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Physical, Thermophysical and Interfacial Properties of Multiphase Polymer Systems: State of the Art, New Challenges and Opportunities

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1.1 Introduction

Multicomponent polymer systems find a wide range of applications in each and every phase of our day-to-day life. Continued research has resulted in the development of super performing macro-, micro- and nanostructured polymeric materials. The new emerging fields of micro- and nano-composites have put forward many challenging opportunities for the use of these smart materials. Polymer physicists, chemists, engineers and technologists show great interest in new strategies for developing high-performance multicomponent systems. Recently, polymer nanostructured multiphase systems have gained much interest due to their unique properties. Characterization of the interphase, physical properties and thermophysical properties are crucial for the understanding of the behavior of these smart materials. A comprehensive understanding of these materials is vital for the industrial use of these materials.

The main objective of this book is to present a survey of recent advances in the area of multiphase polymer systems covering physical, interfacial and thermophysical properties of these materials. After a short presentation of the different existing multiphase polymer systems, followed by a survey of actual scientific production and of application fields for these materials, we present some of the recent developments in the

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area of multicomponent polymer systems that will be highlighted all through the book. The chapter ends with a summary of unresolved issues, perspectives and new challenges for the future.

1.2 Multiphase Polymer Systems

Multiphase polymer systems are characterized by the simultaneous presence of several phases, the two-phase system being the simplest case. Many of the materials described by the term multiphase are two-phase systems that may show a multitude of finely dispersed phase domains. The term 'two-component' is sometimes used to describe flows in which the phases consist of different chemical substances. Multiphase polymer systems in general include polymer blends, composites, nanocomposites, interpenetrating polymer networks (IPNs), and polymer gels.

1.2.1 Polymer Blends

Polymer blends can be considered as a macroscopically homogeneous mixture of two or more polymeric species with synergistic properties. In most cases, blends are homogenous on scales larger than several times the wavelength of visible light. Blends may be either compatible or incompatible. Polymer blends can be broadly divided into three categories: miscible, partially miscible and immiscible blends. A miscible polymer blend is capable of forming a single phase over certain ranges of temperature, pressure, and composition; also it can be thermodynamically stable or metastable, exhibits a single Tg or optical clarity. An immiscible polymer blend means a multiphase system. Although polymer blending is a very attractive way to obtain new materials, most polymers are immiscible and/or incompatible. Reasons for incompatibility are high interfacial tension and poor interfacial adhesion. In general, a miscible blend of two polymers is going to have properties somewhere between those of the two unblended polymers. Whether or not a single phase exists depends on the chemical structure, molar mass distribution and molecular architecture of the components present. The single phase in a mixture may be confirmed by light scattering, X-ray scattering and neutron scattering. Typical dispersed phase morphology of polymer blend is given in Figure 1.1 [1].

1.2.2 Polymer Composites

Generally a composite is defined as a multi-component material comprising multiple different (nongaseous) phase domains in which at least one type of phase domain is a continuous phase. In polymer composites, at least one component is a polymer. Fillers such as fibers, particulate fillers, wood fibers, glass fibers and minerals are used as reinforcements in polymeric matrices.

1.2.3 Polymer Nanocomposites

A nanocomposite is a composite in which at least one of the phases has at least one dimension of the order of nanometers, or structures having nano-scale repeat distances between the different phases that make up the material. Polymeric nanocomposites prepared from high aspect ratio fillers such as carbon nanotubes, layered graphite nanofillers etc. achieve significant improvements in mechanical and electrical properties at low filler concentrations, compared to conventional composites [2, 3], without a significant increase in density (see Figure 1.2). The polymer nanocomposites could be prepared by solution mixing process, in situ intercalation process, latex compounding techniques, and melt mixing techniques (see Figure 1.3). In the case of layered clay nanocomposites, one can achieve different types of morphologies as shown in Figure 1.4.

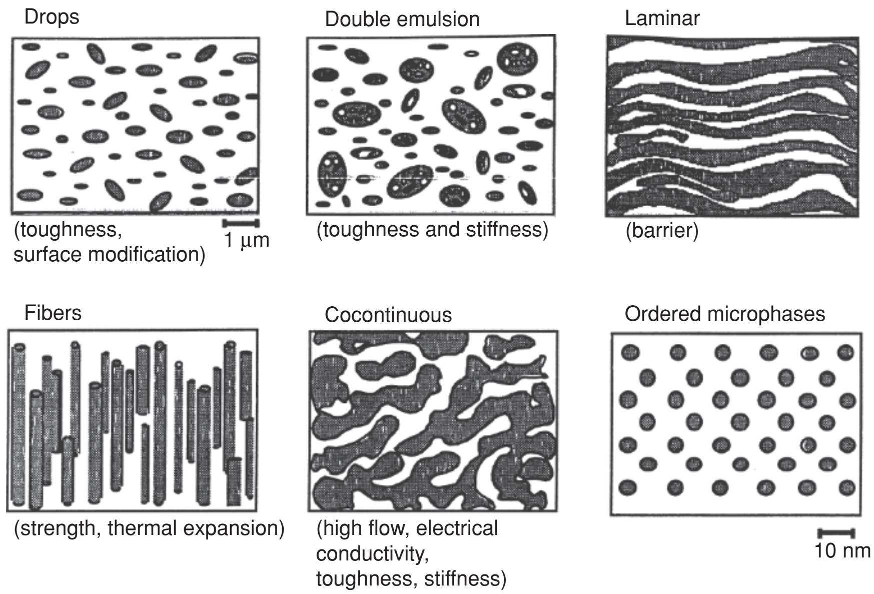

Figure 1.1 *Dispersed phase morphology of polymer blends. Reprinted from [1]. Copyright (2000) with permission from John Wiley and Sons.*

1.2.4 Polymer Gels

Polymer gels consist of a crosslinked polymer network inflated with a solvent such as water. They have the ability to reversibly swell or shrink (up to 1000 times in volume) due to small changes in their environment (pH, temperature, electric field). The swelling behavior of gels is presented in Figure 1.5.

1.2.5 Interpenetrating Polymer Network System (IPNs)

An interpenetrating polymer network (IPN) is a polymer comprising two or more networks which are at least partially interlaced on a polymer scale but not covalently bonded to each other. The network cannot be separated unless chemical bonds are broken. The two or more networks can be envisioned to be entangled in such a way that they are concatenated and cannot be pulled apart, but not bonded to each other by any chemical bond. There are semi-interpenetrating polymer networks and pseudo-interpenetrating polymer

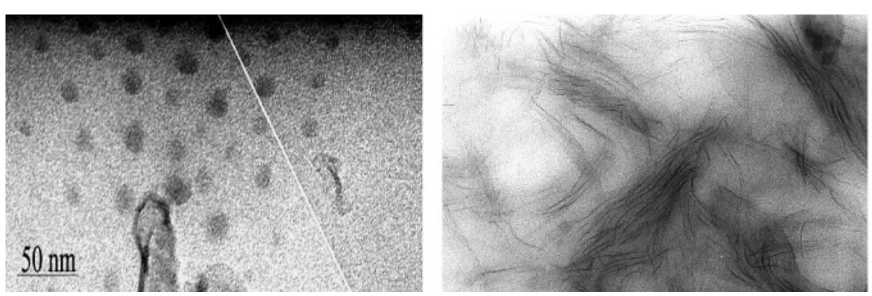

Figure 1.2 *Typical morphology of nanocomposites.*

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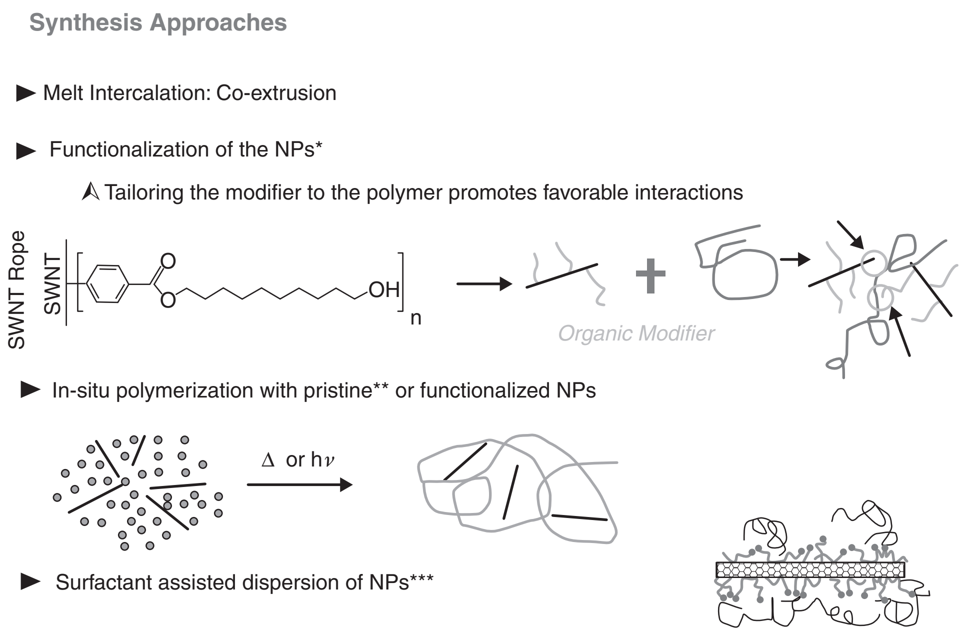

Figure 1.3 Synthesis approach to polymer nanocomposites.

networks. A polymer comprising one or more polymer network(s) and one or more linear or branched polymer(s) is characterized by the penetration on a molecular scale of at least one of the networks by at least some of the linear or branched chains. Semi-interpenetrating polymer networks (SIPNs) may be further described by the process by which they are synthesized. These include sequential SIPNs, simultaneous SIPNs, pseudo-interpenetrating networks, etc. A SIPN is prepared by a process in which the second component

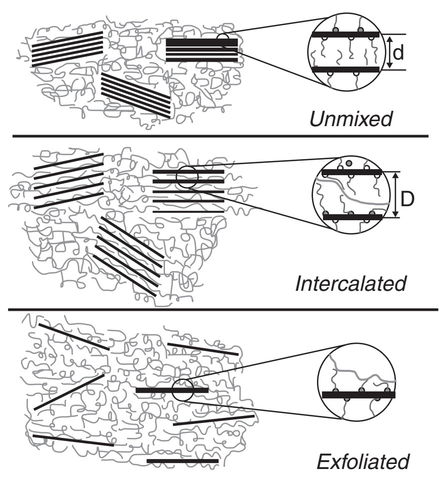

Figure 1.4 Exfoliation and intercalation of clay nanocomposites.

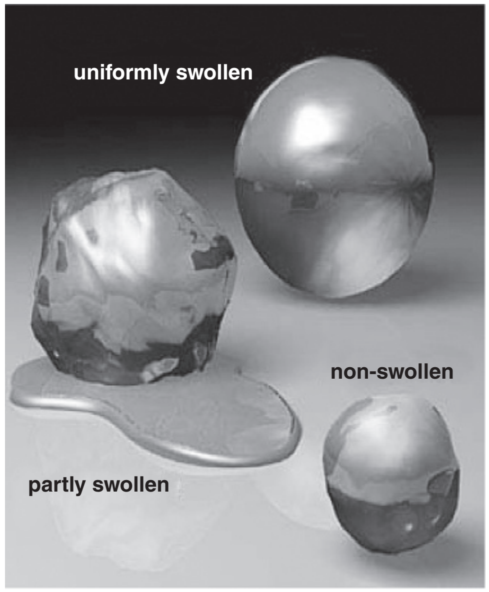

Figure 1.5 *Behavior of gels: Uniformly swollen, partly swollen and non-swollen gels.*

polymer is polymerized or incorporated following the completion of polymerization of the first component polymer, and thus may be referred to as a sequential SIPN. When an SIPN is prepared by a process in which both component polymers are polymerized concurrently, it may be referred to as a simultaneous SIPN. Pseudo-interpenetrating network systems seem to have interpenetrating networks, but actually do not.

1.3 A Short Survey of the Literature and Applications

The 20th century saw great progress in the development and use of polymers and polymer composites; today's broad family of tailor-made materials allows us to realize the latest technological applications; and the future will see polymers used in increasingly innovative ways. Polymers' and polymer composites' almost infinite flexibility and affordability mean that only the imagination of designers limits the ways they can be used. Plastics truly deserve the mantle of material of choice for the 21st century. Just as importantly, polymers' efficiency allows them to make a real contribution to the vital goals of development for several areas in the world. The growth in these polymeric materials continues to outstrip average annual growth in GDP, and this trend looks set to continue [4].

Demand for polymers in all sectors was up in 2000, continuing the growth trend, and with no significant changes in the relative consumption patterns. Unsurprisingly, the Electrical & Electronic sector shows the highest growth, with countless new inventions and applications using polymers and polymer composites materials as an integral material. However, packaging is still the largest user of plastics, representing about 37% of all other sectors in Europe for 2000. The building and construction industry accounted in 2000 about 19% of total consumption as presented in Figure 1.6 and remains one of the main largest users. The applications in the automotive and electrical & electronics sector are also important and increase year after year.

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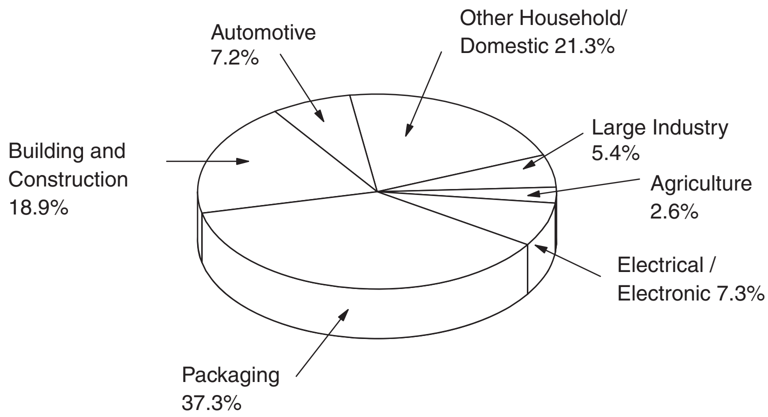

Figure 1.6 *Plastics consumption by industry sector Western Europe 2000.*

If we look at the numbers of scientific work published (using the data base ISI Web of Knowledge®) by each country in the last decade with outputs 'Polymers' with 'Blends', or 'Gels', or 'Nanocomposites' or 'Polymer Composites' we can clearly see in Figure 1.7 that the USA is the leader followed by Asian countries. It is also important to notice that in Western Europe the number of scientific works dedicated to polymers and polymer composites is also important and was the third source of publications in the world.

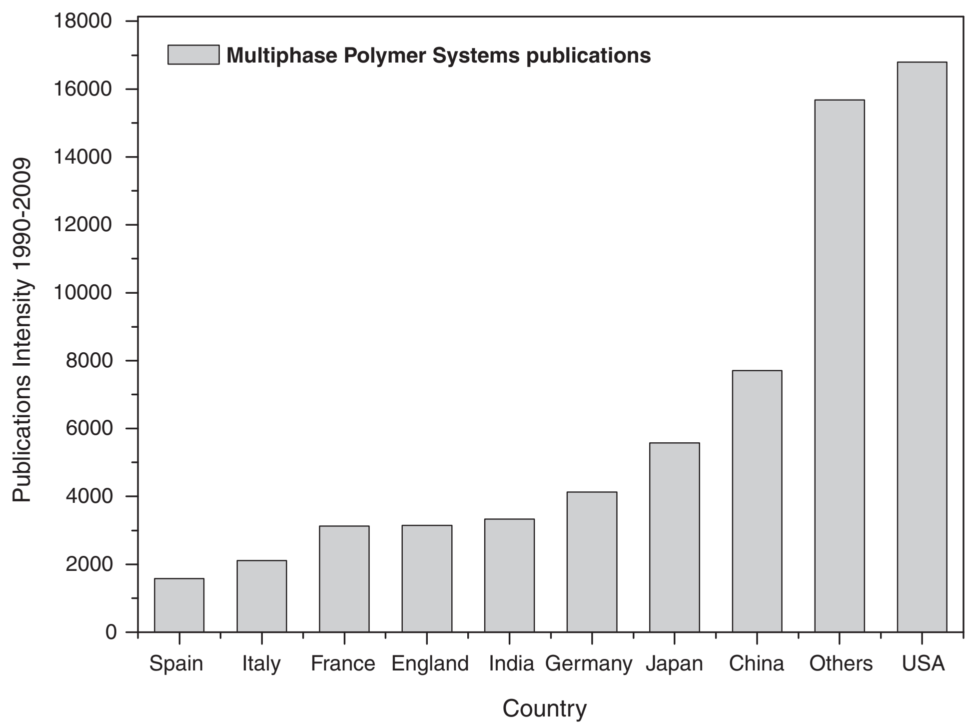

Figure 1.7 *Publications intensity in main country on polymers, blends, gels, nano- and macrocomposites between 1990 and 2009.*

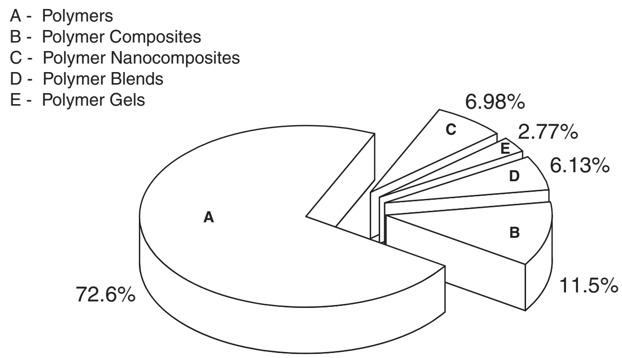

Figure 1.8 *Publications area between 2004 and 2009.*

However, it remains that during the last five years (2004–2009) over 72% of the scientific works were dedicated to polymers (Figure 1.8). Polymer composites and polymer nanocomposites materials and blends represent respectively 11.5%, 8% and about 6% of publications, the rest relating to gels.

1.4 Book Content

This book is intended to deal with most aspects of multiphase polymer systems science. Four transversal main aspects are considered:

1. The modeling of multiphase polymer systems, including theoretical and numerical simulation approaches.
2. The morphological investigation techniques that allow information on the microstructure of these complex systems to be obtained.
3. The physical characterization at macroscopic scale which also brings information on the structure of the material but mainly determines whether the material properties are compatible with its application and use.
4. The life cycling of multiphase polymer systems covering all the steps between the manufacturing process and the recycling.

1.4.1 Modeling and Computer Simulation of Multiphase Composites: From Nanoscale to Macroscale Properties

Predicting the behavior of multiphase polymer composites is an area with vast potential applications, and has attracted a lot of academic work. Chapters 2, 3 and 4 present the state-of-the-art as well as recent applications.

The theoretical approach originates with the Flory-Huggins theory and gives rise to modern powerful predictive methods such as the self-consistent field theory (SCF), which has been applied to the calculation of phase diagrams for diblock copolymer blends, or the study of interfacial properties in binary blends [5, 6]. In Chapter 2 the viscoelastic behavior of polymer nanocomposites in the liquid phase is investigated with recent mesoscale models (sticky reptation model) and the results are quantitatively compared to experiment.

The simulation approach is more recent but recent advances make it a very promising field.

Modeling can be on the microscale (atomistic), the mesoscale (coarse-grain) or macroscale (continuum)

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Recent work focuses on multi-scale modeling in a ‘bottom-up’ approach where properties obtained at a scale are reused on the larger scale, giving these methods real predictive power.

Coarse-grain models and field models are reviewed in detail; dynamical as well as static properties can be investigated with these models. These methods have been applied to miscibility of copolymer blends, or the dynamics of demixing in homopolymer blends.

The behavior of polymer multiphase composites is largely influenced by interfacial properties. Chapter 4 proposes a review of interphase properties, interface modification techniques and interface analysis techniques. Mastering the effects of interface properties is a challenge both for modeling and for manufacturing developments [7, 8].

Another important factor in understanding and mastering macroproperties of immiscible polymer composites is morphology (Chapter 6). Two important factors are analyzed in detail: evolution during processing, and component individual properties. Morphology development can be influenced by compatibilization techniques which modify interfacial properties.

1.4.2 Morphological Investigation Techniques

Morphological characterization of the multiphase polymer system is extremely important since most of the physical and transport properties (mechanical, electrical, thermal) of polymer systems are determined by the scale of dispersion of the component phases.

The length scale (macro, micro and nano) of the dispersion could be monitored by optical light microscopy (phase contrast, polarized), electron microscopy (SEM, TEM), scanning tunneling microscopy, and atomic force microscopy (AFM).

Scattering techniques are also very useful for this; they include light scattering, X-ray scattering (SAXS and WAXS) and neutron scattering techniques.

TEM, AFM, SAXS and SANS techniques can also be of interest in the investigation of the interphase/interface of multiphase polymer systems. Several researchers have looked carefully into the interphase/interface width of several multiphase systems using these techniques.

Spectroscopy is a valuable technique to characterize multiphase polymer systems. These include UV (ultraviolet) spectroscopy, FTIR (Fourier transform infrared spectroscopy), NMR (nuclear magnetic spectroscopy), XPS (X-ray photoelectron spectroscopy), ESR (electron spin resonance spectroscopy). Each technique varies in its sensitivity. For example, NMR spectroscopy and fluorescence spectroscopy can detect heterogeneities in the range of 2–3 nm scale. NMR can generate a lot of information in the nanoscale on the interphase/interface of multiphase polymer systems. XPS can be used for the study of surface chemistry of polymer grafts, colloidal particles, nanocomposites etc, in the nanometer range.

1.4.3 Macroscopic Physical Characterization

Physical properties of polymers and multicomponents systems based on the use of polymers are more strongly dependent on temperature than for other materials such as metals or ceramics. Moreover, the temperature range of use of these systems is thus reduced when compared to other materials. Physical properties of multiphase polymer systems are also closely related to the components’ properties and relative fractions. The structure of the material – for instance the shape, size, dispersion, possible orientation of the dispersed phase – greatly influences macroscopic properties. For instance, crystallization and melting temperatures of nanocomposites are strongly related to the filler content and its dispersion state whereas the thermal expansion coefficient is strongly affected by the alignment of exfoliated platelets as small changes from perfect planar orientation result in significant changes in thermal expansion behavior.

The properties of interest are of two types: bulk properties and phase-transition properties. The bulk properties are mechanical properties, thermophysical properties, electrical properties or permeability. The two main phase-transition properties concern first-order transitions (fusion and crystallization) and the glass transition. All these properties are now accessible thanks to recent progress in experimental techniques that allow measurements in the three physical states over extended ranges of temperature and pressure, including in the vicinity of the critical point (at least in the case of gases and liquids). The possibility of achieving a complete and reliable characterization of multiphase polymer systems is also one reason for the recent and increasing use of these materials. The knowledge of these properties is important for the development of new systems with properties adapted to one particular application, and also for obtaining information on the microstructure of the material. Thus, macroscopic characterization of multiphase polymer systems is important for engineers in industry and for researchers in the field of material science.

Thermophysical properties are important in industry for the knowledge of thermal transport properties and thermal stability of materials. They include thermal conductivity and diffusivity, specific heat, melting and crystallization temperature and enthalpies, coefficient of thermal expansion. Thermal analysis techniques allow information to be obtained on the structure of polymers and multi-components systems and on their phase transitions. Optical techniques allow, for instance, the characterization of the organization of crystalline regions in polymers. Differential Scanning Calorimetry (DSC) is a powerful method for the study of phase transition and for the measurement of specific heat capacity; the recent development of Modulated DSC and the enhanced specifications of recent DSC and MDSC devices have also increased the investigation field of this technique. Chapter 9 will extensively present a survey of thermal analysis applied to the characterization of multi-phase polymer systems. Chapter 10 is devoted to the study of thermophysical properties of multiphase polymer systems (characterization methods, thermophysical behavior, and modeling) [9].

Mechanical behavior is of paramount importance in the design of advanced multiphase polymer materials for many applications in different engineering fields such as aerospace and the automotive industry or civil engineering. The stress–strain behavior, tensile strength, yield strength, elongation at break, hardness, impact behaviors (both notched and unnotched), tear properties, abrasion characteristics and flexural properties are very often determined for the comprehensive understanding of the behavior of multiphase polymer systems. Dynamic mechanical properties are also extremely important for the time-dependent dynamic applications of multiphase polymer systems. Materials reduced to nano-scale can suddenly show very different properties compared to what they exhibit in the macro-scale, enabling unique applications

The rheological behavior of multiphase polymer systems is of great importance for the understanding of the flow behavior of these materials. Viscosity-shear rate relationships are fundamental basic data to evaluate the processability of these materials. Although multiphase polymer systems are pseudoplastic, they might show complex behavior such as Newtonian character, yield stress, thixotropic and rheopectic characteristics. Additionally, phase separation, gelation and vitrification can be very well monitored using sensitive rotation rheometers. Very often, rubber modified thermoplastics and other polymer/polymer blend systems show structure build-up at low shear which eventually get destroyed at higher shear forces. The exfoliation/intercalation in polymer nanocomposites could be well understood by careful rheological measurements. Chapters 7 and 8 will be devoted respectively to mechanical characterization and rheology of multiphase polymer systems [10, 11]. The mechanical reinforcement of polymers using nanoparticles will be exposed in Chapter 25.

Most polymers behave like electrical insulators. A lot of works was devoted in the last 20 years to the development of highly-conducting polymer systems. Different ways were investigated: synthesis of conducting polymers (such as polypyrrole), mixing of common polymers with metal powders, graphite or, more recently, carbone nanotubes to obtain conducting composites. The challenge is to reach electrical conductivity values minimizing the amount of conducting material mixed with the polymer. The use of conducting nanoparticles as filler in a polymeric matrix is the most efficient solution as very small electrical percolation thresholds are observed in these systems. The study of the electrical behavior of insulating

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polymer systems requires the use of characterization techniques specific to dielectric materials, such as broadband dielectric spectroscopy or thermostimulated depolarization currents. Electrical signals obtained by these techniques are the signature of macromolecular chain movements or of interface effects. The large frequency and temperature ranges covered by these techniques allow a lot of information to be obtained on the microstructure of multiphase polymer systems. Chapter 11 will present a synthesis of literature results concerning the development of conductive polymer systems and of the associated characterization techniques and most commonly used models. Dielectric properties will be investigated in Chapter 12 [12].

Diffusion and transport in multiphase polymer systems have attracted a lot of interest recently (Chapter 19). This is due to the fact that multicomponent polymer systems find enormous application in separation technologies, including dialysis, restricted gas transport, pervaporation, gas sorption and vapor sorption. Several factors such as microstructure, dispersion, miscibility, compatibility, interphase adhesion, degree of crosslinking, orientation of the filler particles, phase co-continuity and so on influence the transport process in multiphase polymer systems. Additionally, diffusion and transport could be used as an excellent tool to characterize the morphology and microstructure of multiphase polymer systems.

1.4.4 Life Cycling

Nowadays, the field of applications of multiphase polymer systems is very broad (civil engineering and buildings, electronics, medicine, transports, packaging...). Chapter 23 will give a survey of the existing applications of multiphase polymer systems. Moreover, the continuous development of new materials permits new applications, like fire retardancy applications, which are very important in transport and buildings. This particular topic will be investigated in Chapter 22. Nanoreinforcement of plastics leads to the use of small amounts of fillers to obtain a strong increase of mechanical properties (see Chapters 25 and 6) such as the elastic modulus, even if the use of nanoparticules might cause some health problems. Application allows defining shape and size of the manufactured object and components to be used. All these parameters often impose the use of a particular manufacturing technique. These manufacturing techniques, presented in Chapter 5, are numerous. Classical industrial techniques like extrusion and injection are particularly suitable for the processing of multiphase systems based on the use of thermoplastics. The recent development of new techniques like resin transfer molding has brought new applications concerning processing of fiber-reinforced thermoset composites, particularly in the aeronautics and space industries. Finally, the choice of the manufacturing process greatly influences macroscopic properties of the final material (interfaces between components, non-isotropic properties). Therefore, a strong link exists between applications and the manufacturing process. A good knowledge of ageing processes is also required to determine the lifetime of a given object. The study of ageing processes is quite complex as it requires the use of characterization techniques at different length scales and the development of realistic procedures of accelerated ageing (see Chapter 21). Non-destructive testing techniques are of great interest as they can provide an on-line control of the manufactured products and also an early detection of defects, delaminations, etc, during the normal use of a material (see Chapter 20). Recycling of multiphase polymers is a major issue in order to limit the effect of industrial production on the environment. Recycling will be considered in Chapter 24. Possibilities of recycling are mainly dependent on the components used and on the manufacturing process. Thus the possibilities of recycling have to be considered from the beginning of the development of a new material [13].

1.5 Future Outlook, New Challenges and Opportunities

In the area of multiphase polymer systems (blends, composites, nanocomposites, IPNs, gels) several questions still need to be answered. Concerning polymer blends, more sophisticated techniques are needed to probe the

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very early stages of the phase separation process. Although NMR and fluorescence spectroscopy offer some answer to this, we need to have more fast and easy techniques. Similarly for complex systems, we need to look very carefully at the phase separation mechanisms, spinodal or nucleation and growth. There are many complex polymer systems where both mechanisms operate.

In the area of compatibilization of polymer blends by reactive route, we need to go a long way to characterize the chemistry of the interfacial chemical reactions. For many polymer–polymer blends systems compatibilized by the reactive route, the chemistry of several interfacial reactions has to be well understood. In order for this we need to go for selective extraction followed by NMR and FTIR spectroscopies.

Another important challenge in the area of polymer blends is the online monitoring or in situ monitoring of morphology development during processing. Of course some success has been made in this direction using model systems which are transparent. However, for real polymer systems, we need to undertake more in-depth studies. In this respect, knowledge of the thermophysical properties of polymers over extended ranges of temperature and pressures and in different gaseous environments is undoubtedly necessary to improve the use and lifetime of end-products made of such polymers.In the area of recycling of polymer blends wastes and polymer products, several problems exist which are very important for dealing with waste disposal problems. For effective recycling of polymer blend wastes, we need to have multifunctional compatibilizers which can convert a mixture of a variety of polymer blend materials into useful value-added materials for a number of different applications. However, these techniques have to be more environment-friendly.In the area of composites, the incorporation of naturally-derived macro-, micro- and nanofillers such as cellulose, chitin and starch has recently captured a lot of interest. Since these fillers are derived from waste biomass, the process is highly green and environment-friendly. For polymer nanocomposites, one of the biggest challenges is to reach an excellent dispersion of nanoparticles in the polymer matrix. Although nanoclay is a very efficient reinforcing filler in many polar polymer matrices including nylon, so far we have not been able to achieve good dispersion of the nanoclay in polyolefins (PP, PE) which are one of the plastics with the higher tonnage. More efficient surfactants have to be designed for the excellent dispersion of clay in nonpolar polymer systems such as PP, PE, etc. The extent of intercalation versus exfoliation could not be quantified in many nanoclay-filled polymer systems. We need to have more sophisticated techniques for the exact quantification of the exfoliation process. More environment-friendly and efficient mixing techniques have to be developed for the mixing of nanofillers with various polymer matrices. Of course, strong progress has been made in the use of supercritical carbon dioxide for the processing of various polymer nanocomposites. The orientation of nanoplatelets, such as clay, carbon nanotubes and graphite in the polymer matrix is a major challenge. Perfect alignment of the nanoplatelets will provide excellent properties, particularly gas barrier properties. We need to develop special extrusion techniques, application of magnetic and electrical fields for the orientation of the nanoplatelets. The in situ monitoring of the flow of the polymer nanocomposites during manufacturing requires in-depth research. We still have to go a long way for the successful use of polymer nanocomposites for many commercial applications although some progress has been made in this direction. We should also examine carefully the toxicity aspects of many nanofillers and nanocomposite materials; once the nanofillers enter into our body, elimination will be very difficult. Therefore one has to take extreme care during the handling of the nanofillers in mixing and processing operations. The legal and ethical issues of nanostructured materials have to be addressed carefully.

In the area of IPNs, we have made significant progress for the development of nanostructured IPNs. However, the morphology and phase separation mechanisms of nanostructured IPNs have not been well understood. The design of porous networks based on IPNs has received a lot of attention recently. We believe that such porous IPN materials may find potential applications in separation techniques as chromatography supports, as well as membrane catalysis, and more generally in chemistry in confined medium as nanoreactors. However, such new applications have to be explored in detail. There exists much interest for the development of biopolymer-based IPNs for various applications.

In the case of polymer gels, the development of smart polymer gels with optimum mechanical properties for drug delivery offers enormous opportunites in the medical field. Spatial inhomogeneities present in ionic and nonionic hydrogels depend systematically on network density and on the degree of swelling. The precise quantitative estimation of these inhomogeneities needs more sophisticated and careful analysis. Mechanical instabilities such as buckling, wrinkling, creasing, and folding are commonplace in both natural and synthetic gels over a wide range of length scales. Several advancements have been made on the spontaneous folding behavior of the highly swellable confined nanoscale (thickness below 100 nm) gel films [14]. In fact, the regular self-folding is originated from periodic instabilities (wrinkles) caused by swelling-initiated stresses under confined conditions. Furthermore, folded gel structures can be organized into a regular serpentine-like manner by imposing various boundary conditions on micro-imprinted surfaces. It is important to add that this demonstration of uniform gel to mechanically mediate morphogenesis has far-reaching implications in the creation of complex, large-area, 3D gel nanostructures

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