Metal Compatibilization of Polymer Blends
Development of Optical Fiber/Polymer Interface for Immobilized Sensors
Characterization of Multilayered Automotive Paint Systems Including Depth Profiling and Interface Analysis
Index 30

INTRODUCTION TO INTERFACIAL ASPECTS OF MULTICOMPONENT POLYMER MATERIALS

L. H. Sperling

Polymer Interfaces Center Center for Polymer Science and Engineering Materials Research Center Department of Chemical Engineering Department of Materials Science and Engineering Lehigh University Bethlehem, PA 18015-3194

ABSTRACT

This chapter introduces the interfacial aspects of multicomponent polymer materials, exploring the instruments used, the thickness of the interphases formed, and some of the more interesting results. Five kinds of surfaces and interfaces found in these materials are defined. The properties of silane coupling agents are explored. As an example of the state of the art, recent patents and literature in the field of latex blends are summarized.

INTRODUCTION

The purpose of this chapter is to provide an introduction to the interfacial aspects of multicomponent polymer materials. The basic concepts, instruments, and types of results will be summarized, along with the current status of the field. Some of the key issues and questions will also be raised. The papers that follow, based on the American Chemical Society symposium in Orlando, Florida, held under the auspices of the Polymeric Materials Science and Engineering Division, August, 1996, will delineate recent major research advances in the field.

All real materials have surfaces or interfaces. This simple statement arises from a consideration of the finite size of objects. When people speak of polymer materials, there are five basic classes of surfaces and interfaces(1):

1. A *surface*, referring to that portion of the material commonly exposed to air, that people can see and touch. Strictly speaking a surface, or *free* surface, refers only to a part of a clean, pure material exposed to a vacuum. However, in reality, such surfaces may be

oxidized, oily, or dirty, see Figure 1.

2. A dilute polymer solution-colloid interface, where polymer chains in dilute solution are partly adsorbed onto surfaces, usually colloidal. A single polymer chain may be adsorbed or bound at a number of sites, the remaining mers sticking out into the solution. Fleer, et al.(2) delineate the bonding and other characteristics of such polymer chains. Here, a portion of a chain lying on a solid (colloidal) surface is called a train. Several trains may be separated by portions of polymer sticking into the solution, called loops. The chain ends, which generally also stick out into the solution, are called tails.

While the two items above are not considered in detail in this edited work, there is a great deal of information to be learned from such systems. These systems are somewhat simpler than the blend and composite interfaces described below, and have been easier to treat both theoretically and experimentally.

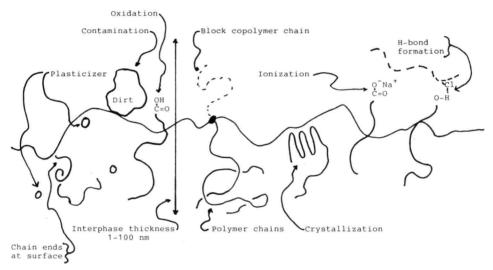


Figure 1. Characteristic features of (a) polymer surfaces, left side, and (b) polymer interfaces, right side.

- 3. A symmetric interface, where two identical polymers are in contact, forming the interface. The healing and fracture of such symmetric polymer interfaces has been treated by Kausch(3) and Wool(4). This interface involves the contact of two melt surfaces, and is important in welding during molding operations, and in latex film formation. The interface heals with time, and disappears, as the chains on both sides intermingle via reptation motions. This interface problem, although extremely important, also will not be emphasized in this book.
- 4. An asymmetric polymer interface, involving two different polymers, Figure 1. The interface may remain indefinitely if the two polymers are immiscible with each other. Important here are the molecular weights of the two polymers, and their capability of forming entanglements with each other. Interpenetration at the interface usually ranges from a depth of a few to several nanometers, depending on how positive the free energy of mixing is. Important factors include the statistical segment length and χ_1 . When the interface is broad, forming entanglements, the term *interphase* is commonly used. This interphase may have physical properties distinctly different from either polymer. The interphase may also contain chemical or physical bonds uniting the two surfaces, such as block or graft copolymers, or hydrogen bonds. There is growing evidence that chain ends

tend to segregate to an interface or surface. However, the excess concentration of chain ends over that in the bulk is small. Figures 2 and 3 illustrate the more common types of interphase phenomena, especially those contributing toward compatibilizing the blend.

5. A composite interface between a polymer and a non-polymer solid phase. Examples include glass fiber reinforced plastics, or calcium carbonate filled materials. Polymers are generally unable to interdiffuse into the contacting surface, but may adhere to it via a variety of chemical and physical bonds. By analogy with the dilute solution-colloid type of interface, in the absence of special bonding modes, it would seem logical that the central portion of the chain tends to form trains, lying on the composite interface, while the tails tend to penetrate into the bulk polymer. Investigations on this point have tended to emphasize theory(5), and are just beginning to understand the actual conformation of the chains. In addition, there is some theoretical evidence that in the lack of bonding or other attractive forces, both asymmetrical polymer blend interfaces and composite interfaces may have lower than expected densities(6), Figure 4, as the phases actually repel one another. This last may arise from positive heats of mixing of the two polymers in blends, or loss of entropy in flattening polymer chains in composite surfaces. Important problems today include an understanding of the fracture toughness of composites, see Figure 5.

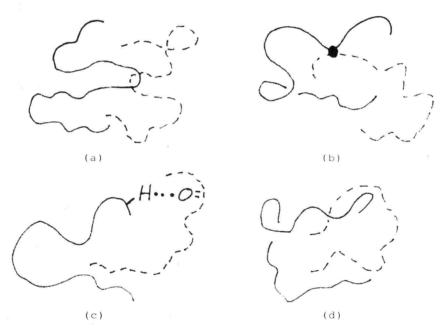


Figure 2. Four major types of phenomena frequently noted at polymer blend interfaces. (a) An entanglement between two chains. (b) A covalent bond, forming a graft copolymer. (c) A hydrogen bond, tending to increase miscibility. (d) Interphase chain conformation. The chain ends tend to interpenetrate, while the center portion tends to orient parallel to the interphase.

Asymmetric polymer blend interfaces and polymer composite types of interfaces will be the subject of the greater portion of this book. Important issues throughout include the effects of molecular weight, entanglement, conformation of the polymer chain near the interface, kinetics of interdiffusion, thermodynamics of miscibility, and bonding capabilities. While the book is not centered on adhesion *per se*, the reader will recognize many aspects of adhesion throughout.

INSTRUMENTAL METHODS FOR POLYMER SURFACES AND INTERFACES

Today, there are a number of ways of measuring surface and interface properties; some of the instruments have been developed only in the last few years. Some of the older, but still very important methods for measuring surface properties include surface tensions and contact angles, and related phenomena will not be discussed here, as they are discussed in detail by Adamson(7) as well as other authors.

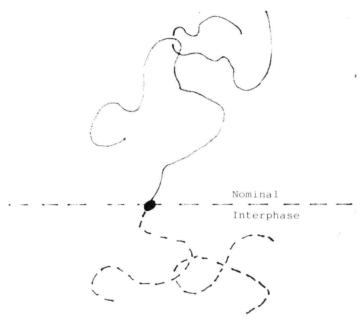


Figure 3. A molecular weight for each block in a block copolymer above a critical molecular weight is required for maximum reinforcement and toughness. Thus, entanglement takes place on both sides of the nominal interphase.

X-ray photoelectron spectroscopy, XPS, sometimes known as electron spectroscopy for chemical analysis, ESCA, measures the electron binding energies of the various elements within 5 nm or so from the surface. ESCA is also sensitive to bonding even when the chemical composition is the same. Since the binding energies differ from one bonding type to another, XPS is sensitive to the chemical environment(8,9). XPS is extremely valuable for identifying chemical structures at surfaces. An important requirement for XPS is that the polymer to be identified have at least one atom different from the atoms of the other polymer(s). Thus, polymers bearing oxygen, sulfur, silicon, or halogen can be quantitatively identified on surfaces in the presence of polymers lacking these atoms. For example, one polymer in a polymer blend may tend to rise to the surface, increasing that components percentage locally, as will be discussed further below. Another example is in the study of the fracture path in polymers. If a polymer blend (or similar) is fractured, does the fracture go through the interphase, termed adhesive fracture, or does it go behind the interphase, through one polymer or the other, termed cohesive fracture, or is it some combination of these features, with the crack wandering(10)?

Atomic force microscopy, AFM, makes use of an atomically sharp tip, usually made of diamond or silicon nitride, drawn across a surface. It is kept in contact by a very soft

spring. The AFM then records contours of constant force to the repulsion generated by the overlap of the electron clouds of the STM tip and those of the surface atoms. Polymeric structures can be resolved to nanometer levels. Figure 6(11) shows the stress-whitened zone of a fractured rubber toughened epoxy. In this particular sample, core-shell latexes were used as the rubber, with SBR as the core and a poly(methyl methacrylate-stat-acrylonitrile) copolymer as the shell. The epoxy itself was based on DER 331 from Dow Chemical, cured with piperidine. The epoxy contained 10 vol-% of the latex. Noting the troughs of particles in Figure 6, the AFM scan strongly suggests cooperative cavitation as the major mode of toughening by the rubber.

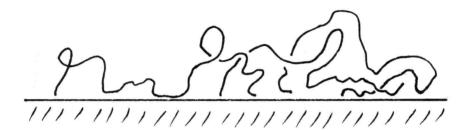


Figure 4. Polymer chain conformation at a wall, modeling a composite system where the chains are not bonded or strongly attracted to the wall surface. Note entropic depletion at the wall.

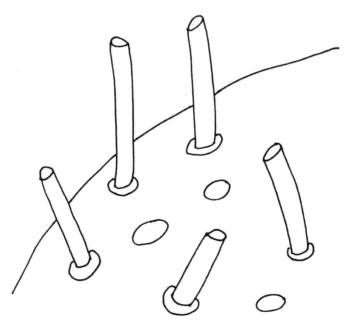


Figure 5. Schematic of fractured fiber composite interface. In general, the fibers break below the surface of the growing crack and pull out, leaving both stubble and holes. Proper bonding between the polymer and the fiber increases the fracture energy of the system significantly.

Transmission electron microscopy, TEM, is in wide use for studies of the interior of polymer blend materials. TEM works by having electrons pass through the sample. Those regions of space with higher density of electrons scatter and/or absorb more electrons per unit volume than less dense regions, creating dark and light regions in the image. Samples can be sectioned down to about 600 Å. For those materials with double bonds, osmium tetroxide makes a wonderful staining agent, although it sometimes over-stains a sample. There are a number of heavy-atom introduction schemes, depending on the chemistry of the polymers involved. TEM is useful in studying the morphology of polymer blends (not necessarily an interface problem, per se), the structure of crazes and craze propagation, cavitation, and shear band formation. Since a major reason why people are so interested in polymer blends is the synthesis of rubber-toughened plastics, TEM plays a major role in many research laboratories.

For the study of the interior of polymer blend and composite samples directly, small-angle neutron scattering, SANS, or small-angle x-ray scattering, SAXS, can be used. Debye, et al. (12) derived the basic theory for SAXS, which can be carried over to SANS with the knowledge that the scattering is nucleus based, rather than electron based. Debye, et al. assumed a randomly structured material, in which a correlation function in exponential form provides the probability of striking a surface at an arbitrary distance from another such point,

$$\gamma(r) = \exp(\frac{-r}{a}) \tag{1}$$

where $\gamma(r)$ is the correlation function for a characteristic distance r between scattering centers, and the quantity a is the correlation distance defining the size of the heterogeneities. The specific surface area, S_{sp} , is defined as the ratio of interfacial surface area, A to the volume,

$$S_{sp} = \frac{4\phi(1-\phi)}{ad} \tag{2}$$

where ϕ is the volume fraction of either phase, and d is the density.

The theory calls for a plot of the excess scattered intensity to the minus one-half power vs. k^2 , where $k = 4\pi\lambda^{-1}\sin(\theta/2)$, where λ is the wavelength, and θ represents the scattering angle. The quantity a can be determined from

$$a = (\frac{\lambda}{2\pi})(\frac{slope}{intercept})^{1/2} \tag{3}$$

The same theory can also be cast in terms of the transverse lengths across the domains, L_1 and L_2 ,

$$L_1 = a/\phi_2, L_2 = a/\phi_1$$
 (4)

Specific surface areas of the order of 50-300 m²/gm are common for polymer blends and composites.

Of course, there is much more information that can be obtained from small-angle scattering, both SANS and SAXS. Often, there are maxima in the scattering curve. In general, the angle of the maxima provides information about the interdomain spacing. The breadth of the peak gives information about the size distribution of the phases. The shape of the tail region yields information about the thickness of the diffuse boundary between

phases, i.e., information about the interphase thickness(13,14,15). For this last, a plot of Is^4 vs. s, where I represents the scattering intensity and $s = 2(sin\theta')/\lambda$, where θ' is half of the full scattering angle is referred to as a Porod law plot. For an ideal two phase system with sharp phase boundaries, the product Is^4 should reach a constant value at high enough s vales. This approach can be used to determine the non-ideal nature of experimental two-phased systems. Positive deviations from Porod's law, i.e., a positive slope in a plot of Is^4 vs. s, can be attributed to thermal density fluctuations or to phase mixing. On the other hand, the presence of interphase material between the two phases results in negative deviations. This provides a fairly sensitive means of determining the interfacial width between phases.

Neutron reflection is one of the newest methods of determining surface and interfacial characteristics of multicomponent polymer materials(16). The method uses systematic differences in the neutron equivalent of refractive index, with is the scattering length. One of the largest differences in scattering lengths is that between the proton and deuteron isotopes, also one of the easiest combinations for the polymer scientist to use. By selective deuteration, the spatial distribution of the different portions of materials can be determined to greater than 1000Å below the surface(17). For example, the layering behavior of diblock copolymers in thin films can be studied in this manner(17).

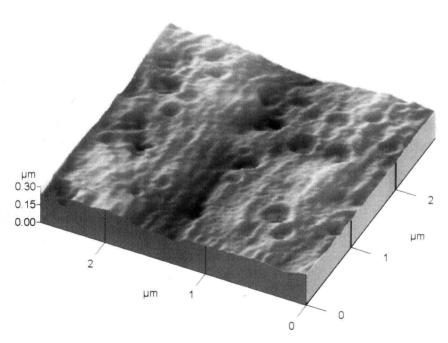


Figure 6. Atomic force microscopy scan of the stress-whitened zone of a rubber-toughened epoxy. The trough of particles down the middle suggests cooperative cavitation. The remains of the rubber core of the particles can be seen inside the craters.

Solid state NMR can be used to determine interphase thickness and morphological details in such materials as polymer blends and core-shell latex particles(18,19). The method used combinations of 1H spin-diffusion, 2-D wideline separation (WISE), cross polarization, high power proton decoupling, and magic angle spinning (CPMAS-NMR), etc., to determine morphological characteristics. Of particular interest, the method makes use of ordinary diffusion kinetics, where the mean-square distance, $< x^2 >$, of the magnetization moves with time, going as $< x^2 > = aDt$, where D represents the spin-diffusion coefficient, and the quantity a depends on the geometry of the packing. Distances across small domains, as well as extent of mixing can be estimated. The experiments are often done in conjunction with TEM, the NMR providing details at very short distances, with the TEM providing the overall morphology. The method is particularly effective in characterizing interphase compositions, especially those where rigid and mobile polymers are in contact.

POLYMER BLEND INTERPHASE THICKNESSES

According to Helfand and Tagami(6), the interphase surface thickness is given by

$$S_{th} = \frac{2b}{(6\chi_{12})^{1/2}} \tag{5}$$

where b is the effective length of a mer, and $\chi_{1,2}$ is the Flory-Huggins interaction parameter. Similarly, the interfacial tension is given by

$$\gamma_{1,2} = (\frac{\chi_{1,2}}{6})^{1/2}bkT \tag{6}$$

For example, the experimental interfacial tension of the polystyrene-blend-poly(methyl methacrylate) pair was found to be 1.5 erg/cm²(20), while the theoretical value is 1.0 erg/cm²(6), values much smaller than their surface tension values. The $\chi_{1,2}$ value for this system is 0.01. The interfacial surface thickness, according to equation (5), is about 50 Å for the polystyrene-blend-poly(methyl methacrylate) pair.

THERMODYNAMICS OF PHASE SEPARATION

By definition, all of the materials to be considered in this book are phase separated; otherwise they would not have interfaces. However, thermodynamics of mixing and demixing plays a critical role in several aspects of the problem. For example, the value of $\chi_{1,2}$, above, is useful in predicting the interphase thickness.

There are three basic thermodynamic theories of mixing: The classical theory, as summarized by Hildebrand and Scott(21), the statistical theory, first developed by Flory(22), and further developed by Scott(23), and Krause(24), and the equation of state theory, first developed also by Flory(25), and further developed by Patterson(26) and by Sanchez(27).

Greatly oversimplifying the theories, the classical theory relies on such concepts as heats of mixing and phase transitions, making few assumptions about the size, shape, and relative positions of the molecules. The free energy of mixing in the classical theory can be expressed.

where ΔG_M is the change in Gibbs' free energy on mixing, ΔH_M is the enthalpy of mixing, and $T\Delta S_M$ represents the absolute temperature times the entropy of mixing.

The statistical theory puts all of the molecules on a lattice, counting the number of molecular arrangements in space to determine the entropy of mixing. Most importantly, this theory assumes incompressibility of the system, ie, no mer sized holes are allowed in the lattice. This important assumption is removed by the equation of state theories, the total volume of the system being a variable. The equation of state theory is the only one of the three theories that predicts a lower critical solution temperature for polymer blends, the type of phase diagram actually observed in most cases. This means that the two polymers will mutually dissolve at low temperatures, and phase separate at some higher temperature.

KINETICS OF PHASE SEPARATION

Phase separation from a homogeneous solution can take place by two main mechanisms: nucleation and growth, NG, and spinodal decomposition, SD(28,29). These occur in different parts of the phase diagram, as illustrated in Figure 7. Greatly oversimplifying, NG results in roughly spherical domains of the minor component nucleating which grow with time. The concentration of this phase does not change with time. In the case of spinodal decomposition, the mixture is placed in an unstable state by a rapid change in temperature or pressure. Concentration fluctuations of a given wavelength grow in amplitude with time and eventually saturate. the morphology at early times is interconnected and bicontinuous. Since the shape of the domains during phase separation controls the interfacial area and several other factors, part of the temperature-composition space of phase separation may be denied to a given final morphology.

In composite systems, of course, neither the kinetics or thermodynamics of phase separation usually play important roles, since the inorganics in use in almost all cases are insoluble in the polymer, and vice versa. However, attractive and repulsive forces are still highly important, as delineated above.

In block copolymers, assuming a regular repeating structure of the chain, the phase morphology is controlled by the composition ratio of the blocks composing the material. Phase morphology may be spherical, cylindrical, alternating lamellae, double diamond, and occasionally other types of morphology, especially where three or more different blocks are on the same chain(30).

The type of classical phase diagram illustrated in Figure 7 cannot exist for block copolymers, because if the block length is kept constant, the overall composition cannot be varied independently. Instead, people talk about the order-disorder transition, ODT, sometimes called the microphase separation transition, MST to describe the phase relationships(31).

Both the polymer blends and block copolymers described above are all amorphous systems. Of course, both polymer blends and blocks can be crystalline. However, the phase morphology is more complex, and so are the interphase relationships. Also, in addition to the interphase structure between the two polymers, there is another interphase to consider, that between the crystalline and amorphous portions of the same kind of chain(32,33). Another case that needs consideration: Does phase separation take place in the melt first, or does crystallization of one or both of the components take place first, before phase separation? In all of these cases, one would expect the structure and