COMPOSITES MATERIALS FOR FOOD PACKAGING

EDITED BY
Giuseppe Cirillo
Marek A Kozlowski
Umile Gianfranco Spizzirri

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Composites Materials for Food Packaging
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Series Editor: Giuseppe Cirillo
Department of Pharmacy, Health and Nutritional Sciences, University of Calabria, Arcavacata di Rende (CS), Italy
E-mail: Giuseppe.cirillo@unica.it

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Publishers at Scrivener
Martin Scrivener (martin@scrivenerpublishing.com)
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Composites Materials for Food Packaging

Edited by
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Preface

In recent years, consumer’s consciousness of the strong relationship between food quality and health has extensively impacted the packaging field. Nowadays, indeed, a packaging material is asked to match the handling and storage conditions with the quality and safety of foodstuffs. As a consequence, scientific literature and industrial R&D activities are plenty with attempts to develop new and effective materials that are able to preserve food from degradation in both normal and stressed environmental conditions, resulting in a consistent enhancement of their shelf-life. The packaging science is thus becoming an interdisciplinary research field, involving the expertise of chemists, physicists, engineers and biologists, with the ultimate aim to match the consumers’ expectation and government’s regulations.

The book is intended as an overview on the recent and more relevant insights in the application of composite materials on food packaging, emphasizing the scientific outcome arising from the physico-chemical properties of such engineered materials with the need of food quality and safety.

Composites, matching the properties of different components, allow the development of innovative and performing strategies for an intelligent food packaging, overcoming the limitations of using only a single material.

The book starts with the description of montmorillonite and halloysite composites, subsequently moving to metal-based materials with special emphasis on silver, zinc, silicium and iron. After the discussion about how the biological influences of such materials can affect the performance of packaging, the investigation of superior properties of sp² carbon nanostructures is reported. Here, carbon nanotubes and graphene are described as starting points for the preparation of highly engineered composites able to promote the enhancement of shelf-life by virtue of their mechanical and electrical features.

Finally, in the effort to find innovative composites, the applicability of biodegradable materials form both natural (e.g. cellulose) and synthetic (e.g. polylactic acid – PLA) origins, with the aim to prove that polymer-based materials can overcome some key limitations such as environmental impact and waste disposal.
Montmorillonite Composite Materials and Food Packaging

Aris E. Giannakas* and Areti A. Leontiou

Laboratory of Food Technology, Department of Business Administration of Food and Agricultural Enterprises, University of Patras, Agrinio, Greece

Abstract

This chapter includes the recent trends in using montmorillonite (MMT)-based composite materials for food packaging applications. MMT is a naturally available phyllosilicate material that belongs to the group of smectites. Over the last few decades, it has found applications in many areas of nanotechnology such as catalysis, adsorption, and filtration. In recent years, it has also generated a wide range of applications in the food packaging industry. MMT has been used as an ideal nanofiller for polymer and biopolymer plastics, which leads to polymer and biopolymer nanocomposite films for food packaging with enhanced thermal and barrier properties. Incorporation of ions such as Ag⁺, Cu²⁺, and Zn²⁺ in clay platelets leads to nanocomposites with enhanced antimicrobial activity. Additionally, many strategies have been developed for immobilization of oxides, enzymes, essential oils, and other bioactive compounds in these platelets. This feature makes the MMT-based composite materials promising nanocarriers for smart and active packaging applications.

Keywords: Montmorillonite, oxides, essential oils, enzymes, antioxidant, antimicrobial, food packaging

1.1 Introduction

The word “nano” comes from the Greek for “dwarf” and denotes nanometer (10⁻⁹ m) [1]. The concept of nanotechnology was introduced by

*Corresponding author: agiannakas@upatras.gr
Richard Feynman in 1959 and the National Nanotechnology Initiative (Arlington, VA, USA), and involves the characterization, fabrication, and/or manipulation of structures, devices, or materials that have at least one dimension (or contain components with at least one dimension) that is approximately 1–100 nm in length. When particle size is reduced below this threshold, the resulting material exhibits physical and chemical properties that are significantly different from the properties of macroscale materials composed of the same substance [2]. Despite an explosion of growth in the area of nanotechnology, food nanotechnology is still a lesser known subfield of the greater nanotechnology spectrum, even among professional nanotechnologists. Potential uses of food nanotechnology include: (i) pesticide, fertilizer, or vaccine delivery; animal and plant pathogen detection; and targeted genetic engineering for agriculture, (ii) encapsulation of flavor or odor enhancers; food textural or quality improvement; new gelation or viscosifying agents for food processing, (iii) nutraceuticals with higher stability and bioavailability for nutrient supplements and (iv) pathogen, gas, or abuse sensors; anticounterfeiting devices; UV-protection and stronger more impermeable, antimicrobial, and antioxidant polymer films for food packaging. In order to enhance mechanical, barrier, antimicrobial, and antioxidant properties and to introduce sensor and UV protection ability in polymer and/or biopolymer films, various inorganic nanostructured materials [1] have been used including TiO$_2$, ZnO nanoparticles, SiO$_2$, carbon nanotubes, and nanoclays.

Nanoclays gathered the attention of the food packaging industry, due to their availability, low cost, significant enhancements, and relatively simple processability [1]. Clays and clay minerals belong to the phyllosilicate group (from the Greek “phyllon”: leaf, and from the Latin “silic”: flint). Clay minerals, that is, layered aluminum silicates, are the most abundant minerals of sedimentation basins (both marine and continental), weathering crusts, and soils [3]. Clay minerals are characterized by two-dimensional sheets of corner sharing SiO$_4$ tetrahedra and/or AlO$_4$ octahedra. The sheet units have the chemical composition (Al, Si)$_3$O$_4$. Each silica tetrahedron shares three of its vertex oxygen atoms with other tetrahedra forming a hexagonal array in two dimensions. The fourth vertex is not shared with another tetrahedron and all of the tetrahedra forming a hexagonal “point” in the same direction; that is, all of the unshared vertices are on the same side of the sheet. In clays, the tetrahedral sheets are always bonded to octahedral sheets formed from small cations, such as aluminum or magnesium, and coordinated by six oxygen atoms. The unshared vertex from the tetrahedral sheet also forms part of one side of the octahedral sheet, but an additional oxygen atom is located
above the gap in the tetrahedral sheet at the center of the six tetrahedra. This oxygen atom is bonded to a hydrogen atom forming an OH group in the clay structure. Clays can be categorized depending on the way that tetrahedral and octahedral sheets are packaged into layers. If there is only one tetrahedral and one octahedral group in each layer, the clay is known as a 1:1 clay. The alternative, known as a 2:1 clay, has two tetrahedral sheets with the unshared vertex of each sheet pointing toward each other and forming each side of the octahedral sheet. The most representative 2:1 clay mineral is bentonite that consists of 90% wt. montmorillonite (MMT) and is a weathering product of volcanic glass.

The structural unit of MMT consists of two tetrahedral sheets that cover one octahedral sheet in between (Figure 1.1). This micaceous clay structure has oxide anions at the tip of the tetrahedral subunits that are oriented toward silicone atoms, which are frequently substituted by aluminum, iron, and cations. However, the octahedral subunits contain aluminum ions that are substituted by silicon ions and surround the hydroxyl atoms present at the axial end of tetrahedral [3–5] planes. The MMT [(Na, Ca)_{0.33} (Al, Mg)_{2} (Si_{4} O_{10}) (OH)_{2} • nH_{2}O] surface is slightly negatively charged because oxide anions dominate the charge-balancing anions (Si^{4+}, Al^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+}) present in the interface and impart as light overall negative charge to the surfaces of the sheets clay minerals. The MMT particles are plate-shaped, typically 1 nm in thickness and

![Figure 1.1 Structure of Montmorillonite (available online).](image-url)
Composites Materials for Food Packaging

0.2–2 microns in diameter [6]. MMT has an excellent sorption property and possesses sorption sites available within its inter-layer space as well as on the outer surface and edges. Depending on the place of origin, MMT contains variable amounts of sodium and calcium along with water for hydration. Sodium montmorillonite (Na-MMT) hydrates more than calcium montmorillonite (Ca-MMT). Cation exchange capacity (cmol/kg), specific surface area (m²/g), and basal interlayer spacing are maximum for MMT compared to other clays such as illite, kaolinite, and muscovite-type layered silicate [6].

Most polymers are considered to be organophilic compounds. In order to render the layered silicates miscible with nonpolar polymers, one must exchange the alkali counter-ions with a cationic–organic surfactant [1, 7, 8]. Alkylammonium ions are mostly used, although other “onium” salts can be used, such as sulfonium and phosphonium. Surfactants can also be used to improve the dispersability of the clay. The surfactants were able to increase spacing between clay layers (d-spacing) to different extents, depending on the number of polar units in the copolymer molecule. The resulting clays are called organomodified layered silicates (OMLS) and in the case of montmorillonite, they are abbreviated as OMMT (organically modified MMT). Organoclays are cheaper than most other nanomaterials, since they come from readily available natural sources and are produced in existing, full-scale production facilities [8]. In Table 1.1, the most cited commercial OMMT are mentioned.

The main advantages of MMT and OMMT nanoclays that make them ideal nanostructures for food packaging applications are as follows: (i) because of its hydrophilic nature MMT can be easily mixed with hydrophobic polymers [9, 10] such as polyvinylalcohol (PVOH), polylactide acid (PLA), and biopolymers [11–13] such as starch, chitosan, and proteins to give packaging films improved mechanical, thermomechanical, and oxygen and water vapor barrier properties; (ii) OMMT can be easily mixed with most polymers which are mainly hydrophobic and biopolymers to improve their mechanical properties and water vapor and oxygen barrier properties; (iii) because of its high ion exchange capacity, MMT can be modified with cation Ag⁺ or Cu²⁺ nanoparticles (NPs) to give excellent antimicrobial nanofillers; (iv) MMT’s large specific surface area can be modified with antioxidant and antimicrobial agents such as essential oils to give promising nanocarriers for smart packaging application; (v) pillar- ing of metal oxides in the interlayer space of MMT gives rise to a new class of nanosensors for food packaging applications; and (vi) enzymes can be adsorbed or bonded in the surface of MMT to give composites for active packaging applications.
Table 1.1 Chemical composition of the main commercial montmorillonite cited.

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<td>Montmorillonite (MMT) Na₀.₂Ca₀.₁Al₂Si₄O₁₀(OH)₂(H₂O)₁₀</td>
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</tr>
<tr>
<td>Cloisites 30B</td>
<td>Modified MMT</td>
<td>Quaternary ammonium salt (MT₂EtOH) 90 meq/100 g clay</td>
</tr>
<tr>
<td>Cloisites 20A</td>
<td>Modified MMT</td>
<td>Quaternary ammonium salt (2M₂HT) 95 meq/100 g clay</td>
</tr>
<tr>
<td>Cloisites 93A</td>
<td>Modified MMT</td>
<td>Ternary ammonium salt (M₂HT) 90 meq/100 g clay</td>
</tr>
<tr>
<td>Cloisites 15A</td>
<td>Modified MMT</td>
<td>Quaternary ammonium salt (2M₂HT) 125 meq/100 g clay</td>
</tr>
<tr>
<td>Cloisites 10A</td>
<td>Modified MMT</td>
<td>Quaternary ammonium salt (2M₂BHT) 125 meq/100 g clay</td>
</tr>
<tr>
<td>Clay1</td>
<td>Modified MMT</td>
<td>Quaternary ammonium salt (HDTA) 6-fold the CEC of raw clay</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(raw clay with a cation exchange capacity (CEC) 92.6 meq/100 g clay)</td>
</tr>
<tr>
<td>Clay2</td>
<td>Modified MMT</td>
<td>Quaternary ammonium salt (HDTA þ ACO) HDTA in 5.75-fold and ACO in 0.25-fold of the CEC of raw clay (92.6 meq/100 g clay)</td>
</tr>
<tr>
<td>Oligo(styrene-co-acrylonitrile) MMT</td>
<td>Modified MMT</td>
<td>Quaternary ammonium salt of poly(styrene-co-acrylonitrile)(CEC 0.9 meq/g clay)</td>
</tr>
</tbody>
</table>
1.2 Polymer/MMT-Based Packaging Materials

Polymer/MMT materials are a class of polymer/layered nanocomposites. Polymer/layered nanocomposites (PNCs), in general, can be classified into three different types, namely (i) intercalated NCs, (ii) flocculated NCs, and (iii) exfoliated NCs [9] (see Figure 1.2). In the first case, polymer chains are inserted into layered structures such as clays, which take place in a crystallographically regular fashion, with a few nanometers repeat distance, irrespective of the ratio of polymer to the layered structure. In the second case, flocculation of intercalated and stacked layers to some extent takes place due to the hydroxylated edge-edge interactions of the clay layers. Finally, separation of the individual layers in the polymer matrix occurs in the third type by average distances that depend only on the loading of layered material such as clay. In this new family of composite materials, high storage modulus, increased tensile and flexural properties, heat distortion temperature, decrease in gas permeability, and unique properties such as self-extinguishing behavior and tunable biodegradability are observed, compared to matrix material or conventional micro- and macrocomposite materials [9, 10].

Polymers most frequently used in food packaging are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene terephthalate (PET). However, despite their enormous versatility, a limiting property of polymeric materials in food packaging

![Figure 1.2](https://example.com/figure1.2.png)
is their inherent permeability to gases and vapors, including oxygen, carbon dioxide, and organic vapors [14]. The penetration of gas into polymer has a critical effect on their service performance. Permeability is a critical performance issue in many areas such as packaging. For this reason, clay-reinforced nanocomposite has received significant consideration in recent years. Clay nanoparticles have a nanolayer structure with the layers separated by interlayer galleries. Later, the impressive decrease of permeability was attributed to the large aspect ratio of the clay layers, which should increase the tortuosity of the path of the gas as it diffuses into the NCs as shown in Figure 1.3. These layered structured materials such as MMT forces gas traveling through the film to follow a tortuous path through the polymer matrix surrounding the silicate particles (Figure 1.3), thereby increasing the effective path length for diffusion. Another issue of great importance is the observed decrease in water vapor permeability (WVP) in evaluating such polymer–clay composites for use in food packaging protective coatings and other applications where efficient polymer barrier properties are needed [9, 10].

To take advantage of the addition of clay, a homogeneous dispersion of the clay in the polymer matrix must be obtained. It was reported that entropic and enthalpic factors determine the morphological arrangement of the clay nanoparticles in the polymer matrix. Dispersion of clay in a polymer requires sufficiently favorable enthalpic factors that are achieved when polymer clay interactions are favorable. For most polar polymers, the use of alkyl-ammonium surfactants is adequate to offer sufficient excess enthalpy and promote formation of homogeneous NCs. The most widely

![Figure 1.3](Image available online.)
Composites Materials for Food Packaging

used clay filler for the enhancement of gas barrier property of polymer clay NCs is MMT as it has large cation exchange capacity [14].

Hereafter, we review the most remarkable studies of last decade of polymer/MMT composites focusing on studies where PE, PS, PP, and PET polymers were used for packaging applications. From these studies, gas barrier properties with mechanical and thermomechanical properties are reviewed.

1.2.1 Polyethylene(PE)/MMT-Based Packaging Materials

New composites that include PE as the matrix are widely used in many applications with better mechanical and physical properties compared to the polymer alone. Polyethylene composites can be used in packaging, electrical, thermal energy storage, automotive, biomedical, and space applications. Polyethylene can be classified into several different categories but mostly does not depend on its density and branching [15]. The main forms of PE are high-density polyethylene (HDPE), high molecular weight HDPE (HMWHDPE), ultrahigh molecular weight density polyethylene (UHMW-HDPE), linear low-density polyethylene (LLDPE), and very low-density polyethylene (VLDPE). These are divided based on density and branching. Generally, the most used PE grades are HDPE, low-density polyethylene (LDPE), and medium-density polyethylene (MDPE). Table 1.2 shows the density values for some types of PE. Low-density polyethylene is a branched thermoplastic, having many relatively long branches of the main molecular chain. This prevents the molecules from packing closely together; irregular packing causes low crystallinity content. Low-density polyethylene is flexible and has low tensile and compressive strength compared to HDPE because of irregular packing of polymer chains. Generally, LDPE is the most common form of PE used in food packaging materials, rigid containers, and plastic film applications [15].

Jacquelot et al. [16] used a commercial organo-modified MMT, bearing a dimethyl tallow benzyl ammonium ion as quaternary ammonium (OMMT) and low density maleic anhydride-grafted polyethylene as a compatibilizer to prepare PE/OMMT films. It was shown that the introduction of a maleated polyethylene compatibilizer was required to improve the clay nanoplatelet dispersion in the metallocene polyethylene-based NCs. Increasing the MMT content led to a significant increase of the barrier properties. Interfacial agents such as oxidized paraffins were shown to be more effective to reduce the gas permeability than maleated polyethylene and the dependence of the gas transport properties was discussed not
only as a function of the clay dispersion but also as a function of the clay/compatibilizer and compatibilizer/matrix interaction.

Zhong et al. [17] prepared LDPE, HDPE/ethylene vinyl acetate copolymer (EVA)/OMMT (OMMT = Cloisite1 20A) NCs in a twin-screw extruder. The resulting organoclay-polyethylene NCs were then blown into films. Tensile properties and oxygen permeability of these nanocomposite films were investigated to understand the effects of organoclay on different types of polyethylene. It was found that the OMMT-enhancing effects are the function of the matrix. The mechanical and oxygen barrier properties of OMMT/EVA systems increased with clay loading. Both the tensile modulus and oxygen barrier of EVA doubled at 5 wt% clay. Maleic anhydride grafted polyethylene (MAPE) usually is used as a compatibilizer for LDPE- and HDPE-based NCs. However, the MAPEs were found to weaken the oxygen barrier of the PEs, especially for HDPE. This is believed to be a result of less compactness caused by the large side groups and the increase in polarity of the MAPEs. Incorporating 5 wt% clay improves the oxygen barrier by 30% and the tensile modulus by 37% for the LDPE/MAPE system.

Arunvisut et al. [18] prepared (LDPE)/OMMT NCs, which can be used in packaging industries, by melt-mix organoclay with polymer matrix (LDPE) and compatibilizer, polyethylene grafted maleic anhydride (PEMA). For the organic modification of MMT, we used hydrogenated tallowalkyl dimethyl ammonium chloride. Tensile modulus and tensile strength at yield were improved when clay contents increased because of the reinforcing behavior of clay on both TD and MD tests. Tensile modulus

<table>
<thead>
<tr>
<th>GSE (%)</th>
<th>E. coli O157:H7</th>
<th>L. monocytogenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>0.5</td>
<td>13.63 ± 0.34*</td>
<td>29.53 ± 0.33</td>
</tr>
<tr>
<td>0.7</td>
<td>14.29 ± 0.25</td>
<td>32.68 ± 0.13</td>
</tr>
<tr>
<td>1.0</td>
<td>14.51 ± 0.02</td>
<td>33.85 ± 0.90</td>
</tr>
<tr>
<td>1.2</td>
<td>14.76 ± 0.25</td>
<td>34.68 ± 0.47</td>
</tr>
</tbody>
</table>

ND, Not detected; E. coli, Escherichia coli; L. monocytogenes, Listeria monocytogenes.

*Mean values with different letters within a column are significantly different by Duncan’s multiple range test at $p < 0.05$. 

Table 1.2 Antimicrobial activity of the barley protein (BP)/Cloisite Na+ composite films containing grapefruit seed extract (GSE) against the pathogenic bacteria. Reprinted with permission from Reference [76].
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of 7 wt% of clay in the nanocomposite was 100% increasing from neat LDPE in TD tests and 17% increasing in MD tests. However, elongation at yield decreased when increased in clay loading. Oxygen permeability tests of LDPE/clay NCs also decreased by 24% as the clay content increased to 7 wt% (Figure 1.4).

Xie et al. [19] prepared LDPE/OMMT NCs by twin-screw extruder and hot-press. OMMT was first modified with dodecyl dimethylbenzyl ammonium (DDA) salt and octadecyl trimethyl ammonium (OTA) salt. CO₂ and O₂ barrier properties of NCs were increased by seven times and four times with 0.5 wt% OTA-MMT loading, respectively. At 2 wt% OTA-MMT loading, WVP of LDPE has also decreased about 2.5 times. Compared with pure PE film, 49.5% and 178% improvement of tensile strength of NCs films were obtained by addition of only 4 wt% DDA-OMMT and OTA-MMT, respectively. In addition, with only 0.5 wt% OMMT loading, the onset degradation temperature of NCs increased by 23 °C and 26 °C for LDPE/DDA-OMMT and LDPE/OTA-OMMT, respectively.

Hosseinkhanli et al. [20] prepared LDPE/poly(ethylene-covinyl acetate) (EVA) NCs containing organoclay (Nanomer I31Ps, a MMT modified by an alkylamine) by one- and two-step procedures through melt blending. The resultant NCs were then processed via the film-blowing method. Obtained films from the two-step-procedure compound showed enhanced oxygen barrier properties and mechanical behavior as compared to the properties of the films produced via the one-step procedure. A more recent report of the same group [21] used zinc-neutralized carboxylate ionomer as a compatibilizer to prepare (LDPE)/OMMT (Nanomer I31PS) NCs by

![Figure 1.4](image-url)  
**Figure 1.4** Gas permeability of LDPE and LDPE/clay NCs for 1, 3, 5, and 7 wt% clay. Reprinted with permission from Reference [18].
melt blending in a twin-screw extruder by using different mixing methods. Barrier properties and tensile modulus of the films were improved by increasing the OMMT content. In addition, tensile strength increased in the machine direction, but it decreased in the transverse direction by increasing the clay content.

1.2.2 Polystyrene(PS)/MMT-Based Packaging Materials

Polystyrene (PS) is a highly commercialized thermoplastic material which is used in a variety of applications including packaging. In the last two decades, one of the rapidly growing areas for plastics is the packaging industry. This is due to ease, low price, safety, and good aesthetic qualities of plastics.

Nazarenko et al. prepared three polystyrene (PS)/clay hybrid systems via in situ polymerization of styrene in the presence of unmodified sodium MMT (NaMMT) clay, MMT modified with zwitterionic cationic surfactant octadecyldimethyl betaine (C18DMB), and MMT modified with polymerizable cationic surfactant vinylbenzylidimethyldodecylammonium chloride (VDAC). The PS/NaMMT composite was found to exhibit a conventional composite structure consisting of unintercalated micro- and nanoclay particles homogeneously dispersed in the PS matrix. The PS/C18DMB-MMT system exhibited an intercalated layered silicate nanocomposite structure consisting of intercalated tactoids dispersed in the PS matrix. Finally, the PS/VDAC-MMT system exhibited features of both intercalated and exfoliated NCs. Systematic statistical analysis of aggregate orientation, characteristic width, length, aspect ratio, and number of layers using multiple TEM micrographs enabled the development of representative morphological models for each of the nanocomposite structures. Oxygen barrier properties of all three PS/clay hybrid systems were measured as a function of mineral composition and analyzed in terms of traditional Nielsen and Cussler approaches. A modification of the Nielsen model has been proposed, which considers the effect of layer aggregation (layer stacking) on a gas barrier.

Giannakas et al. [22] prepared PS/OMMT NCs via the solution-blending method, using CHCl$_3$ and CCl$_4$ as solvents. The clay used was organically modified by hexadecyltrimethyl-ammonium bromide (CTAB) at various surfactant loadings. An intercalated nanocomposite structure was obtained using CHCl$_3$ as a solvent while an exfoliated or partially exfoliated structure was probably the predominated form in the case of CCl$_4$, as shown by X-ray diffraction measurements. Enhancement in thermal stability and in water barrier properties was observed for PS-NCs compared
to that of a pristine polymer as indicated by thermogravimetric analysis and water vapor transmission measurements. This increment was more prevalent for NCs prepared with carbon tetrachloride as a solvent.

Dunkerley and Schmidt [23] prepared model polystyrene (PS)/dimethylditallow modified MMT (DMDT-MMT) NCs via a novel spray casting technique capable of creating homogeneous, free-standing nanocomposite films. This approach provides a single experimental methodology for producing films of pure polymer, pure organoclay, or any intermediate composition, with consistently high levels of layer orientation in all cases. They studied the barrier properties of obtained films and focused on enveloping a nanocomposite barrier model. The results of oxygen permeation analysis (OPA) performed on these model materials (0–100 vol% organoclay in 10% increments) are compared to the results from all models commonly used for nanocomposite barrier properties modeling, both before and after the addition of a correction factor for actual layer orientation as measured by 2D wide-angle X-ray diffraction (WAXD), and with fitting parameters limited to physically meaningful values. Substantial improvements were reported in barrier properties in spite of the absence of exfoliation, with the model fits implying that the permeating species remain sensitive to the aspect ratio of individual platelets at all organoclay contents. While all models match our experimental data at low organoclay contents, significant differentiation occurs as the organoclay content is increased. Finally, they confirmed that the permeability of these materials followed an Arrhenius relation vs. temperature, albeit scaled to lower values as a function of inorganic content.

Arora et al. [24] used tetraethyl ammonium bromide (TEAB), tetrabutyl ammonium bromide TBAB, and cetyltrimethyl ammonium bromide (CTAB) to modify NaMMT and observed a significant improvement in the mechanical properties of PS/OMMT NCs prepared with modified clays as compared to commercial organoclay, which followed the order as: PS/TBAB system > PS/CTAB system > PS/TEAB system. Thermogravimetric analysis (TGA) demonstrated that $T_{10}$, $T_{50}$, and $T_{max}$ were more in case of PS NCs prepared using modified organoclay than nanoclay [nanolin DK4] and maximum being in the case of the PS/CTAB system. The results of differential scanning calorimetry (DSC) confirmed that the glass transition temperature of all the NCs was higher as compared to neat polystyrene. The NCs having 2% of TBAB modified clay showed better oxygen barrier performance as compared to PS.

Yank et al. [25] applied a supercritical CO$_2$ (scCO$_2$) processing method to pre-disperse commercial OMMT (Cloisite® 10A 20A and 30B) for further solvent mixing with polystyrene (PS) to form NCs with significant