Recent Advances in Polymer Nano- composites

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Preface

There has been enormous interest in the commercialization of nanocomposites for a variety of applications, and several of these will be successful in the near future. Over the last ten years, several different types of polymer nanocomposites have become the dominant class of multicomponent polymer systems. A large number of scientific publications, industrial patents, international conferences, and exhibitions are devoted to this class of materials.

This book mainly focuses on the preparation, properties, characterization, and applications of polymer nanocomposites. The various manufacturing techniques, analysis of morphology, filler dispersion, interfacial interactions, etc. have been described in detail. For nanocomposites, filler dispersion, intercalation/exfoliation, orientation and filler–matrix interaction are the main parameters that determine the physical, thermal, transport, mechanical, and rheological properties of the nanocomposites. The ultimate properties of the nanocomposites have been correlated with the key parameters of filler dispersion and filler–matrix interaction. The use of various sophisticated instrumental techniques for the characterization of these nanocomposites has been reviewed in this book.

Although there are published data and books on polymer nanocomposites, there is no specific book dedicated to all types of nanofillers. It is important to add that none of the existing books cover all range of nanofillers from spherical to two dimensional (0D to 2D fillers). The main objective of this book is to summarize in a fairly comprehensive manner many of the recent technical accomplishments in the area of polymer nanocomposites. The book is intended to serve as a one-stop reference resource for important research accomplishments in the area of polymer nanocomposites. Prominent researchers from industry, academia and government/private research laboratories across the globe have contributed the various chapters in the book. The book will be a very valuable reference source for university and college faculties, professionals, post-doctoral research fellows, senior graduate students, polymer technologists, and researchers from R&D laboratories working in the area of polymer nanocomposites.

Chapter 1 discusses the role of interface, preparation, structure–property relationship, and applications of layered silicate rubber latex nanocomposites. The interface has a strong influence on the properties of polymer nanocomposites. The influence of various compatibilising agents and interfacial agents on the morphology, structure and properties has been discussed in detail. The polymer–filler interaction and filler dispersion on the properties of the nanocomposites have been correlated with the interface.

The structure, mechanical, electrical, and thermal characteristics of polymer–graphite nanocomposites has been discussed in Chapter 2. The graphite structure and property modification by methods like intercalation with alkali metals followed by exfoliation with aqueous solvents, inserting sulfuric acid between the carbon layers of graphite to expanded graphite, heat exfoliation of the graphite, and ultrasonication to separate loosely connected graphite nanosheets into individual nanoplatelets are discussed. The mechanical

and electrical properties of graphite polyamide nanocomposites, graphite polypropylene nanocomposites, and graphite epoxy nanocomposites are discussed in the chapter. Chapter 3 mainly concentrates on three types of PANi-containing nanocomposites: (1) composites with nanostructured materials, such as clay and certain metal compounds of which the cavities have been filled with PANi by *in situ* polymerization or impregnation techniques, (2) composites with nanoscaled metal particles, metals oxides and silica particles embedded in PANi, (3) composites with carbon nanotubes and graphite. Their properties and applications are also elaborated in this chapter.

Chapter 4 briefly describes the theoretical reason of modification of either nanoclays or polymeric matrix for the preparation of high performance nanocomposites. The chapter deals with polypropylene, polyethylene, and EVA copolymer nanocomposites. The various processing conditions which affect morphology and final characteristics of prepared nanocomposites has been elaborated. The morphological, mechanical, and thermal characterization of the above-mentioned polymer nanocomposites are also discussed in the chapter. Chapter 5 emphasizes the preparation and characterization of PMMA, PAN and the other acrylic-based polymer nanocomposites by the addition of inorganic nanofillers. The mechanistic understanding of the different preparation approaches and the effects after the addition of various inorganic nanoparticles and their potential applications are elaborated here.

Chapter 6 reports the state of the art regarding polyurethane (PU) nanocomposites, from processing and characterization to specific properties and end-use applications. The different parameters determining PU nanocomposites are studied in detail. In this chapter, nanocomposites based on thermoplastic or waterborne PU, PU foams, blends of polymers, and fillers both "inert" or "reactive" have been elaborated. The correlation between the fundamental nanocomposite structure and properties such as mechanical, permeation, barrier, thermal stability, flame retardancy etc. have been established by taking into consideration the filler–volume fraction as well as the aspect ratio. The emerging applications of PU nanocomposites in the biomedical field and other contemporary domains are also presented in this chapter.

Chapter 7 covers major activities for designing novel nanoarchitectures for emerging technologies with emphasis on synthesis, structure and optical properties of polymer–metal chalcogenide (CdS, PbS, CdSe, HgS, and Ag_2S etc.) nanocomposites. Basic synthetic routes and typical polymer matrices (homopolymers, random- and block-copolymers, conductive polymers, and biopolymers) are considered. The role of the surface fictionalizations of semiconductor nanoparticles as a means of preparing ordered composite structures is also discussed. Concerns of possible influences of semiconductor nanoparticles on the physical properties of the host matrix are also addressed.

It has been demonstrated that the addition of a small quantity of cellulose whiskers to various polymers greatly improves their dynamic mechanical properties in particular their stiffness at $T > T_g$ of the matrix. At higher fiber content, composites with impressive mechanical properties (modulus up to > 25 GPa, strength > 450 GPa) were obtained using nanofibrillated wood pulp and bacterial cellulose. In Chapter 8, a brief review of the literature on the production, structure, and properties of cellulose whiskers and nanofibrils together with their polymer composites is given.

Rapid progress made in the synthesis and development of nanoscale materials has motivated researchers to alter the constituent phases of traditional fiber-reinforced composites and sandwich constructions with the nanosized fillers. In Chapter 9, recent developments made in the field of polymeric nanocomposites for structural material applications

are reviewed. This article reveals the recent progress made in the field of nanotechnology as applied to structural polymeric composites. Particular focus is given to carbon-fiber-reinforced nanophased composites and sandwich constructions. The article elaborates the modification of matrices, modification or the synthesis of nanophased fibers, the modification of foam and the fabrication of nanophased structural-fiber-reinforced and sandwich composites. Emphasis is given to the evaluation of thermal, thermomechanical, mechanical (both quasi-static), and dynamic properties.

A better understanding of the chemorheology of the unfilled or filled thermosetting resins is of great importance to many industries including integrated chip manufacturers, aerospace technologies, automotive manufacturers, and many other specialized applications. Convenient and rapid techniques for the determination of chemorheology and cure kinetics can lead to a better understanding of the cure processing of thermosetting-resin-based nanocomposites. This will provide enough experimental data to optimize these processes and thereby reduce design and operating costs in the industry. Mechanical methods such as the dynamic torsional vibration method (DTVM) can be used successfully to investigate the curing process in several thermosetting resin systems. Chapter 10 highlights the utilization of DTVM to study the cure behavior of several thermosetting-resin-based nanocomposites, with particular reference to layered silicate-reinforced polymer nanocomposites.

NMR can be used in different ways to investigate composites of polymers with inorganic compounds and diverse polymer nanocomposites. Nanocomposites may contain noncrystalline and crystalline phases. NMR allows the determination of their relative contents and description of their different motional properties. NMR can also discriminate between the different crystalline forms in these systems. Chapter 11 gives a brief survey of NMR theory required to investigate polymer nanocomposites. It also describes the NMR studies of solid polymer electrolytes, nanocomposites prepared with conducting polymers, and the characterization and dynamics of the nanocomposites or some of their precursors.

The characterization of the structure of polymer nanocomposites by the techniques of small-angle scattering of neutrons and X-rays is reviewed in Chapter 12. This review focuses on structure determination in polymer nanocomposites by scattering methods, namely small angle neutron scattering and small angle X-ray scattering. It concentrates on the case of soft and continuous polymer matrices with inclusions of hard, nanometric filler particles like carbon black, silica and silicates.

Nanocomposites have been shown to contribute to certain flame retardant mechanisms where their high surface area to volume ratio gives an advantage, and some unique fire retardant attributes are added. Chapter 13 considers the mechanism of degradation and combustion, and then provides examples of the type of additives that can retard the combustion process at each stage. Synergisms between additives are included and explained. Recent examples of nanocomposites and hybrids of nano- and micro-composites are provided where the nanoparticles enhanced fire retardance.

The rapid growth of the miniature electronic and computer-related industries has caused great demand for smaller and lighter batteries with high level of energy and safety characteristics. Chapter 14 reviews the state-of-the-art of nanocomposite polymer electrolytes and encompasses their electrochemical and physical properties for the applications in lithium–polymer batteries especially for elevated temperature applications. The experimental procedure and the role of nanofillers on the ionic conductivity, compatibility with lithium metal anode and their cycling ability are discussed in this chapter. The electrochemical characteristics such as electrochemical impedance, transference number,

interfacial properties of Li/CPE/Li cells, and the cycling behavior of PVdF–HFP nanocomposite electrolytes with transition metal oxide cathode materials are also discussed.

The unique physical properties of nanocomposites have been explored by several industrial sectors. Chapter 15 looks at clay–polymer-based nanocomposite materials for applications in multilayered imaging elements and display components. The chapter mainly focuses on clay–polymer-based nanocomposite materials for applications in multilayered imaging elements and display components. The applications of clay–polymer nanocomposites in photographic and inkjet media and display components are well illustrated.

Contents

1 Preparation, Structure–Property Relationship, and Applications of Layered Silicate Rubber Latex Nanocomposites

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1.1 Introduction

Polymeric nanocomposites can be considered as an important category of organic–inorganic hybrid materials, in which inorganic nanoscale building blocks (e.g., nanoparticles, nanotubes, or nanometer-thick sheets) are dispersed in an organic polymer matrix [1–5]. When compared to conventional composites based on micrometer-sized fillers, the interface between the filler particles and the matrix in polymer nanocomposites constitutes a much greater area within the bulk material, and hence influences the composite's properties to a much greater extent, even at a rather low filler loading [6–8]. Polymer nanocomposites reinforced by relatively small amounts of ultrafine nanoparticles (most often clay platelets) proved exceptionally promising engineering materials with unexpectedly high stiffness–toughness ratio, gas barrier properties, flame retardence, etc. The real interest in nanotechnology is to create revolutionary properties and functions by tailoring materials and designing devices on the nanometer scale.

According to a report, the total worldwide market for polymer nanocomposites reached 11.1 million kg worth 90.8 million US$ in 2003. This market is expected to expand at an average annual growth rate of 18.4% to reach 211 million US$ by 2008.

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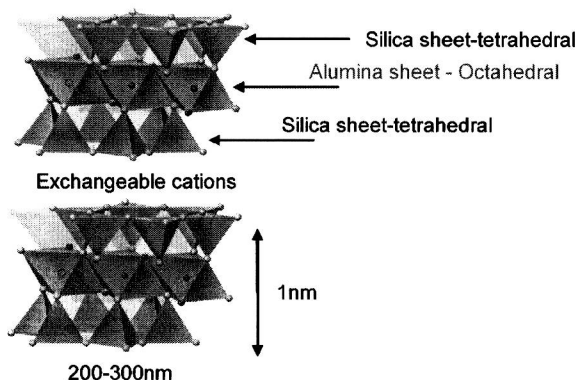
Figure 1.1.   Schematic representation of (tetrahedral–octahedral–tetrahedral) montmorillonite (MMT) clay [3].
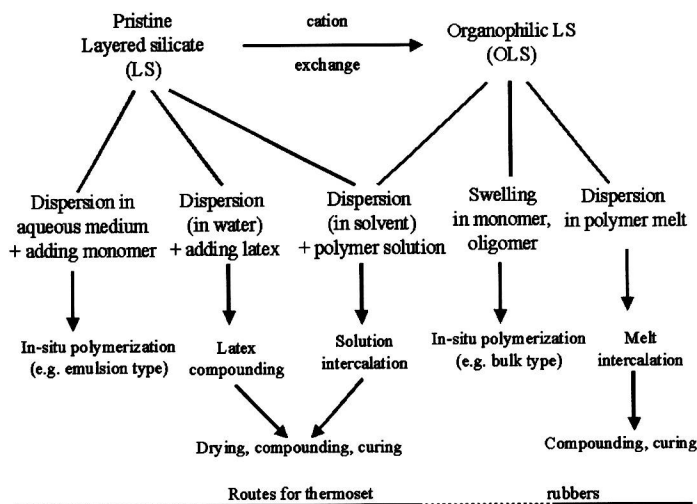
Polymer-layered silicate nanocomposites (PLSN) are the foremost members of such high-performance nanocomposites. Improvements in mechanical, thermal, and barrier properties, flame retardency, etc., are claimed for this class of polymer nanocomposites that could not be achieved by conventional fillers at such low loading (typically <10 phr). This class of material uses different types of clay, such as smectite, laponite, kaolinite, etc., among which smectite group of clays are most widely used due to its layered structure, very high surface area (700–800 m^2/g), higher cation exchange capacity (90–125 meq/100 g clay), and high aspect ratio (100–300). Cations like ammonium ion with long aliphatic hydrocarbon chains compatibilize the silicates with polymers and enhance the interaction with a polymer by enlarging the interlayers (lamina), generating organically modified layered silicates (LS) or simply organoclays. Each layer is constructed from a two-silicon tetrahedron fused to an alumina octahedron (Figure 1.1).

1.2   Production of Rubber–Clay Nanocomposites

Currently, numerous procedures for the preparation of polymer nanocomposites have been proposed [3–8], using the following approaches:

- Direct intercalation of nanoscale building blocks into a polymer melt or solution.
- *In situ* generation of nanoscale building blocks in a polymer matrix.
- Polymerization of monomers in presence of nanoscale building blocks.
- A combination of polymerization and formation of nanoscale building blocks (e.g., sol–gel method, intercalation of monomers into layered structures followed by polymerization, etc.).

The key issue of these techniques is that the geometry, spatial distribution, and volume content of the nanofillers must be effectively controlled through adjusting the preparation conditions to ensure the structural requirements of nanocomposites. The preparation of rubber–clay nanocomposites slightly differs from the above scenario as some methods are not ideal (e.g., *in situ* polymerization) and rubbers are available in various forms (latex, solution, and dry), which offer additional possibilities (e.g., latex compounding). Scheme 1.1 shows the possible production routes of thermoset-rubber–LS nanocomposites. Further, the melt intercalation method, which is strongly recommended for dry form

Scheme 1.1. Possible preparation routes of rubber-layered silicate nanocomposites [4].

of rubber, is not included here as the main theme of our discussion is latex-based nanocomposites [4].

Modification of the clay by organic molecules ("organophilization") is not always a necessary step in the production of polymer nanocomposites. In general, two types of organic–inorganic hybrids are distinguished – intercalated (in which polymer chains are diffused between the silicate layers) and exfoliated (in which the silicate layers of ca.1 mm thickness are fully delaminated and dispersed in the polymer matrix). Pristine-layered silicates usually contain hydrated Na^+ or K^+ ions. In aqueous dispersions, the clay "swells" (i.e., its layers are separated due to hydration of the interstitial cations), which facilitates the intercalation of the rubber molecules when the dispersion is mixed with latex.

It is further emphasized that a dramatic improvement in the properties of polymer–clay nanocomposites can only be achieved by ensuring the initial penetration (intercalation) of polymer molecules into the interlayer space (galleries) of clay tactoids and subsequently by forcing these layers apart to complete delamination (exfoliation) of the clay monolayers (1 nm thickness) throughout a polymer matrix. Apparently, the major outcome of this technology is the achievement of a maximum possible area for polymer–filler interaction by eliminating the initial aggregated state of clay nanolayers.

1.3   Characterization of Nanocomposites

1.3.1   X-Ray Diffraction Technique

X-Ray diffraction (XRD) is the most widely used technique for the characterization of polymer nanocomposites [7,8]. The change in the interlayer spacing, that is, "d" spacing of the latex nanocomposites, is observed from the peak position in the XRD pattern in accordance with the Bragg's equation

$$n\lambda = 2d \sin\theta, \tag{1.1}$$

Structure	Initial XRD spectra	Final XRD spectra

Immiscible system

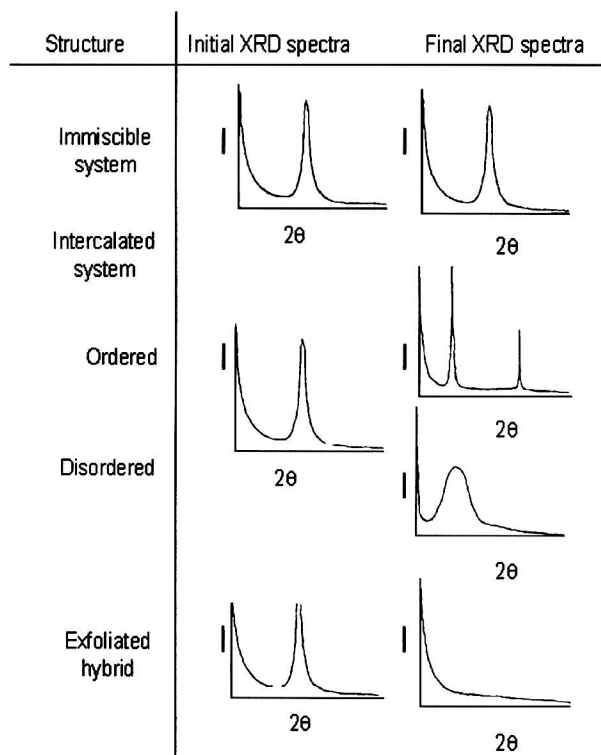Intercalated system

Ordered

Disordered

Exfoliated hybrid

Figure 1.2. Schematic representation of XRD spectra of possible polymer-layered silicate nanocomposites structures [7,8].

where n is the order of diffraction, λ is the wavelength of X-rays, d is the interlayer spacing, and θ is the angle of diffraction. The XRD method has been used to characterize the formation of structure in polymer–silicate hybrids by monitoring the position, shape, and intensity of the basal reflection from the silicate layers. Figure 1.2 summarizes the general character of the X-ray spectra for various types of PLSN structures. For immiscible mixtures of polymer and organophilic-layered silicates (OLS), the basal reflection does not change upon blending with the polymer. On the other hand, the finite-layer expansion associated with intercalated structures results in a new basal reflection that corresponds to the larger gallery height. A decrease in the degree of coherent layer stacking (i.e., a more disordered system) results in peak broading and intensity loss. In contrast, the extensive layer separation, beyond the resolution of Bragg–Brento geometry, of exfoliated structures does not result in a new, observable, basal reflection [7,8].

1.3.2   Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a powerful technique used for the characterization of PLNC. It gives a direct measure of the spatial distribution of silicate layers, morphology, and structural effects of a selected area of the sample; however, the limitation is that it requires substantial skill in specimen preparation and analysis. Figure 1.3 shows
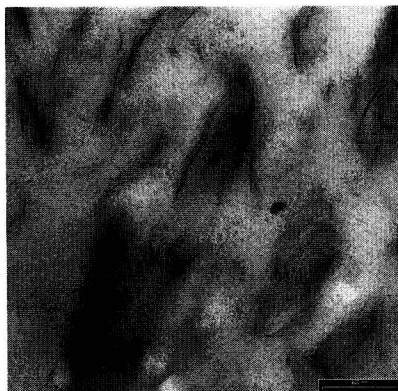
Figure 1.3. TEM picture of natural rubber (NR) nanocomposites containing 10 phr MMT–ODA (note that ODA is octadecyl amine used as modifier for MMT) [9].

the exfoliation of LS (MMT–ODA) at a loading of 10 phr [9]. Here, the black strands-like portion in the photograph shows the fully separated silicate sheets.

1.3.3 Differential Scanning Calorimeter

Differential scanning calorimeter (DSC) measurements of PLSN are helpful for the identification of the extent of intercalation. The interactions of the intercalated polymer chains with the host species reduce its segmental mobility, thereby increasing its glass transition temperature T_g up to five units. Accordingly, PMMA/organically modified MMT shows increase in T_g with MMT content [10]. It is due to the confinement of the intercalated polymer chains between the sheets of the clay that prevents the segmental motions of the polymer chains'.

1.3.4 Dynamic Mechanical Thermal Analysis

Similar to DSC, dynamic mechanical thermal analysis (DMTA) can also provide information about the T_g of PLSN. The magnitude of the storage modulus (E') gives an idea about the level of reinforcement, and hence the intercalation in MMT–ODA and MMT–TMDA composites compared to the microcomposite – NR–silica system (Figure 1.4). It is also reported that damping peak in the tan δ curves decreases upon the addition of silicates due to the restricted mobility of chain segments (Figure 1.5). Moreover, dynamic mechanical studies on MMT–ODA systems indicate the presence of a separate relaxation event, which has been attributed to less-mobile chains within the interfacial region [9]. This may be due to the higher level of intercalation in MMT–ODA (interlayer distance 2.10 nm) compared to MMT–TMDA (interlayer distance 1.85 nm).

1.3.5 Transport Properties

Due to the large aspect ratio of the LS, the permeability of PLSN decreases drastically. The substantial decrease can be explained by the increase in tortuosity of the path of the gas as it diffuses into the nanocomposite [11]. The barrier improvement is predicted by tortuous path model to be a function of the volume fraction ϕ and the aspect ratio of the
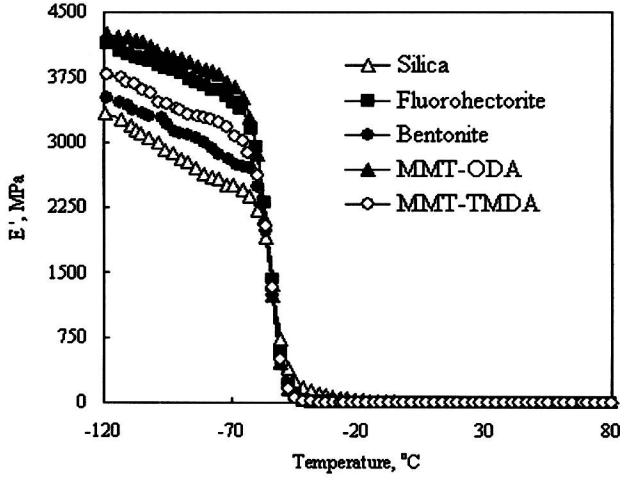
Figure 1.4. Complex storage modulus (E') as a function of temperature for different silicate-filled NR nanocompoites [9]. Note that ODA is octadecylamine and TMDA is methyl tallow bis-2-hydroxyl ethyl quaternary ammonium, used as modifiers for MMT.

Figure 1.5. Mechanical loss (tan δ) as a function of temperature for different silicate-filled nanocompoites [9]. Note that ODA is octadecyl amine and TMDA is methyl tallow bis-2-hydroxyl ethyl quaternary ammonium, used as modifiers for MMT.
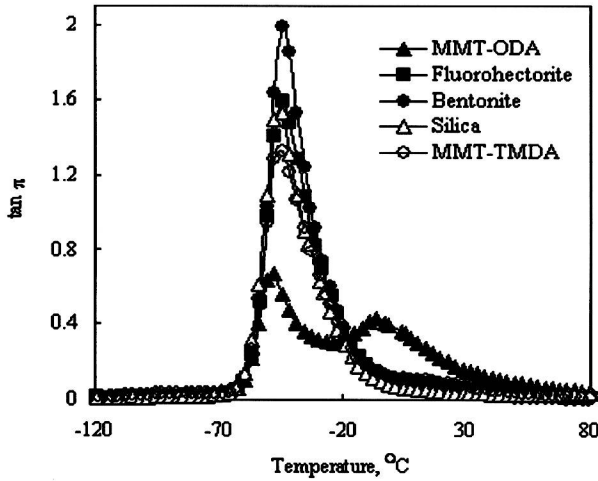
silicate layers α; higher aspect ratios provide grater barrier improvements according to the following equation for permeability:

$$PN = \frac{(1 - \phi) \times PM}{1 + \alpha\phi/2},$$ (1.2)

where PN represents the permeability of the resulting nanocomposites and PM the permeability of the matrix polymer. Toyota researchers reported that the water absorption of
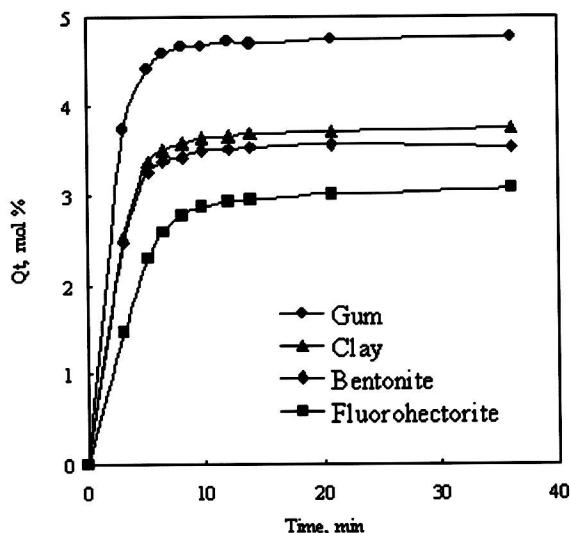
Figure 1.6. Swelling behavior of the LS-filled (nano) composites in toluene at 25 °C [18].

nylon–clay hybrid reduced by 40% as compared to the pure polymer [12]. The gas permeability in rubber–clay hybrids was also reduced by 30% with 4 vol.% of exfoliated clay [13]. There is substantial reduction in free volume upon the addition of nanofillers to polymer matrix due to the increased polymer–filler interaction [14]. The dispersed nanocomposites exhibit increased solvent resistance compared to immiscible hybrids (Figure 1.6). The exfoliated silicate layers prevent solvent molecules to diffuse and damage the polymer network [15].

1.3.6   Thermal Stability

The thermal stability of nanocomposites increased with the amount of silicate layers in the composites [16]. Polymer–clay nanocomposites were characterized by a single weight loss with the beginning of the degradation shifted to much higher temperature. A possible reason for the high thermal stability of nanocomposites might be the well-dispersed inorganic material (silicate) with high thermal stability and great barrier properties, which prevent the heat to transmit quickly and limit the continuous decomposition of the nanocomposites.

1.3.7   Fourier Transmission Infrared Spectroscopy

Fourier transmission infrared spectroscopy (FT-IR) can be effectively used for the characterization of PLSN. This is essentially due to the shift in the Si–O stretching (1005/cm) and Si–O bending (476/cm) vibrations (frequency) to lower wavelengths [17] (Figure 1.7) due to the interaction of the silicate (intercalation/exfoliation) with the polymer in the composite.