

Review

Polymer Nanocomposites

Masami Okamoto 

Advanced Polymeric Nanostructured Materials Engineering, Graduate School of Engineering, Toyota Technological Institute, 2-12-1 Hisakata, Tempaku, Nagoya 468 8511, Japan; okamoto@toyota-ti.ac.jp

Abstract: In the last 20 years, there has been a strong emphasis on the development of polymer nanocomposites, where at least one of the dimensions of the filler material is of the order of a nanometer. Polymer nanocomposites are fundamentally different from traditional filled polymers because of the immense internal interfacial area and the nanoscopic nature of the nanomaterials. The new multifunctional properties derived from the nano-structure of nanocomposites provide an opportunity to circumvent the traditional properties associated with traditional composites. Numerous examples can be found in the literature that show significant improvements in multifunctional properties of the nanocomposites and this new class materials now being introduced in structural applications, such as gas barrier film, flame retardant product, and other load-bearing applications. This review offers a comprehensive review on the basic concept, technology and application for polymer nanocomposites.

Keywords: polymer nanocomposites; nanomaterials; internal interfacial area; nano-structure; multifunctional properties



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1. Introduction

For the past five decades, we have devoted ourselves to macrocomposites, such as filler reinforced polymer matrix composites, in which the length scale of the filler or the fiber diameters is in micrometers (Figure 1). Polymer composites are manufactured commercially for many diverse applications, such as automobiles, sporting goods, aerospace components, and so on. Over the last 20 years, we have been discovering polymer nanocomposites [1], where the length scale of the reinforcement (nanomaterials) is on the nanometer scale, as shown in Figure 1. Polymer nanocomposites have the potential to significantly impact growth at every level of the world economy in the 21st century. This surge in the field of polymer composites has been greatly facilitated by the advent of scanning tunneling microscopy and scanning probe microscopy in the early 1980s.

The nano-filler (nanomaterials) in the polymer nanocomposites have ultra-large interfacial area per unit volume, and distances between the filler and filler components (correlation length ξ) are close to polymer random coil/chain size with 20 nm in diameter [2]. In addition, the nano-fillers are on the same order of magnitude as the polymer coil. At the same time, the correlation length between filler particles ξ is smaller than the average value of the particle diameter D ($\xi \leq D$) with increasing filler content, indicating the formation of the highly geometric constraints. That is, the spatial-linked-like structure of the dispersed filler particles is formed [3]. Low concentrations necessary to influence in a matrix polymer have generated much interest in the field of the polymer nanocomposites. As a result, very unusual material properties are induced by molecular interaction between polymer coils/chains and nano-fillers. This is not possessed in the conventional macrocomposites. Furthermore, we can fabricate and process many polymeric nanocomposites via a similar way of conventional polymer-based macrocomposites, indicating them to be particularly attractive from a manufacturing point of view [1].

Basic structure

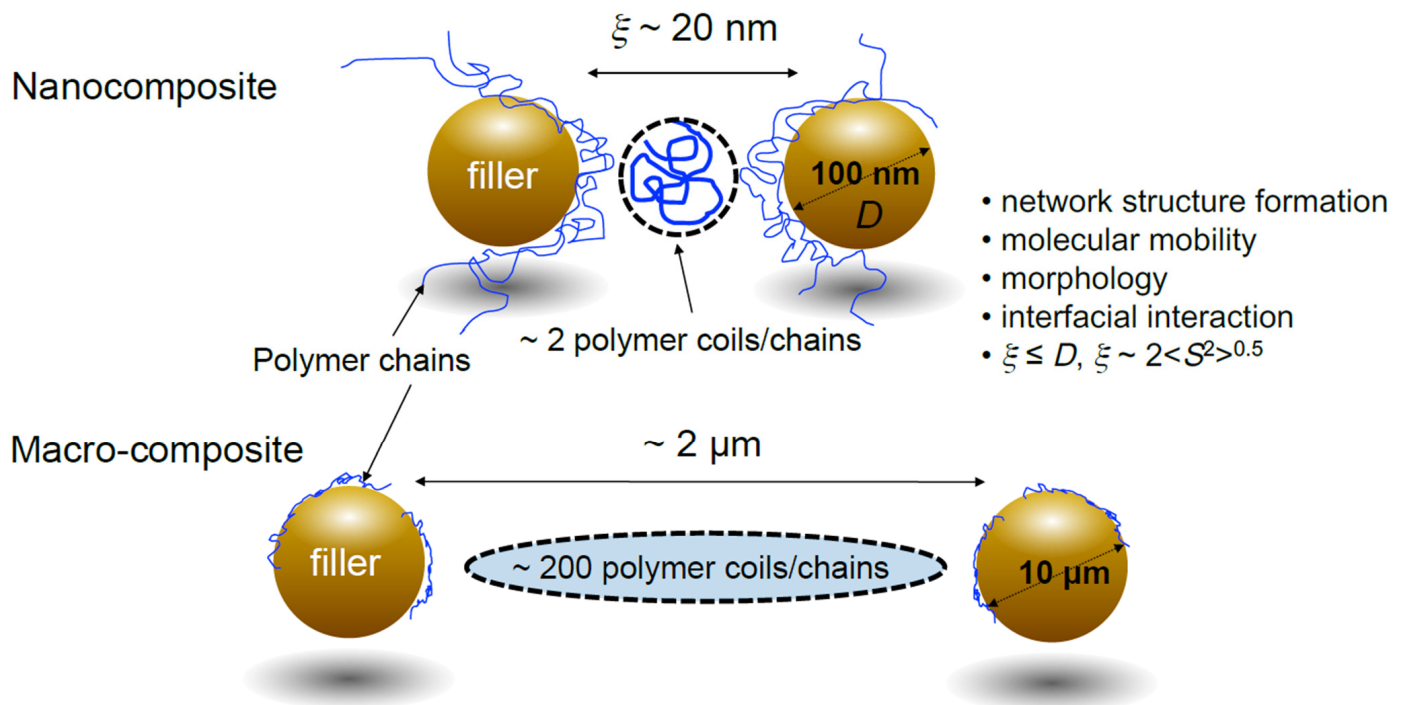
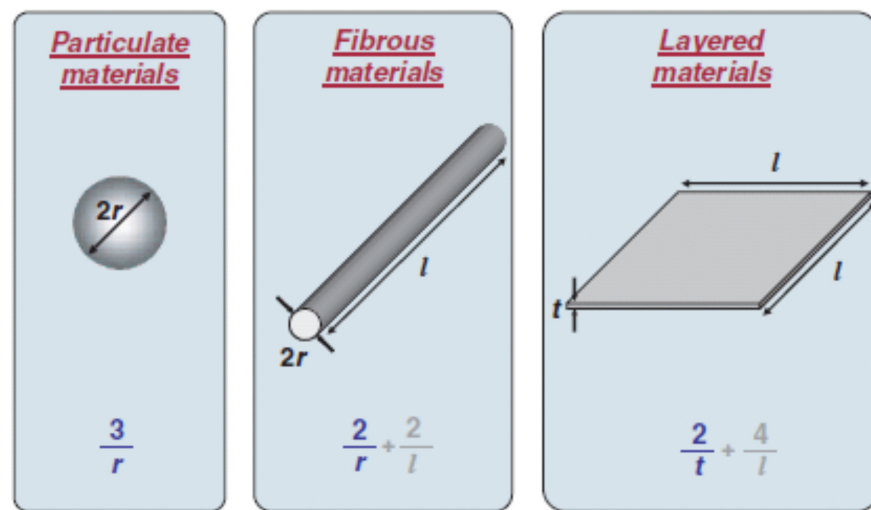


Figure 1. Typical particle reinforcements/geometries in nano- and macro-composites. The correlation length between filler particles ξ is smaller than average value of the particle diameter D ($\xi \leq D$) with increasing filler content. In general, the ξ value ($\cong 30 \text{ nm}$) corresponds to the random coil size of polymer. The root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$ is around 10 nm, which is calculated by $\langle S^2 \rangle^{1/2} = 4.0 \times 10^{-2} M_w^{1/2}$ [2]. The polymeric chain mobility presumably is decreased in translational motion. The morphological difference comes from the loading amount of filler particles.

2. Nanomaterials

In the case of particles, platelets, or fibers, the surface area per unit volume is inversely proportional to the material's diameter D . The surface/volume ratio R is $6/D$. The smaller the diameter, the larger the surface area per unit volume. Figure 2 shows common particle geometries and their value of R [4]. For the fiber and layered (platelet) materials, the first term in the equation is dominant, but second term ($2/l$ and $4/l$) has very small effect as compared with the first term. Therefore, a change in D from the micrometer to nanometer range affects the value of R by three orders of magnitude [4].

Typical nano-fillers under investigation include, nanoparticles, nanotubes, nanofibers, fullerenes, and nanowires, where are classified into three classes by their geometries, such as one-, two-, or three-dimensional nanoscale materials, as shown in Figure 2 [5,6]. Figure 3 shows the schematic illustration of several nano-fillers with dimensions. Silica, nano-silicon carbide ($n\text{-SiC}$), carbon black, fullerenes, polyhedral oligomeric silsesquioxanes (POSS), allophane nanoball are classified as nanoparticle reinforcing agents. Carbon nanofibers, carbon nanotubes and nanofibers (halloysite, nickel nanostrand: NiNs) are fibrous materials. In the case of the filler having a nanometer thickness and a high aspect ratio (50–1000) platelet structure, it is classified as a layered nanomaterial, such as an organically modified layered silicate (Figure 3) [1,3,5].



- Nano-silica
- Nano-silicon carbide
- Nano-zinc oxide
- Nano-silver
- Carbon black
- POSS
- Others ($n\text{-BaTiO}_3$, $n\text{-CaCO}_3$)
- Carbon nanofibers
- Carbon nanotubes
- Halloysite nanotubes
- Nickel nanostrand (NiNs)
- Layered silicate (Montmorillonite)
- Layered double hydroxide (LDHs)
- Layered titanate
- Nanographene platelets

Figure 2. Common particle reinforcements/geometries and their respective surface area-to-volume ratios R . Source: Reproduced with permission from [6]. © 2005, Elsevier Ltd.

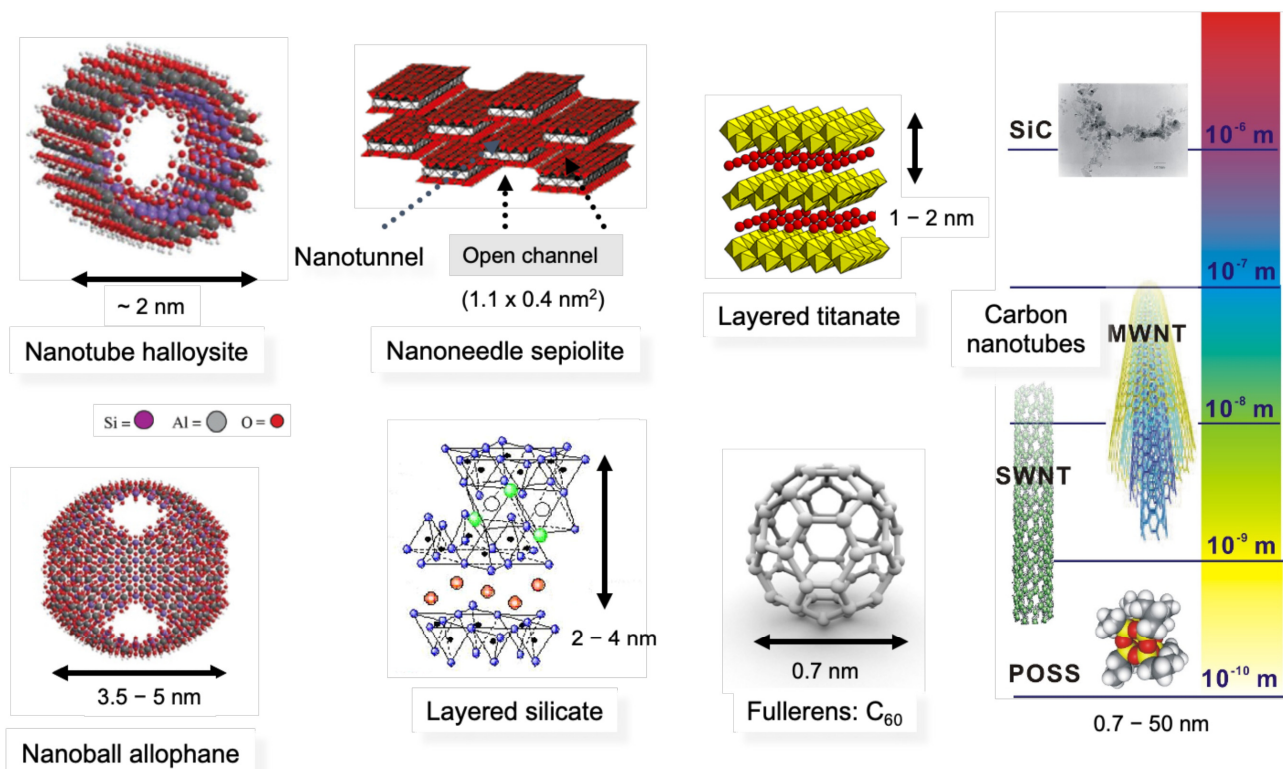


Figure 3. Schematic illustration of several nano-fillers (nanomaterials) with dimension. Polyhedral oligomeric silsesquioxanes (POSS), carbon nanotubes (single-wall nanotube (SWNT) and multi-wall nanotube (MWNT)), nanofiber (halloysite), nanoneedle (sepiolite), nanoballs (fullerens, allophane), layered nanomaterials (layered silicate, layered titanate), and silicon carbide (SiC).

3. Multifunctional Properties

Polymer nanocomposites have interphases that dominate the composite properties due to the very small size of the nano-filler component. For nano-fillers, at least one dimension is on the nanometer scale, as shown in Figures 2 and 3. The polymers are thermoplastic, thermoset, or rubber and elastomer. The polymer–nano-filler interface is the dominant factor for the nanocomposite properties. The interaction between the polymer molecule is entirely a molecular-level interaction. The surface chemistry and bulk mixing dynamics have affected the incorporation of nanoparticles into the polymer matrix. Since the invention of polymer nanocomposite in 1993 [7], polymer nanocomposites have become an important class of materials that offer superior properties as compared with those of conventional macrocomposites. A new property is the multifunctional properties that extend their scope of application to new areas.

This new class of materials is now being introduced in structural applications, such as gas barrier film, flame retardant product, and other load-bearing applications (Figure 4). The polymer nanocomposites exhibit other property enhancement such as thermal (stability and conductivity) ablation, electrical, optical, tribological, chemical resistance. These multifunctional properties of polymer nanocomposites are discussed in detail in the literature [8–18]. It is a very complex matter to understand the reason why the property enhancement takes place in polymer nanocomposites. Table 1 summarizes the advantages/disadvantages to illustrate this point in new material.

The researchers of Toyota Central Research & Development (TCRD) reported work based on Nylon-6-clay nanocomposites [7]. The resulting composite with a loading of only 4.2 wt% organically modified layered silicate possessed a double modulus, a 50% enhanced strength, and an increase in heat distortion temperature of 80 °C, as compared with the neat Nylon-6 [19]. In recent years, for nanocomposite fabrication, organically modified layered silicate (organoclay) has been used in various polymer systems including epoxy, polyurethanes, and so on [1].

The US Army research laboratory investigated the ballistic impact strength of polycarbonate-layered silicate nanocomposites [6,20]. Nanocomposites showed an important role in longer-range missiles. Koo and colleague investigated the nanocomposites for high-temperature application by cyanate ester, epoxy, phenolic, nylon-11, etc., and the feasibility of using these materials for fire retardant coating, rocket production insulation, rocket nozzle ablative materials, damage tolerant performance [21]. Nanoclay plays an important role in reducing the flammability of coating system for solid rocket exhaust plumes (3600 °C) at very high velocity. Flammability enhancement by organoclay is an important issue for many applications as compared to pure polymer systems [1].



Figure 4. Schematic illustration of three different types of thermodynamically achievable polymer-layered silicate nanocomposites. Reproduced with permission from [1]. © 2003, Elsevier Ltd.

Table 1. Advantages/disadvantages of polymer nanocomposites.

Improved Properties	Disadvantages
Mechanical properties (tensile strength, stiffness, toughness)	Melt viscosity increase
Gas permeability	Dispersion difficulties of nano-fillers
Free volume reduction in matrix polymer	Haze properties
Heat resistance	Sedimentation
Flame retardant	Color issues
Dimensional stability	Cost of creating nano-fillers
Thermal expansion	Safety of nano-fillers
Electrical conductivity	
Proton conductivity	
Field emission	
Ablation resistance	
Chemical resistance	
Optical properties	
Biodegradability	
Crystallization control	
Rheological properties	
Processability	

NASA Langley Center developed transparent nanocomposites with organically modified layered silicate. Those are lightweight and durable and suitable for aerospace applications [6,22]. Using nanoclays in carbon fiber/epoxy reinforced composites cryogenic storage system has been developed [23]. Both mechanical and thermal expansion characteristics were improved to avoid micro cracking and thermal cycling because of the temperature range from -196 to 125 °C for space application.

4. Structure and Characterization Techniques for Nanocomposites

Nanomaterials provide reinforcing efficiency with their high aspect ratio. The properties of a nanocomposite are greatly affected by the size scale of the component phases and the degree of mixing between the two phases. Depending on the nature of the components used (layered silicate or nanofiber) and the method of preparation, the obtained properties may be different [1].

Of particular interest has been recently developed nanocomposites consisting of a polymer and layered silicate because they often exhibit remarkably improved mechanical and various other properties [1,3,5,8], as compared with pure polymer or conventional macrocomposites. Layered silicates have a layer thickness in the order of 1 nm and very high aspect ratio (e.g., 10–1000). Therefore, a few weight percent of layered silicate properly dispersed throughout the polymer matrix provides a much larger surface area for polymer/filler interaction than conventional composites. Depending on the strength of interfacial interaction between polymer matrix and layered silicate (modified or not), three different types of polymer-layered silicate (PLS) nanocomposites are thermodynamically achievable (Figure 4).

(1) Intercalated nanocomposites: in an intercalated nanocomposite, the insertion of polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the silicate layer (clay) to polymer ratio. Properties of the composites typically resemble those of ceramic materials.

(2) Flocculated nanocomposites: conceptually this is same with intercalated nanocomposites; however, silicate layers are sometimes flocculated due to hydroxylated edge–edge interaction of the silicate layers. The length of the oriented collections in the range of 300–800 nm is far larger than the original silicate layer (mean diameter 150 nm) [24]. Such flocculation presumably is governed by an interfacial energy between polymer matrix and organoclays and controlled by ammonium cation-matrix polymer interaction. The polarity of the matrix polymer is of fundamental importance in controlling the nanoscale structure.

(3) Exfoliated nanocomposites: in exfoliated nanocomposites, the individual silicate layers are separated in a continuous polymer matrix by an average distance that is entirely dependent on the layered silicate loading. Usually, the clay content of an exfoliated nanocomposite is much lower than that of intercalated nanocomposites.

The preparative methods are broadly classified into three main categories.

(1) Intercalation of polymer or pre-polymer from solution

This is based on a solvent system in which polymer or pre-polymer is soluble and the silicate layers are swellable. The layered silicate is first swollen in a solvent, such as water, chloroform or toluene, etc. When the polymer and layered silicate solutions are mixed, the polymer chains intercalate and displace the solvent within the interlayer of the silicate. Upon solvent removal, the intercalated structure remains, resulting in polymer-layered silicate (PLS) nanocomposites.

(2) In situ intercalative polymerization method

In this method, the organically modified layered silicate is swollen within the liquid monomer or a monomer solution so as the polymer formation can occur in between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator or by an organic initiator or catalyst fixed through cation exchange inside the interlayer before the swelling step by the monomer.

(3) Melt intercalation method

This method involves annealing, statically or under shear, a mixture of the polymer and organically modified layered silicate above the softening point of the polymer. This method has great advantages over either in situ intercalative polymerization or polymer solution intercalation. Firstly, this method is environmentally benign due to the absence of organic solvents. Secondly, it is compatible with current industrial processes, such as extrusion and injection molding. Melt intercalation method allows the use of polymers which were previously not suitable for in situ polymerization or solution intercalation method. Other possibilities are exfoliation adsorption, and template synthesis [1,13]. Nowadays, this solvent-free method is much preferred for practical industrial material production by its high efficiency and possibility of avoiding environmental hazards.

Analogously, in fibrous or particle-reinforced polymer nanocomposites, dispersion of the nanoparticle and adhesion at the particle–matrix interface play pivotal roles in determining the mechanical properties of the nanocomposite. Without proper dispersion, the nanomaterial will not offer improved mechanical properties over that of conventional composites, in fact, a poorly dispersed nanomaterial may degrade the mechanical properties [1]. Graphite and graphene platelets have a similar geometry (layered sheet structure) with clay; therefore, a clay polymer reinforcement concept is also applicable. Additionally, optimizing the interfacial bond between the particle and the matrix, one can tailor the properties of the overall composite, similar to what is performed on macrocomposites. For example, good adhesion at the interface will improve properties such as interlaminar shear strength, delamination resistance, fatigue, and corrosion resistance.

Various techniques for nanocomposite characterization have been employed. The structure of the nanocomposites has typically been established using a Wide-angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS) analysis, scanning electron microscopy (SEM), and transmission electron microscope (TEM) observation [1,16]. The structure of the PLS nanocomposites has typically been established using WAXD analysis and TEM observation. Due to its easiness and availability WAXD is most commonly used to probe the PLS nanocomposite structure and sometimes to study the kinetics of the polymer melt intercalation [1,16]. By monitoring the position, shape, and intensity of the basal reflections from the distributed silicate layers, the nanocomposite structure either intercalated or exfoliated may be identified. For example, in case of exfoliated nanocomposites, the extensive layer separation associated with the delamination of the

original silicate layers in the polymer matrix results in the eventual disappearance of any coherent X-ray diffraction from the distributed silicate layers.

On the other hand, for intercalated nanocomposites, the finite layer expansion associated with the polymer intercalation results in the appearance of a new basal reflection corresponding to the larger gallery height. Although, WAXD offers a convenient method to determine the interlayer spacing of the silicate layers in the original layered silicates and in the intercalated nanocomposites (within 1–4 nm); however, little can be said about the spatial distribution of the silicate layers or any structural in-homogeneities in the PLS nanocomposites.

Additionally, some layered silicates initially do not exhibit well-defined basal reflection. Thus, peak broadening and intensity decreases are very difficult to study systematically. Therefore, conclusions concerning the mechanism of nanocomposites formation and their structure based solely on WAXD patterns are only tentative. On the other hand, TEM allows a qualitative understanding of the internal structure, spatial distribution of the various phases, and defect structure through direct visualization. However, special care must be exercised to guarantee a representative cross section of the sample.

With SEM, we can obtain images of surface features associated with a sample. In addition, two other microscopies, scanning probe microscopy (SPM) and scanning tunneling microscopy (STM) are useful to analyze nanotube research [16]. The SPM uses the interaction between a sharp tip and a surface to obtain an image. For STM, a sharp conducting tip is held sufficiently close to a surface (typically ~0.5 nm), such that electrons can ‘tunnel’ across the gap [16]. This method provides surface structural and electronic information at atomic level. The invention of the STM inspired the development of other ‘scanning probe’ microscopes, such as atomic force microscope (AFM) [16]. The AFM uses a sharp tip to scan the entire sample. Raman spectroscopy has also proven to be a useful probe for carbon-based material properties [16].

5. Types of Polymers so far Used for Polymer-Layered Silicate (PLS) Nanocomposites

Before describing commercial examples of polymer nanocomposites, we summarize the large variety of polymer systems that have so far been used in nanocomposites preparation with layered silicate can be conventionally classified as below (Tables 2–6).

Table 2. Vinyl polymer classification.

Vinyl Polymer Systems	References
methyl methacrylate (MMA)	[25–38]
MMA copolymers	[39–42]
polyacrylates	[43–45]
polyacrylic acid	[46,47]
polyacrylonitrile (AN)	[48–51]
polystyrene (S)	[52–77]
4-vinylpyridine	[78]
polyacrylamide	[79–81]
polytetrafluoro ethylene	[82]
poly(vinyl alcohol)	[83–86]
poly(N-vinyl pyrrolidone)	[87–91]
poly(vinyl pyrrolidinone)	[92,93]
poly(vinyl pyridine)	[94]
poly(ethylene glycol)	[95]
poly(ethylene vinyl alcohol)	[96]
poly(vinylidene fluoride)	[97]
poly(<i>p</i> -phenylenevinylene)	[98]
polybenzoxazole	[99]
poly(S-co-AN)	[100]
ethyl vinyl alcohol copolymer	[101]
PS-polyisoprene diblock copolymer	[102,103]
other	[104]

Several technologically important polycondensates and rubbers have also been used in the nanocomposite preparation with layered silicate (Table 3).

Table 3. Condensation polymers and rubbers classification.

Condensation Polymer Systems	References
Nylon-6	[6,18,105–127]
Other polyamides	[128–134]
poly(ϵ -caprolactone) (PCL)	[135–146]
Poly(ethylene terephthalate) (PET)	[147–153]
poly (trimethylene terephthalate)	[154,155]
poly(butylene terephthalate)	[156]
polycarbonate	[157,158]
Polyethylene oxide	[159–179]
polyethylene oxide copolymers	[180,181]
poly (ethylene imine)	[182]
poly (dimethyl siloxane)	[183–188]
polybutadiene	[189]
polybutadiene copolymers	[190–192]
epoxidized natural rubber	[193,194]
epoxy polymer resins	[195–216]
phenolic resins	[217,218]
polyurethanes	[219–223]
polyurethane uera	[224]
polyimides	[225–240]
poly(amic acid)	[241,242]
polysulphone	[243]
polyetherimide	[244,245]
fluoropoly(ether-imide)	[246]

Polyolefines such as polypropylene (PP) and polyethylene (PE) have been used and are shown in Table 4.

Table 4. Polyolefines classification.

Polyolefines	References
PP	[247–284]
PE	[285–294]
PE oligomers	[295]
poly(ethylene-co-vinyl acetate)	[296]
ethylene propylene diene methylene linkage	[297]
poly(1-butene)	[298]

In addition to the above-mentioned conventional polymers, several interesting developments have also taken place in the preparation of PLS nanocomposites with some specialty polymers (Table 5).

Table 5. Specialty polymers.

Specialty Polymers	References
polypyrrole	[299–304]
poly (N-vinylcarbazole)	[305,306]
polyaniline	[307–320]
poly(<i>p</i> -phenylene vinylene)	[321]
liquid crystalline polymers	[322–326]
hyper branch polymers	[327]
cyanate ester	[328]
Nafion®	[329]
Aryl-ethany-terminated imide oligomer	[330]

Today, tremendous amounts and varieties of plastics, notably polyolefin, polystyrene and poly (vinyl chloride), are currently produced mostly from fossil fuels, consumed and discarded into the environment, ending up as spontaneously undegradable wastes. Their disposal by incineration always produces large amounts of CO₂ and contributes to global warming, and some but not all of them even release toxic gases and again makes global pollution. For these reasons, there is an urgent need for the development of “green polymeric materials” that would not involve the use of toxic or noxious components in their manufacture and could allow to be composted to naturally occurring degradation products. Accordingly, polylactide (PLA) is of increasing commercial interest because it is made from renewable sources and readily biodegradable.

Okamoto and colleagues [24] have started the preparation, characterization and materials properties of various kinds of biodegradable polymers/layered silicate nanocomposites having properties suitable for a wide-range of applications (Table 6).

Table 6. Biodegradable polymers.

Biodegradable Polymers	References
Poly(lactide (PLA)	[24,331–340]
poly (butylene succinate)	[341–343]
PCL	[135–146]
unsaturated polyester	[344]
poly(hydroxy butyrate	[345–347]
aliphatic polyester	[348–351]

6. Commercial Market Opportunities

The first commercial example of polymer nanocomposites in automotive applications was nylon-6–clay nanocomposites used for making timing belt covers (the Toyota Motor Company, 1991) [352]. More significantly, these nanocomposites were used in under the hood application in the Toyota Camry [20]. Related to the early successful development, General Motors Corporation (GMC) developed a step assist component for 2002 GMC Safari and Chevrolet Astro vans, which are made of thermoplastic polyolefin–clay nanocomposite. This nanocomposite showed lighter and stiffer, more robust at low temperatures, and easily recyclable. GMC also tried to use these nanocomposites in the lateral protection wire of the 2004 Chevrolet Impala and 2005 Hummer H2 cargo because they are 7% lighter in weight and present a better surface appearance (Figure 5a,c,d).

Putsch and Sud-Chemie jointly prepared Elan XP, a compound of polypropylene and polystyrene compatibilized by clay, which is used as an interior air vent for the Audi A4 and a Volkswagen van (Figure 5f).

InMat Inc. has developed several applications for their nanocomposite coatings. The nanocomposite coating of the Wilson tennis balls maintains the internal pressure for an extended period of time (Figure 5h). The Wilson tennis balls have a double core, which is coated by a polymer–clay nanocomposite which acts as a gas barrier, doubling the ball’s shelf life. This technology was extended to the rubber industry and was incorporated into soccer balls or into bicycle tires.

The barrier properties of polymer nanocomposite have also been extended to liquid or molecule, such as water, since these liquids are responsible for polymer deterioration in some instances. Ube Industries reveal significant reduction in fuel transmission via polyamide-6/66 polymers by incorporation of nano-clay particles, resulting in reduced fuel emission for fuel tank and fuel line components (Figure 5b).

Improvement in barrier resistance in nanocomposites plays an important role in beverage applications. When the layers are delaminated, it increases the effective path length for molecular diffusion and the path becomes highly tortuous to reduce the effect of gas and moisture transmission through the film [1]. Based on the barrier properties, nanocomposite packaging films made in PET have been studied as replacements for conventional polymer

films [24]. Coor Inc. developed commercial PET–clay nanocomposite product for beer bottles (Figure 5i). Unitika Ltd. developed PLA–clay nanocomposite for bottle applications [24].

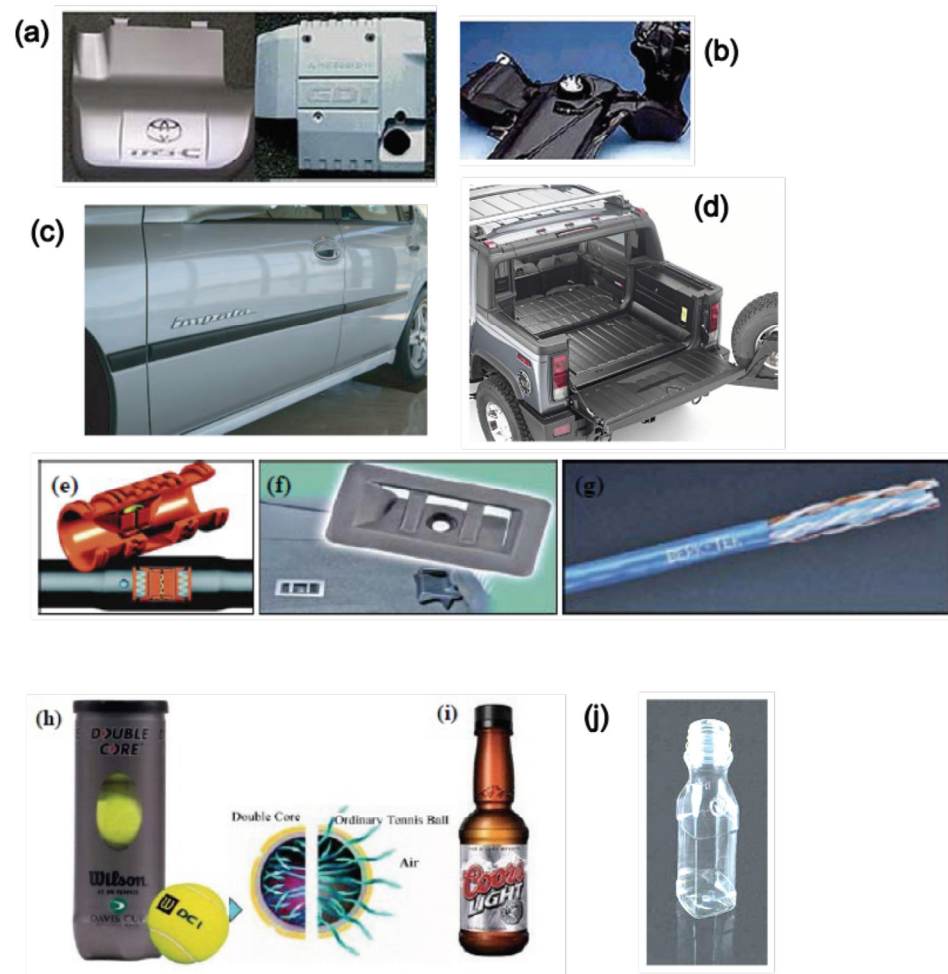


Figure 5. (a) Toyota and Mitsubishi engine covers and (b) gasoline tank injection-molded from polyamide-6/clay nanocomposites. (c) GMC's Chevrolet Impala 2004: nanocomposite application and (d) Polypropylene/EPDM-based nanocomposite: GMC's 2005 Hummer H2 cargo bed uses ~7 lb, Trough the courtesy of M. Verbrugge, General Motors Corporation (GMC). (e) Geoflow's linear low-density polyethylene/clay nanocomposite drip emitter for irrigation tubing ensures timed release of herbicide from the plastic. (f) Putsch and Sud-Chemie jointly prepared Elan XP, a compound of polypropylene and polystyrene compatibilized by clay, which is used as an interior air vent for the Audi A4 and a Volkswagen van. (g) Due to the good flame retardancy of polymer/clay materials, Nexans' introduced cable jacketing nanocomposite, the first such product for plenum cable used in office buildings. (h) Wilson's double-core tennis balls uses. (i) Coor's beer bottles. (j) Low O₂ gas permeability poly(*L*-lactic acid) bottles from Unitika Ltd. [353].

Thermal stability and fire retardancy have been investigated for commodity polymers. Due to the good flame retardancy of polymer–clay nanocomposite materials, Nexans' introduced cable jacketing nanocomposite, the first such product for plenum cable used in office buildings (Figure 5g).

In some cases, the value of polymer nanocomposites technology relates to value-added performance of medical and agricultural applications not present in neat polymer but occurs via the low-volume introduction of organically modified clay nanoparticles. For example, Geoflow's linear low-density polyethylene–clay nanocomposite drip emitter for irrigation tubing ensures timed release of herbicide from the plastic (Figure 5e).

7. Future Outlook

The potential of nanocomposites in various sectors of research and application is promising in many parts of the world. With only moderate success in the last two decades, researchers need to continue exploring strategies for optimization. Until now, there are some niche applications where nanotechnology is in the market, but the main impact is at least 10 years away [354].

Biodegradable polymer-based nanocomposites have a great deal of future promise for potential applications as high-performance biodegradable materials. These are entirely new types of materials based on plant and nature materials (organoclay). When disposed of in compost, these are safely decomposed into CO₂, water, and humus through the activity of microorganisms. The CO₂ and water will become corn or sugarcane again through plant photosynthesis. Undoubtedly, their unique properties originating from the controlled nanostructure paves the way for a much broader range of applications (already commercially available through Unitika Ltd., Japan), and opens a new dimension for plastics and composites [24].

Sustainability needs to be further enhanced based on the Life Cycle Assessment (LCA) presented in the study on biodegradable polymer-based nanocomposites. On the other hand, to enable complete recycling, society must also require manufacturers to present LCA and assessment results comparable to research efforts on all environmental impacts of nanocomposite materials.

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References

1. Sinha Ray, S.; Okamoto, M. Polymer/Layered Silicate Nanocomposites: A Review from Preparation to Processing. *Prog. Polym. Sci.* **2003**, *28*, 1539–1641. [\[CrossRef\]](#)
2. Anastasiadis, S.H.; Russel, T.P.; Satija, S.K.; Majkrzak, C.F. The morphology of symmetric diblock copolymers as revealed by neutron reflectivity. *J. Chem. Phys.* **1990**, *92*, 5677–5691. [\[CrossRef\]](#)
3. Okamoto, M. Clay-based Polymeric Nanocomposites: Network formation and solid-state shear processing. In *Processing Polymer Nanocomposites*; Kenig, S., Ed.; Carl Hanser Verlag GmbH & Co.: Munich, Germany, 2019; pp. 255–295.
4. Thostenson, E.; Li, C.; Chou, T. Review Nanocomposites in Context. *J. Compo. Sci. Tech.* **2005**, *65*, 491–516. [\[CrossRef\]](#)
5. Schmidt, D.; Shah, D.; Giannelis, E.P. New Advances in Polymer/Layered Silicate Nanocomposites. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 205–212. [\[CrossRef\]](#)
6. Hussain, F.; Hojjati, M.; Okamoto, M.; Gorga, R.E. Review article: Polymer-matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview. *J. Composite Mater.* **2006**, *40*, 1511–1575. [\[CrossRef\]](#)
7. Usuki, A.; Kawasumi, M.; Kojima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O.J. Swelling Behavior of Montmorillonite Cation Exchanged for V-amino Acids by E-caprolactam. *J. Mater. Res.* **1993**, *8*, 1174–1178. [\[CrossRef\]](#)
8. Utracki, L.A. *Clay-Containing Polymeric Nanocomposites*; Rapra Technology Ltd.: Shawbury, UK, 2004.
9. Advani, S.G. (Ed.) *Processing and Properties of Nanocomposites*; World Scientific & Imperial College Press: London, UK, 2007.
10. Ruiz-Hitzky, E.; Ariga, K.; Lvov, Y.M. (Eds.) *Bio-Inorganic Hybrid Nanomaterials*; Wiley-VCH: Weinheim, Germany, 2008.
11. Lau, A.K.-T.; Hussain, F.; Lafdi, K. (Eds.) *Nano-and Biocomposites*; CRC Press: Boca Raton, FL, USA; Taylor and Francis: New York, NY, USA, 2009.
12. Avérous, L.; Pollet, E. (Eds.) *Environmental Silicate Nano-Biocomposites*; Springer: London, UK, 2012.
13. Thomas, S.; Stephen, R. (Eds.) *Rubber Nanocomposites: Preparation, Properties, and Application*; John Wiley & Sons: Singapore, 2010.
14. Gao, F. (Ed.) *Advances in Polymer Nanocomposites: Types and Application*; Woodhead Publishing: Cambridge, UK, 2012.
15. Theng, B.K.G. (Ed.) *Formation and Properties of Clay-Polymer Complexes in Developments in Clay Science*; Elsevier: Amsterdam, The Netherlands, 2012; Volume 4.
16. Mittal, V. (Ed.) *Characterization Techniques for Polymer Nanocomposites*; Wiley-VCH: Weinheim, Germany, 2012.
17. Sinha Ray, S. (Ed.) *Clay-Containing Polymer Nanocomposites: From Fundamental to Real Applications*; Elsevier: Amsterdam, The Netherlands, 2013.

18. Sinha Ray, S. (Ed.) *Environmentally Friendly Polymer Nanocomposites: Types, Processing and Properties*; Woodhead Publishing: London, UK, 2013.
19. Okada, A.; Usuki, A. The Chemistry of Polymer-Clay Hybrids. *Mater. Sci. Eng. C* **1995**, *3*, 109–115. [[CrossRef](#)]
20. Hsieh, A.J. *Ballistic Impact Measurements of Polycarbonate Layered Silicate Nanocomposites*; ANTEC; Cambridge University Press: Cambridge, UK, 2001.
21. Koo, J.; Pilato, L. Polymer Nanostructured Materials for High Temperature Applications. *SAMPE J.* **2005**, *41*, 7–15.
22. Transparent Nanocomposites for Aerospace Applications. *Adv. Compos. Bull.* 2004. Available online: <https://www.technical-textiles.net> (accessed on 10 January 2023).
23. Timmerman, J.; Hayes, B.; Seferis, J. Nanoclay Reinforcement Effects on the Cryogenic Micro Cracking of Carbon Fiber/Epoxy Composites. *Compo. Sci. Tech.* **2002**, *62*, 1249–1258. [[CrossRef](#)]
24. Ray, S.S.; Yamada, K.; Okamoto, M.; Ogami, A.; Ueda, K. New Polylactide/Layered Silicate Nanocomposites. 3. High-Performance Biodegradable Materials. *Chem. Mater.* **2003**, *15*, 1456–1465.
25. Blumstein, A.; Malhotra, S.L.; Watterson, A.C. Polymerization of monolayers. V. Tacticity of the insertion poly(methyl methacrylate). *J. Polym. Sci. Part A-2 Polym. Phys.* **1970**, *8*, 1599–1615. [[CrossRef](#)]
26. Lee, D.C.; Jang, L.W. Preparation and characterization of PMMA–clay composite by emulsion polymerization. *J. Appl. Polym. Sci.* **1996**, *61*, 1117–1122. [[CrossRef](#)]
27. Chen, G.; Chen, X.; Lin, Z.; Ye, W.; Yao, K. Preparation and properties of PMMA/clay nanocomposite. *J. Mater. Sci. Lett.* **1999**, *18*, 1761–1763. [[CrossRef](#)]
28. Chen, G.; Yao, K.; Zhao, J. Montmorillonite clay/poly(methylmethacrylate) hybrid resin and its barrier property to the plasticizer within poly(vinyl chloride) composite. *J. Appl. Polym. Sci.* **1999**, *73*, 425–430. [[CrossRef](#)]
29. Tabtiang, A.; Lumlong, S.; Venables, R.A. Influence of preparation method upon structure and relaxation characteristics PMMA/clay composites. *Eur. Polym. J.* **2000**, *36*, 2559–2568. [[CrossRef](#)]
30. Tabtiang, A.; Lumlong, S.; Venables, R.A. The effects of shear and thermal history upon the microstructure of solution polymerized poly(methyl methacrylate)/clay composites. *Polym. Plast. Technol. Eng.* **2000**, *39*, 293–303. [[CrossRef](#)]
31. Okamoto, M.; Morita, S.; Taguchi, H.; Kim, Y.H.; Kotaka, T.; Tateyama, H. Synthesis and structure of smectic clay/poly(methyl methacrylate) and clay polystyrene nanocomposites via in situ intercalative polymerization. *Polymer* **2000**, *41*, 3887–3890. [[CrossRef](#)]
32. Bandyopadhyay, S.; Giannelis, E.P. Thermal and thermomechanical properties of PMMA nanocomposites. *Polym. Mater. Sci. Eng.* **2000**, *82*, 208–209.
33. Huang, X.; Brittain, W.J. Synthesis and characterization of PMMA nanocomposites by suspension and emulsion polymerization. *Macromolecules* **2001**, *34*, 3255–3260. [[CrossRef](#)]
34. Zeng, C.; Lee, L.J. Poly(methyl methacrylate) and polystyrene/clay nanocomposites prepared by in-situ polymerization. *Macromolecules* **2000**, *34*, 4098–4103. [[CrossRef](#)]
35. Salahuddin, N.; Shehata, M. Poly(methyl methacrylate)–montmorillonite composites: Preparation, characterization and properties. *Polymer* **2001**, *42*, 8379–8385. [[CrossRef](#)]
36. Bottcher, H.; Hallensleben, M.L.; Nu, S.; Wurm, H.; Bauer, J.; Behrens, P. Organic/inorganic hybrids by living/controlled ATRP grafting from layered silicates. *J. Mater. Chem.* **2002**, *12*, 1351–1354. [[CrossRef](#)]
37. Zerda, A.S.; Caskey, T.C.; Lesser, A.J. Highly concentrated, intercalated silicate nanocomposites: Synthesis and characterization. *Macromolecules* **2003**, *36*, 1603–1608. [[CrossRef](#)]
38. Su, S.; Wilkie, C.A. Exfoliated poly(methyl methacrylate) and polystyrene nanocomposites occur when the clay cation contains a vinyl monomer. *J. Polym. Sci. Part B Polym. Phys.* **2003**, *41*, 1124–1135. [[CrossRef](#)]
39. Forte, C.; Geppi, M.; Giamberini, S.; Ruggeri, G.; Veracini, C.A.; Mendez, B. Structure determination of clay/methylmethacrylate copolymer interlayer complexes by means of ¹³C solid state nmr. *Polymer* **1998**, *39*, 2651–2656. [[CrossRef](#)]
40. Dietsche, F.; Thomann, Y.; Thomann, R.; Mulhaupt, R. Translucent acrylic nanocomposites containing anisotropic laminated nanoparticles derived from intercalated layered silicates. *J. Appl. Polym. Sci.* **2000**, *75*, 396–405. [[CrossRef](#)]
41. Okamoto, M.; Morita, S.; Kotaka, T. Dispersed structure and ionic conductivity of smectic clay/polymer nanocomposites. *Polymer* **2001**, *42*, 2685–2688. [[CrossRef](#)]
42. Okamoto, M.; Morita, S.; Kim, Y.H.; Kotaka, T.; Tateyama, H. Dispersed structure change of smectic clay/poly(methylmethacrylate) nanocomposites by copolymerization with polar comonomers. *Polymer* **2001**, *42*, 1201–1206. [[CrossRef](#)]
43. Seckin, T.; Onal, Y.; Aksoy, I.; Yakinci, M.E. Synthesis and characterization of novel polyacrylate–clay sol–gel materials. *J. Mater. Sci.* **1996**, *31*, 3123–3127. [[CrossRef](#)]
44. Dietsche, F.; Mulhaupt, R. Thermal properties and flammability of acrylic nanocomposites based upon organophilic layered silicates. *Polym. Bull.* **1999**, *43*, 395–402. [[CrossRef](#)]
45. Chen, Z.; Huang, C.; Liu, S.; Zhang, Y.; Gong, K. Synthesis, characterization and properties of clay–polyacrylate hybrid materials. *J. Appl. Polym. Sci.* **2000**, *75*, 796–801. [[CrossRef](#)]
46. Billingham, J.; Breen, C.; Yarwood, J. Adsorption of polyamine, polyacrylic acid and poly(ethylene glycol) on montmorillonite: An situ study using ATR-FTIR. *Vib. Spectrosc.* **1997**, *14*, 19–34. [[CrossRef](#)]
47. Lin, J.; Wu, J.; Yang, Z.; Pu, M. Synthesis and properties of poly(acrylic acid)/mica superabsorbent nanocomposite. *Macromol. Rapid. Commun.* **2001**, *22*, 422–424. [[CrossRef](#)]

48. Blumstein, R.; Blumstein, A.; Parikh, K.K. Synthesis and properties of polyacrylonitrile/clay nanocomposite. *Appl. Polym. Symp.* **1994**, *25*, 81–89.
49. Sugahara, Y.; Satahara, S.; Kuroda, K.; Kato, C. Evidence for the formation of interlayer polyacrylonitrile in kaolinite. *Clays Clay Miner.* **1988**, *36*, 343–348. [[CrossRef](#)]
50. Bergaya, F.; Kooli, F. Intercalated polyacrylonitrile/clay nanocomposite. *Clay Miner.* **1991**, *26*, 33–40. [[CrossRef](#)]
51. Choi, Y.S.; Wang, K.H.; Xu, M.; Chung, I.J. Synthesis of exfoliated polyacrylonitrile/Na-MMT nanocomposites via emulsion polymerization. *Chem. Mater.* **2002**, *14*, 2936–2939. [[CrossRef](#)]
52. Kato, C.; Kuroda, K.; Takahara, H. Preparation and electrical properties of quaternary ammonium montmorillonite–polystyrene complexes. *Clays Clay Miner.* **1981**, *29*, 294–298. [[CrossRef](#)]
53. Akelah, A. Polystyrene/clay nanocomposites. In *Polymers and Other Advanced Materials: Emerging Technologies and Business Opportunities*; Prasad, P.N., Mark, J.E., Ting, F.J., Eds.; Plenum Press: New York, NY, USA, 1995; pp. 625–630.
54. Vaia, R.A.; Jant, K.D.; Kramer, E.J.; Giannelis, E.P. Microstructural evaluation of melt-intercalated polymer-organically modified layered silicate nanocomposites. *Chem. Mater.* **1996**, *8*, 2628–2635. [[CrossRef](#)]
55. Park, C.I.; Park, O.O.; Lim, J.G.; Kim, H.J. The fabrication of syndiotactic polystyrene/organophilic clay nanocomposites and their properties. *Polymer* **2001**, *42*, 7465–7475. [[CrossRef](#)]
56. Akelah, A.; Moet, M. Polymer–clay nanocomposites: Freeradical grafting of polystyrene on to organophilic montmorillonite interlayers. *J. Mater. Sci.* **1996**, *31*, 3589–3596. [[CrossRef](#)]
57. Sikka, M.; Cerini, L.N.; Ghosh, S.S.; Winey, K.I. Melt intercalation of polystyrene in layered silicates. *J. Polym. Sci. Part B Polym. Phys.* **1996**, *34*, 1443–1449. [[CrossRef](#)]
58. Laus, M.; Camerani, M.; Lelli, M.; Sparnacci, K.; Sandrolini, F.; Francescangeli, O.F. Hybrid nanocomposites based on polystyrene and a reactive organophilic clay. *J. Mater. Sci.* **1998**, *33*, 2883–2888. [[CrossRef](#)]
59. Doh, J.G.; Cho, I. Synthesis and properties of polystyrene–organoammonium montmorillonite hybrid. *Polym. Bull.* **1998**, *41*, 511–518. [[CrossRef](#)]
60. Porter, T.L.; Hagerman, M.E.; Reynolds, B.P.; Eastman, M.E. Inorganic/organic host–guest materials: Surface and interclay reactions of styrene with copper(II)-exchanged hectorite. *J. Polym. Sci. Part B Polym. Phys.* **1998**, *36*, 673–679. [[CrossRef](#)]
61. Hasegawa, N.; Okamoto, H.; Kawasumi, M.; Usuki, A. Preparation and mechanical properties of polystyrene/clay hybrid. *J. Appl. Polym. Sci.* **1999**, *74*, 3359–3364. [[CrossRef](#)]
62. Noh, M.W.; Lee, D.C. Synthesis and characterization of PS–clay nanocomposite by emulsion polymerization. *Polym. Bull.* **1999**, *42*, 619–626. [[CrossRef](#)]
63. Weimer, M.W.; Chen, H.; Giannelis, E.P.; Sogah, D.Y. Direct synthesis of dispersed nanocomposites by in situ living free radical polymerization using a silicate-anchored initiator. *J. Am. Chem. Soc.* **1999**, *121*, 1615–1616. [[CrossRef](#)]
64. Fu, X.; Qutubuddin, S. Polymer–clay nanocomposites: Exfoliation of organophilic montmorillonite nanolayers in polystyrene. *Polymer* **2001**, *42*, 807–813. [[CrossRef](#)]
65. Chen, G.; Liu, S.; Zhang, S.; Qi, Z. Self-assembly in a polystyrene/montmorillonite nanocomposite. *Macromol. Rapid Commun.* **2000**, *21*, 746–749. [[CrossRef](#)]
66. Lim, Y.T.; Park, O.O. Rheological evidence for the microstructure of intercalated polymer/layered silicate nanocomposite. *Macromol. Rapid Commun.* **2000**, *21*, 231–235. [[CrossRef](#)]
67. Hoffman, B.; Dietrich, C.; Thomann, R.; Friedrich, C.; Mulhaupt, R. Morphology and rheology of polystyrene nanocomposites based upon organoclay. *Macromol. Rapid Commun.* **2000**, *21*, 57–61. [[CrossRef](#)]
68. Zilg, C.; Thomann, R.; Baumert, M.; Finter, J.; Mulhaupt, R. Organic/inorganic hybrid materials and nanocomposites based upon layered silicate modified with cyclic imidines. *Macromol. Rapid Commun.* **2000**, *21*, 1214–1219. [[CrossRef](#)]
69. Wu, H.D.; Tseng, C.R.; Chang, F.C. Chain conformation and crystallization behavior of the syndiotactic polystyrene nanocomposites studied using Fourier transform infrared analysis. *Macromolecules* **2001**, *34*, 2992–2999. [[CrossRef](#)]
70. Xiao, P.; Xiao, M.; Gong, K. Preparation of exfoliated graphite/polystyrene composite by polymerization-filling technique. *Polymer* **2001**, *42*, 4813–4816. [[CrossRef](#)]
71. Tseng, C.-R.; Wu, J.-Y.; Lee, H.-Y.; Chang, F.-C. Preparation and crystallization behavior of syndiotactic polystyrene–clay nanocomposites. *Polymer* **2001**, *42*, 10063–10070. [[CrossRef](#)]
72. Zhu, J.; Morgan, A.B.; Lamelas, F.J.; Wilkie, C.A. Fire properties of polystyrene–clay nanocomposites. *Chem. Mater.* **2001**, *13*, 3774–3780. [[CrossRef](#)]
73. Zeng, Q.H.; Wang, D.Z.; Yu, A.B.; Lu, G.Q. Synthesis of polymer–montmorillonite nanocomposites by in situ intercalative polymerization. *Nanotechnology* **2002**, *13*, 549–553. [[CrossRef](#)]
74. Beyer, F.L.; Tan, N.C.B.; Dasgupta, A.; Galvin, M.E. Polymerlayered silicate nanocomposites from model surfactants. *Chem. Mater.* **2002**, *14*, 2983–2988. [[CrossRef](#)]
75. Gilman, J.W.; Awad, W.H.; Davis, R.D.; Shields, J.; Harris, R.H., Jr.; Davis, C.; Morgan, A.B.; Sutto, T.E.; Callahan, J.; Trulove, P.C.; et al. Polymer/layered silicate nanocomposites from thermally stable trialkylimidazolium-treated montmorillonite. *Chem. Mater.* **2002**, *14*, 3776–3785. [[CrossRef](#)]
76. Argoti, S.D.; Reeder, S.; Zhao, H.; Shipp, D.A. Polystyrene nanocomposites using atom transfer radical polymerization. *Polym. Prepr.* **2002**, *43*, 267–268.

77. Gelfer, M.Y.; Hyun, H.S.; Liu, L.; Hsiao, B.S.; Chu, B.; Rafailovich, M.; Si, M.; Zaitsev, V. Effect of organoclays on morphology and thermal and rheological properties of polystyrene and poly(methyl methacrylate) blends. *J. Polym. Sci. Part B Polym. Phys.* **2003**, *41*, 44–54. [\[CrossRef\]](#)
78. Friedlander, H.Z.; Frink, C.R. Organized polymerization. III. Monomers intercalated in montmorillonite. *J. Polym. Sci. Part B* **1964**, *2*, 475–479. [\[CrossRef\]](#)
79. Churochkina, N.A.; Starodoubtsev, S.G.; Khokhlov, A.R. Swelling and collapse of the gel composites based on natural and slightly charged poly(acrylamide) gels containing Na⁺-montmorillonite. *Polym. Gels Netw.* **1998**, *6*, 205–215. [\[CrossRef\]](#)
80. Gao, D.; Heimann, R.B.; Williams, M.C.; Wardhaugh, L.T.; Muhammad, M. Rheological properties of poly(acrylamide)–bentonite composite hydrogels. *J. Mater. Sci.* **1999**, *34*, 1543. [\[CrossRef\]](#)
81. Xia, X.; Yih, J.; D'Souza, N.A.; Hu, Z. Swelling and mechanical behavior of poly(N-isopropylacrylamide)/Na⁺ montmorillonite layered silicates composite gels. *Polymer* **2003**, *44*, 3389–3393. [\[CrossRef\]](#)
82. Wheeler, A. Poly(vinyl alcohol)/clay nanocomposites. U.S. Patent 2,847,391, 12 August 1958.
83. Ogata, N.; Kawakage, S.; Ogihara, T. Poly(vinyl alcohol)–clay and poly(ethylene oxide)–clay blend prepared using water as solvent. *J. Appl. Polym. Sci.* **1997**, *66*, 573–581. [\[CrossRef\]](#)
84. Matsuyama, H.; Young, J.F. Intercalation of polymers in calcium silicate hydrate: A new synthetic approach to biocomposites. *Chem. Mater.* **1999**, *11*, 16–19. [\[CrossRef\]](#)
85. Strawhecker, K.E.; Manias, E. Structure and properties of poly(vinyl alcohol)/Na⁺-montmorillonite nanocomposites. *Chem. Mater.* **2000**, *12*, 2943–2949. [\[CrossRef\]](#)
86. Wang, Y.; Wang, Y.; Yan, D. Properties of poly(vinyl alcohol)/montmorillonite nanocomposite fiber. *Polym. Prepr.* **2003**, *44*, 1102–1103.
87. Francis, C.W. Adsorption of polyvinylpyrrolidone on reference clay minerals. *Soil Sci.* **1973**, *115*, 40–54. [\[CrossRef\]](#)
88. Carrado, K.A.; Xu, L. In-situ synthesis of polymer–clay nanocomposites from silicate gel. *Chem. Mater.* **1998**, *10*, 1440–1445. [\[CrossRef\]](#)
89. Gultek, A.; Seckin, T.; Onal, Y.; Icduygu, G. Preparation and phenol captivating properties of polyvinylpyrrolidone–montmorillonite hybrid materials. *J. Appl. Polym. Sci.* **2001**, *81*, 512–519. [\[CrossRef\]](#)
90. Levy, R.; Francis, C.W. Interlayer adsorption of polyvinylpyrrolidone on montmorillonite. *J. Colloid Interface Sci.* **1975**, *50*, 442–450. [\[CrossRef\]](#)
91. Koo, C.M.; Ham, H.T.; Choi, M.H.; Kim, S.O.; Chung, I.J. Characteristic of poly(vinyl pyrrolidone)-layered silicate nanocomposites prepared by attrition ball milling. *Polymer* **2003**, *44*, 681–689. [\[CrossRef\]](#)
92. Komori, Y.; Sugahara, Y.; Kuroda, K. Direct intercalation of poly(vinylpyrrolidinone) into kaolinite by a refined guest displacement method. *Chem. Mater.* **1999**, *11*, 3–6. [\[CrossRef\]](#)
93. Nisha, A.; Rajeswari, M.K.; Dhamodharan, R. Intercalative redox polymerization and characterization of poly(n-vinyl-2-pyrrolidinone) in the gallery of vermiculite: A novel inorganic–organic hybrid material. *J. Appl. Polym. Sci.* **2000**, *76*, 1825–1830. [\[CrossRef\]](#)
94. Fournaris, K.G.; Karakassides, M.A.; Petridis, D.; Yiannakopoulou, K. Clay–polyvinylpyridine nanocomposites. *Chem. Mater.* **1999**, *11*, 2372–2381. [\[CrossRef\]](#)
95. Parfitt, R.L.; Greenland, D.J. The adsorption of poly(ethylene glycols) on clay minerals. *Clay Miner.* **1970**, *8*, 305–315. [\[CrossRef\]](#)
96. Zhao, X.; Urano, K.; Ogasawara, S. Adsorption of poly(ethylene vinyl alcohol) from aqueous solution on montmorillonite clays. *Colloid Polym. Sci.* **1989**, *267*, 899–906. [\[CrossRef\]](#)
97. Priya, L.; Jog, J.P. Intercalated poly(vinylidene fluoride)/clay nanocomposites: Structure and properties. *J. Polym. Sci. Part B Polym. Phys.* **2003**, *41*, 31–38. [\[CrossRef\]](#)
98. Oriakhi, C.O.; Zhang, X.; Lerner, M.M. Synthesis and luminescence properties of a poly(p-phenylenevinylene)/montmorillonite layered nanocomposite. *Appl. Clay. Sci.* **1999**, *15*, 109–118. [\[CrossRef\]](#)
99. Hsu, S.L.C.; Chang, K.C. Synthesis and properties of polybenzoxazole–clay nanocomposites. *Polymer* **2002**, *43*, 4097–4101. [\[CrossRef\]](#)
100. Kim, S.W.; Jo, W.H.; Lee, M.S.; Ko, M.B.; Jho, J.Y. Preparation of clay-dispersed poly(styrene-co-acrylonitrile) nanocomposites using poly(1-caprolactone) as a compatibilizer. *Polymer* **2001**, *42*, 9837–9842. [\[CrossRef\]](#)
101. Artzi, N.; Nir, Y.; Nakris, M.; Seigmann, A. Melt blending of ethylene–vinyl alcohol copolymer/clay nanocomposites: Effect of the clay type and processing conditions. *J. Polym. Sci. Part B Polym. Phys.* **2002**, *40*, 1741–1753. [\[CrossRef\]](#)
102. Ren, J.; Silva, A.S.; Krishnamoorti, R. Linear viscoelasticity of disordered polystyrene–polyisoprene block copolymer based layered-silicate nanocomposites. *Macromolecules* **2000**, *33*, 3739–3746. [\[CrossRef\]](#)
103. Mitchell, C.A.; Krishnamoorti, R. Rheological properties of diblock copolymer/layered-silicate nanocomposites. *J. Polym. Sci. Part B Polym. Phys.* **2002**, *40*, 1434–1443. [\[CrossRef\]](#)
104. Mark, J.E. Ceramic reinforced polymers and polymermodified ceramics. *Polym. Eng. Sci.* **1996**, *36*, 2905–2920. [\[CrossRef\]](#)
105. Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. Synthesis of nylon-6–clay hybrid. *J. Mater. Res.* **1993**, *8*, 1179–1183. [\[CrossRef\]](#)
106. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. Mechanical properties of nylon6–clay hybrid. *J. Mater. Res.* **1993**, *8*, 1185–1189. [\[CrossRef\]](#)

107. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. Synthesis of nylon-6 hybrid by montmorillonite intercalated with 1-caprolactam. *J. Polym. Sci. Part A Polym. Chem.* **1993**, *31*, 983–986. [\[CrossRef\]](#)
108. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. One-pot synthesis of nylon 6–clay hybrid. *J. Polym. Sci. Part A Polym. Chem.* **1993**, *31*, 1755–1758. [\[CrossRef\]](#)
109. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. Sorption of water in nylon 6–clay hybrid. *J. Appl. Polym. Sci.* **1993**, *49*, 1259–1264. [\[CrossRef\]](#)
110. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O.; Kaji, K. Fine structure of nylon 6–clay hybrid. *J. Polym. Sci. Part B Polym. Phys.* **1994**, *32*, 625–630. [\[CrossRef\]](#)
111. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O.; Kaji, K. Novel preferred orientation in injection-molded nylon 6–clay nanocomposites. *J. Polym. Sci. Part B Polym. Phys.* **1995**, *33*, 1039–1045. [\[CrossRef\]](#)
112. Usuki, A.; Koiwai, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. Nylon 6/clay nanocomposites. *J. Appl. Polym. Sci.* **1995**, *55*, 119–123. [\[CrossRef\]](#)
113. Alexandre, M.; Dubois, P. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Mater. Sci. Eng. R* **2000**, *28*, 1–63. [\[CrossRef\]](#)
114. Liu, L.M.; Qi, Z.N.; Zhu, X.G. Studies on nylon 6/clay nanocomposites by melt-intercalation process. *J. Appl. Polym. Sci.* **1999**, *71*, 1133–1138. [\[CrossRef\]](#)
115. Wu, S.H.; Wang, F.Y.; Ma, C.-C.M.; Chang, W.C.; Kuo, C.T.; Kuan, H.C.; Chen, W.J. Mechanical, thermal and morphological properties of glass fiber and carbon fiber reinforced polyamide-6 and polyamide-6/clay nanocomposites. *Mater. Lett.* **2001**, *49*, 327–333. [\[CrossRef\]](#)
116. Lincoln, D.M.; Vaia, R.A.; Wang, Z.G.; Hsiao, B.S. Secondary structure and elevated temperature crystallite morphology of nylon-6/layered silicate nanocomposites. *Polymer* **2001**, *42*, 1621–1631. [\[CrossRef\]](#)
117. Medellin-Rodriguez, F.J.; Burger, C.; Hsiao, B.S.; Chu, B.; Vaia, R.A.; Phillips, S. Time-resolved shear behavior of end-tethered nylon 6–clay nanocomposites followed by non-isothermal crystallization. *Polymer* **2001**, *42*, 9015–9023. [\[CrossRef\]](#)
118. Dennis, H.R.; Hunter, D.L.; Chang, D.; Kim, S.; White, J.L.; Cho, J.W.; Paul, D.R. Effect of melt processing conditions on the extent of exfoliation in organoclay-based nanocomposites. *Polymer* **2001**, *42*, 9513–9522. [\[CrossRef\]](#)
119. VanderHart, D.L.; Asano, A.; Gilman, J.W. Solid-state NMR investigation of paramagnetic nylon-6 clay nanocomposites. 1. Crystallinity, morphology, and the direct influence of Fe_3^+ on nuclear spins. *Chem. Mater.* **2001**, *13*, 3781–3795. [\[CrossRef\]](#)
120. Shelley, J.S.; Mather, P.T.; DeVries, K.L. Reinforcement and environmental degradation of nylon 6/clay nanocomposites. *Polymer* **2001**, *42*, 5849–5858. [\[CrossRef\]](#)
121. Fornes, T.D.; Yoon, P.J.; Keskkula, H.; Paul, D.R. Nylon 6 nanocomposites: The effect of matrix molecular weight. *Polymer* **2001**, *42*, 9929–9940. [\[CrossRef\]](#)
122. Liu, X.; Wu, Q. Phase transition in nylon 6/clay nanocomposites on annealing. *Polymer* **2002**, *43*, 1933–1936. [\[CrossRef\]](#)
123. Fornes, T.D.; Yoon, P.J.; Hunter, D.L.; Keskkula, H.; Paul, D.R. Effect of organoclay structure on nylon-6 nanocomposite morphology and properties. *Polymer* **2002**, *43*, 5915–5933. [\[CrossRef\]](#)
124. Kamal, M.R.; Borse, N.K.; Garcia-Rejon, A. The effect of pressure and clay on the crystallization behavior and kinetics of polyamide-6 in nanocomposites. *Polym. Eng. Sci.* **2002**, *42*, 1883–1896. [\[CrossRef\]](#)
125. Bureau, M.N.; Denault, J.; Cole, K.C.; Enright, G.D. The role of crystallinity and reinforcement in the mechanical behavior of polyamide-6/clay nanocomposites. *Polym. Eng. Sci.* **2002**, *42*, 1897–1907. [\[CrossRef\]](#)
126. Uribe-Arocha, P.; Mehler, C.; Puskas, J.E.; Altstadt, V. Effect of sample thickness on the mechanical properties of molded polyamide-6 and polyamide-6 clay nanocomposites. *Polymer* **2003**, *44*, 2441–2446. [\[CrossRef\]](#)
127. Hasegawa, N.; Okamoto, H.; Kato, M.; Usuki, A.; Sato, N. Nylon 6–montmorillonite nanocomposites prepared by compounding nylon 6 with Na-montmorillonite slurry. *Polymer* **2003**, *44*, 2933–2937. [\[CrossRef\]](#)
128. Ding, Y.; Jones, D.J.; Maires-Torres, P.; Roziere, J. Twodimensional nanocomposites: Alternating inorganic–organic polymer layers in zirconium phosphate. *Chem. Mater.* **1995**, *7*, 562–571. [\[CrossRef\]](#)
129. Reichert, P.; Kressler, J.; Thomann, R.; Mulhaupt, R.; Stoppelmann, G. Nanocomposites based on a synthetic layer silicate and polyamide-12'. *Acta Polym.* **1998**, *49*, 116–123. [\[CrossRef\]](#)
130. Hoffman, B.; Kressler, J.; Stoppelmann, G.; Friedrich, C.; Kim, G.M. Rheology of nanocomposites based on layered silicate and polyamide-12'. *Colloid Polym. Sci.* **2000**, *278*, 629–636. [\[CrossRef\]](#)
131. Giza, E.; Ito, H.; Kikutani, T.; Okui, N. Structural control of polyamide 6/clay nanocomposites fibers in-line drawing process. *J. Polym. Eng.* **2000**, *20*, 403–425. [\[CrossRef\]](#)
132. Kim, G.M.; Lee, D.H.; Hoffmann, B.; Kresler, J.; Stoppelmann, G. Influence of nanofillers on the deformation process in layered silicate/polyamide-12 nanocomposites. *Polymer* **2001**, *42*, 1095–1100. [\[CrossRef\]](#)
133. Nair, S.V.; Goettler, L.A.; Lysek, B.A. Toughness of nanoscale and multiscale polyamide-6,6 composites. *Polym. Eng. Sci.* **2002**, *42*, 1872–1882. [\[CrossRef\]](#)
134. Liu, X.; Wu, Q.; Zhang, Q.; Mo, Z. Phase transition in polyamide-66/montmorillonite nanocomposites on annealing. *J. Polym. Sci. Part B Polym. Phys.* **2003**, *44*, 6367. [\[CrossRef\]](#)
135. Messersmith, P.B.; Giannelis, E.P. Polymer-layered silicate nanocomposites: In-situ intercalative polymerization of ϵ -caprolactone in layered silicates. *Chem. Mater.* **1993**, *5*, 1064–1066. [\[CrossRef\]](#)

136. Jimenez, G.; Ogata, N.; Kawai, H.; Ogihara, T. Structure and thermal/mechanical properties of poly(ϵ -caprolactone)–clay blend. *J. Appl. Polym. Sci.* **1997**, *64*, 2211–2220. [[CrossRef](#)]
137. Krishnamoorti, R.; Giannelis, E.P. Rheology of end-tethered polymer layered silicate nanocomposites. *Macromolecules* **1997**, *30*, 4097–4102. [[CrossRef](#)]
138. Pantoustier, N.; Alexandre, M.; Degee, P.; Calberg, C.; Jerome, R.; Henrist, C.; Cloots, R.; Rulmont, A.; Dubois, P. Poly(ϵ -caprolactone) layered silicate nanocomposites: Effect of clay surface modifiers on the melt intercalation process. *e-Polymer* **2001**, *9*, 1–9. [[CrossRef](#)]
139. Shima, R.; Utracki, L.A.; Garcia-Rejon, A. Pressure–volume–temperature relations of a poly- ϵ -caprolactam and its nanocomposite. *Compos. Interfaces* **2001**, *8*, 345–353.
140. Pantoustier, N.; Lepoittevin, B.; Alexandre, M.; Kubies, D.; Calberg, C.; Jerome, R.; Dubois, P. Biodegradable polyester layered silicate nanocomposites based on poly(ϵ -caprolactone). *Polym. Eng. Sci.* **2002**, *42*, 1928–1937. [[CrossRef](#)]
141. Lepoittevin, B.; Pantoustier, N.; Devalckenaere, M.; Alexandre, M.; Kubies, D.; Calberg, C.; Jerome, R.; Dubois, P. Poly(ϵ -caprolactone)/clay nanocomposites by in-situ intercalative polymerization catalyzed by dibutyltin dimethoxide. *Macromolecules* **2002**, *35*, 8385–8390. [[CrossRef](#)]
142. Lepoittevin, B.; Devalckenaere, M.; Pantoustier, N.; Alexandre, M.; Kubies, D.; Calberg, C.; Jerome, R.; Dubois, P. Poly(ϵ -caprolactone)/clay nanocomposites prepared by melt intercalation: Mechanical, thermal and rheological properties. *Polymer* **2002**, *43*, 4017–4023. [[CrossRef](#)]
143. Gorrasi, G.; Tortora, M.; Vittoria, V.; Pollet, E.; Lepoittevin, B.; Alexandre, M.; Dubois, P. Vapor barrier properties of polycaprolactone montmorillonite nanocomposites: Effect of clay dispersion. *Polymer* **2003**, *44*, 2271–2279. [[CrossRef](#)]
144. Utracki, L.A.; Simha, R.; Garcia-Rejon, A. Pressure–volume–temperature dependence of poly- ϵ -caprolactam/clay nanocomposites. *Macromolecules* **2003**, *36*, 2114–2121. [[CrossRef](#)]
145. Lepoittevin, B.; Pantoustier, N.; Devalckenaere, M.; Alexandre, M.; Calberg, C.; Jerome, R.; Henrist, C.; Rulmont, A.; Dubois, P. Polymer/layered silicate nanocomposites by combined intercalative polymerization and melt intercalation: A master batch process. *Polymer* **2003**, *44*, 2033–2040. [[CrossRef](#)]
146. Wu, T.M.; Cheng, J.-C.; Yan, M.-C. Crystallization and thermoelectric behavior of conductive-filler-filled poly(ϵ -caprolactone)/poly(vinyl butyral)/montmorillonite nanocomposites. *Polymer* **2003**, *44*, 2553–2562. [[CrossRef](#)]
147. Ke, Y.C.; Long, C.; Qi, Z. Crystallization, properties, and crystal and nanoscale morphology of PET–clay nanocomposites. *J. Appl. Polym. Sci.* **1999**, *71*, 1139–1146. [[CrossRef](#)]
148. Sekelik, D.J.; Stepanov Enazarenko, S.; Schiraldi, D.; Hiltner, A.; Baer, E. Oxygen barrier properties of crystallized and talc-filled poly(ethylene terephthalate). *J. Polym. Sci. Part B Polym. Phys.* **1999**, *37*, 847–857. [[CrossRef](#)]
149. Matayabas, J.C., Jr.; Turner, S.R.; Sublett, B.J.; Connell, G.W.; Barbee, R.B. Nanocomposite technology for enhancing the gas barrier of polyethylene terephthalate. *PCT Int. Appl. Wo.* **1998**, *98*, 29499.
150. Takekoshi, T.; Khouri, F.F.; Campbell, J.R.; Jordan, T.C.; Dai, K.H.; General Electric Co. PET nanocomposites prepared by in situ incorporation of varying amounts of four different organoclays. U.S. Patent 5,530,052, 25 June 1996.
151. Tsai, T.Y. Polyethylene terephthalate–clay nanocomposites. In *Polymer–Clay Nanocomposites*; Pinnavaia, T.J., Beall, G.W., Eds.; John Wiley and Sons: Chichester, UK, 2000; pp. 173–189.
152. Davis, C.H.; Mathias, L.J.; Gilman, J.W.; Schiraldi, D.A.; Shields, J.R.; Trulove, P.; Sutto, T.E.; Delong, H.C. Effects of melt-processing conditions on the quality of poly(ethylene terephthalate) montmorillonite clay nanocomposites. *J. Polym. Sci. Part B Polym. Phys.* **2002**, *40*, 2661–2666. [[CrossRef](#)]
153. Imai, Y.; Nishimura, S.; Abe, E.; Tateyama, H.; Abiko, A.; Yamaguchi, A.; Aoyama, T.; Taguchi, H. High-modulus poly(ethylene terephthalate)/expandable fluorine mica nanocomposites with a novel reactive compatibilizer. *Chem. Mater.* **2002**, *14*, 477–479. [[CrossRef](#)]
154. Liu, Z.; Yan, D.; Chen, K. Preparation of poly(trimethylene terephthalate)/montmorillonite nanocomposite by melt intercalation. *Polym. Prepr.* **2003**, *44*, 1138–1139.
155. Duan, Q.; Yan, D. Poly(trimethylene terephthalate)–montmorillonite nanocomposite made by in situ polymerization. *Polym. Prepr.* **2003**, *44*, 1140–1141.
156. Chisholm, B.J.; Moore, R.B.; Barber, G.; Khouri, F.; Hempstead, A.; Larsen, M.; Olson, E.; Kelley, J.; Balch, G.; Caraher, J. Nanocomposites derived from sulfonated poly(butylene terephthalate). *Macromolecules* **2002**, *35*, 5508–5516. [[CrossRef](#)]
157. Huang, X.; Lewis, S.; Brittain, W.J.; Vaia, R.A. Synthesis of polycarbonate-layered silicate nanocomposites via cyclic oligomers. *Macromolecules* **2000**, *33*, 2000–2004. [[CrossRef](#)]
158. Mitsunaga, M.; Ito, Y.; Sinha Ray, S.; Okamoto, M.; Hironaka, K. Polycarbonate/clay nanocomposites: Nanostructure control and foam processing. *Macromol. Mater. Eng.* **2003**, *288*, 543–548. [[CrossRef](#)]
159. Wu, J.; Lerner, M.M. Structural, thermal, and electrical characterization of layered nanocomposites derived from sodium-montmorillonite and polyethers. *Chem. Mater.* **1993**, *5*, 835–838. [[CrossRef](#)]
160. Vaia, R.A.; Vasudevan, S.; Krawiec, W.; Scanlon, L.G.; Giannelis, E.P. New polymer electrolyte nanocomposites: Melt intercalation of poly(ethylene oxide) in mica-type silicates. *Adv. Mater.* **1995**, *7*, 154–156. [[CrossRef](#)]
161. Wong, S.; Vasudevan, S.; Vaia, R.A.; Giannelis, E.P.; Zax, D. Dynamics in a confined polymer electrolyte: A ^7Li and ^2H NMR study. *J. Am. Chem. Soc.* **1995**, *117*, 7568–7569. [[CrossRef](#)]

162. Vaia, R.A.; Sauer, B.B.; Tse, O.K.; Giannelis, E.P. Relaxations of confined chains in polymer nanocomposites: Glass transition properties of poly(ethylene oxide) intercalated in montmorillonite. *J. Polym. Sci. Part B Polym. Phys.* **1997**, *35*, 59–67. [\[CrossRef\]](#)
163. Aranda, P.; Galvan, J.C.; Ruiz-Hitzky, E. Isotropic PEO–clay nanocomposites prepared by microwave-assisted blending intercalation. In *Organic/Inorganic Hybrid Materials: MRS Symposium Proceedings*; Laine, R.M., Sanchez, C., Brinker, J.F., Giannelis, E.P., Eds.; Cambridge University Press: Warrendale, PA, USA, 1998; Volume 519, pp. 375–380.
164. Hatharasinghe, H.L.M.; Smalley, M.V.; Swenson, J.; Williams, C.D.; Heenan, R.K.; King, S.M. Neutron scattering study of vermiculite–PEO mixtures. *J. Phys. Chem. B* **1998**, *102*, 6804–6808. [\[CrossRef\]](#)
165. Hernan, L.; Morales, J.; Santos, J. Synthesis and characterization of poly(ethylene oxide) nanocomposites of misfit layer chalcogenides. *J. Solid State Chem.* **1998**, *141*, 327–329. [\[CrossRef\]](#)
166. Harris, D.J.; Bonagamba, T.J.; Schmidt-Rhor, K. Conformation of poly(ethylene oxide) intercalated in clay and MoS₂ studied by two dimensional double-quantum NMR. *Macromolecules* **1999**, *32*, 6718–6724. [\[CrossRef\]](#)
167. Chen, W.; Xu, Q.; Yuan, R.Z. Modification of poly(ethylene oxide) with polymethylmethacrylate in polymer-layered silicate nanocomposites. *J. Mater. Sci. Lett.* **1999**, *18*, 711–713. [\[CrossRef\]](#)
168. Bujdak, J.; Hackett, E.; Giannelis, E.P. Effect of layer charge on the intercalation of poly(ethylene oxide) in layered silicates: Implications on nanocomposite polymer electrolytes. *Chem. Mater.* **2000**, *12*, 2168–2174. [\[CrossRef\]](#)
169. Schmidt, G.; Nakatani, A.I.; Butler, P.D.; Karim, A.; Han, C.C. Shear orientation of viscoelastic polymer–clay solutions probed by flow birefringence and SANS. *Macromolecules* **2000**, *33*, 7219–7222. [\[CrossRef\]](#)
170. Xiao, Y.; Hu, K.A.; Yu, Q.C.; Wu, R.J. Preparation of polyethylene oxide/Li_xV_{2–δ}O_{4–δ} nanocomposites. *J. Appl. Polym. Sci.* **2001**, *80*, 2162–2166. [\[CrossRef\]](#)
171. Choi, H.J.; Kim, S.G.; Hyun, Y.H.; Jhon, M.S. Preparation and rheological characteristics of solvent-cast poly(ethylene oxide)/montmorillonite nanocomposites. *Macromol. Rapid Commun.* **2001**, *22*, 320–325. [\[CrossRef\]](#)
172. Hyun, Y.H.; Lim, S.T.; Choi, H.J.; Jhon, M.S. Rheology of poly(ethylene oxide)/organoclay nanocomposites. *Macromolecules* **2001**, *34*, 8084–8093. [\[CrossRef\]](#)
173. Liao, B.; Song, M.; Liang, H.; Pang, Y. Polymer-layered silicate nanocomposites. 1. A study of poly(ethylene oxide)/Na⁺-montmorillonite nanocomposites as polyelectrolytes and polyethylene-block-poly(ethylene glycol) copolymer/Na⁺-montmorillonite nanocomposites as fillers for reinforcement of polyethylene. *Polymer* **2001**, *42*, 10007–10011.
174. Chen, H.W.; Chang, F.C. The novel polymer electrolyte nanocomposite composed of poly(ethylene oxide), lithium triflate and mineral clay. *Polymer* **2001**, *42*, 9763–9769. [\[CrossRef\]](#)
175. Chen, H.W.; Chiu, C.Y.; Wu, H.D.; Shen, I.W.; Chang, F.C. Solidstate electrolyte nanocomposites based on poly(ethylene oxide), poly(oxypropylene) diamine, mineral clay and lithium perchlorate. *Polymer* **2002**, *43*, 5011–5016. [\[CrossRef\]](#)
176. Shen, Z.; Simon, G.P.; Cheng, Y.B. Comparison of solution intercalation and melt intercalation of polymer–clay nanocomposites. *Polymer* **2002**, *43*, 4251–4260. [\[CrossRef\]](#)
177. Lim, S.K.; Kim, J.W.; Chin, I.; Kwon, Y.K.; Choi, H.J. Preparation and interaction characteristics of organically modified montmorillonite nanocomposite with miscible polymer blend of poly(ethylene oxide) and poly(methyl methacrylate). *Chem. Mater.* **2002**, *14*, 1989–1994. [\[CrossRef\]](#)
178. Strawhecker, K.E.; Manias, E. Crystallization behavior of poly(ethylene oxide) in the presence of Na⁺-montmorillonite fillers. *Chem. Mater.* **2003**, *15*, 844–849. [\[CrossRef\]](#)
179. Chaiko, D.J. New poly(ethylene oxide)–clay composites. *Chem. Mater.* **2003**, *15*, 1105–1110. [\[CrossRef\]](#)
180. Fischer, H.R.; Gielgens, L.H.; Koster, T.P.M. Ethylene oxide copolymers/clay nanocomposites. In *Organic/Inorganic Hybrid Materials: MRC Symposium Proceedings*; Laine, R.M., Sanchez, C., Brinker, J.F., Giannelis, E.P., Eds.; Cambridge University Press: Warrendale, PA, USA, 1998; Volume 519, pp. 517–520.
181. Fischer, H.R.; Gielgens, L.H.; Koster, T.P.M. Nanocomposites from polymers and layered minerals. *Acta. Polym.* **1999**, *50*, 122–126. [\[CrossRef\]](#)
182. Wei, L.; Rocci-Lane, M.; Brazis, P.; Kannevorf, C.R.; Kim, Y.I.; Lee, W.; Choy, J.H.; Kanatzidis, M.G. α-RuCl₃/polymer nanocomposites: The first group of intercalative nanocomposites with transition metal halides. *J. Am. Chem. Soc.* **2000**, *122*, 6629–6640.
183. Burnside, S.D.; Giannelis, E.P. Synthesis and properties of new poly(dimethylsiloxane) nanocomposites. *Chem. Mater.* **1995**, *7*, 1597–1600. [\[CrossRef\]](#)
184. Wang, S.J.; Long, C.; Wang, X.; Li, Q.; Qi, Z. Synthesis and properties of silicone rubber organomontmorillonite hybrid nanocomposites. *J. Appl. Polym. Sci.* **1998**, *69*, 1557–1561. [\[CrossRef\]](#)
185. Takeuchi, H.; Cohen, C. Reinforcement of poly(dimethylsiloxane) elastomers by chain-end anchoring to clay particles. *Macromolecules* **1999**, *32*, 6792–6799. [\[CrossRef\]](#)
186. Burnside, S.D.; Giannelis, E.P. Nanostructure and properties of polysiloxane-layered silicate nanocomposites. *J. Polym. Sci. Part B Polym. Phys.* **2000**, *38*, 1595–1604. [\[CrossRef\]](#)
187. Bokobza, L.; Nugay, N. Orientational effect of mica in fumed silica reinforced composites. *J. Appl. Polym. Sci.* **2001**, *81*, 215–222. [\[CrossRef\]](#)
188. Osman, M.A.; Atallah, A.; Muller, M.; Suter, U.W. Reinforcement of poly(dimethylsiloxane) networks by mica flakes. *Polymer* **2001**, *42*, 6545–6556. [\[CrossRef\]](#)
189. Nugay, N.; Kusefoglu, S.; Erman, B. Swelling and staticdynamic mechanical behavior of mica-reinforced linear and star-branched polybutadiene composites. *J. Appl. Polym. Sci.* **1997**, *66*, 1943–1952. [\[CrossRef\]](#)

190. Akelah, A.; El-Borai, M.A.; El-Aal, M.F.A.; Rehab, A.; Abou-Zeid, M.S. New catalytic systems based on intercalated polymer-montmorillonite supports. *Macromol. Chem. Phys.* **1999**, *200*, 955–963. [[CrossRef](#)]
191. Zhang, L.; Wang, Y.; Wang, Y.; Sui, Y.; Yu, D. Morphology and mechanical properties of clay/styrene-butadiene rubber nanocomposites. *J. Appl. Polym. Sci.* **2000**, *78*, 1873–1878. [[CrossRef](#)]
192. Wang, Y.; Zhang, L.; Tang, C.; Yu, D. Preparation and characterization of rubber-clay nanocomposites. *J. Appl. Polym. Sci.* **2000**, *78*, 1879–1883. [[CrossRef](#)]
193. Manna, A.K.; Tripathy, D.K.; De, P.P.; De, S.K.; Chatterjee, M.K.; Pfeiffer, D.G. Bonding between epoxidized natural rubber and clay in presence of silane coupling agent. *J. Appl. Polym. Sci.* **1999**, *72*, 1895–1903. [[CrossRef](#)]
194. Vu, Y.T.; Mark, J.E.; Pham, L.H.; Engelhardt, M. Clay nanolayer reinforcement of *cis*-1,4-polyisoprene and epoxidized natural rubber. *J. Appl. Polym. Sci.* **2001**, *82*, 1391–1403. [[CrossRef](#)]
195. Messersmith, P.B.; Giannelis, E.P. Synthesis and characterization of layered silicate-epoxy nanocomposites. *Chem. Mater.* **1994**, *6*, 1719–1725. [[CrossRef](#)]
196. Lan, T.; Pinnavaia, T.J. Clay-reinforced epoxy nanocomposites. *Chem. Mater.* **1994**, *6*, 2216–2219. [[CrossRef](#)]
197. Wang, M.S.; Pinnavaia, T.J. Clay-polymer nanocomposites formed from acidic derivatives of montmorillonite and an epoxy resin. *Chem. Mater.* **1994**, *6*, 468–474. [[CrossRef](#)]
198. Lan, T.; Kaviratna, P.D.; Pinnavaia, T.J. Mechanism of clay tactoid exfoliation in epoxy-clay nanocomposites. *Chem. Mater.* **1995**, *7*, 2144–2150. [[CrossRef](#)]
199. Wang, Z.; Lan, T.; Pinnavaia, T.J. Hybrid organic-inorganic nanocomposites formed from an epoxy polymer and a layered silicic acid (Magadiite). *Chem. Mater.* **1996**, *8*, 2200–2204. [[CrossRef](#)]
200. Shi, H.; Lan, T.; Pinnavaia, T.J. Interfacial effects on the reinforcement properties of polymer-organoclay nanocomposites. *Chem. Mater.* **1996**, *8*, 1584–1587. [[CrossRef](#)]
201. Pinnavaia, T.J.; Lan, T.; Wang, Z.; Shi, H.; Kaviratna, P.D. Mechanism of clay tactoid exfoliation in epoxy-clay nanocomposites. In *Nanotechnology: Molecularly Designated Materials*; ACS Symposium Series; Chow, G.M., Gonsalves, K.E., Eds.; American Chemical Society: Washington, DC, USA, 1996; Volume 622, pp. 244–250.
202. Wang, Z.; Pinnavaia, T.J. Hybrid organic-inorganic nanocomposites: Exfoliation of magadiite nanolayers in an elastomeric epoxy polymer. *Chem. Mater.* **1998**, *10*, 1820–1826. [[CrossRef](#)]
203. Wang, Z.; Massam, J.; Pinnavaia, T.J. Epoxy-clay nanocomposites. In *Polymer-Clay Nanocomposites*; Pinnavaia, T.J., Beall, G.W., Eds.; John Wiley and Sons: New York, NY, USA, 2000; pp. 127–149.
204. Lee, D.C.; Jang, J.W. Characterization of epoxy-clay hybrid composite prepared by emulsion polymerization. *J. Appl. Polym. Sci.* **1998**, *68*, 1997–2005. [[CrossRef](#)]
205. Zilg, C.; Mulhaupt, R.; Finter, J. Morphology and toughness/stiffness balance of nanocomposites based upon anhydridecured epoxy resins and layered silicates. *Macromol. Chem. Phys.* **1999**, *200*, 661–670. [[CrossRef](#)]
206. Kornmann, X.; Lindberg, H.; Berglund, L.A. Synthesis of epoxy-clay nanocomposites: Influence of the nature of the clay on structure. *Polymer* **2001**, *42*, 1303–1310. [[CrossRef](#)]
207. Jiankun, L.; Yucai, K.; Zongneng, Q.; Xiao-Su, Y. Study on intercalation and exfoliation behavior of organoclays in epoxy resin. *J. Polym. Sci. Part B Polym. Phys.* **2001**, *39*, 115–120. [[CrossRef](#)]
208. Chin, I.J.; Albrecht, T.; Kim, H.C.; Russell, T.P.; Wang, J. On exfoliation of montmorillonite in epoxy. *Polymer* **2001**, *42*, 5947–5952. [[CrossRef](#)]
209. Zerda, A.S.; Lesser, A.J. Intercalated clay nanocomposites: Morphology, mechanics, and fracture behavior. *J. Polym. Sci. Part B Polym. Phys.* **2001**, *39*, 1137–1146. [[CrossRef](#)]
210. Kornmann, X.; Thomann, R.; Mulhaupt, R.; Finter, J.; Berglund, L.A. High performance epoxy-layered silicate nanocomposites. *Polym. Eng. Sci.* **2002**, *42*, 1815–1826. [[CrossRef](#)]
211. Feng, W.; Ait-Kadi, A.; Riedl, B. Polymerization compounding: Epoxy-montmorillonite nanocomposites. *Polym. Eng. Sci.* **2002**, *42*, 1827–1835. [[CrossRef](#)]
212. Becker, O.; Varley, R.; Simon, G. Morphology, thermal relaxations and mechanical properties of layered silicate nanocomposites based upon high-functionality epoxy resins. *Polymer* **2002**, *43*, 4365–4373. [[CrossRef](#)]
213. Chen, J.S.; Poliks, M.D.; Ober, C.K.; Zhang, Y.; Wiesner, U.; Giannelis, E.P. Study of the interlayer expansion mechanism and thermal-mechanical properties of surface-initiated epoxy nanocomposites. *Polymer* **2002**, *43*, 4895–4904. [[CrossRef](#)]
214. Kong, D.; Park, C.H. Real time exfoliation behavior of clay layers in epoxy-clay nanocomposites. *Chem. Mater.* **2003**, *15*, 419–424. [[CrossRef](#)]
215. Park, J.H.; Jana, C.H. The relationship between nano and micro-structures and mechanical properties in PMMA-epoxy-nanoclay composites. *Polymer* **2003**, *44*, 2091–2100. [[CrossRef](#)]
216. Park, J.H.; Jana, C.H. Mechanism of exfoliation of nanoclay particles in epoxy-clay nanocomposites. *Macromolecules* **2003**, *36*, 2758–2768. [[CrossRef](#)]
217. Choi, M.H.; Chung, I.J.; Lee, J.D. Morphology and curing behaviors of phenolic resin-layered silicate nanocomposites prepared by melt intercalation. *Chem. Mater.* **2000**, *12*, 2977–2983. [[CrossRef](#)]
218. Wang, H.; Zhao, T.; Zhi, L.; Yan, Y.; Yu, Y. Synthesis of novolac/layered silicate nanocomposites by reaction exfoliation using acid-modified montmorillonite. *Macromol. Rapid. Commun.* **2002**, *23*, 44–48. [[CrossRef](#)]
219. Wang, Z.; Pinnavaia, T.J. Nanolayer reinforcement of elastomeric polyurethane. *Chem. Mater.* **1998**, *10*, 3769–3771. [[CrossRef](#)]

220. Chen, T.K.; Tien, Y.I.; Wei, K.H. Synthesis and characterization of novel segmented polyurethane/clay nanocomposite via poly(ϵ -caprolactone)/clay. *J. Polym. Sci. Part A Polym. Chem.* **1999**, *37*, 2225–2233. [\[CrossRef\]](#)
221. Tien, Y.I.; Wei, K.H. Hydrogen bonding and mechanical properties in segmented montmorillonite/polyurethane nanocomposites of different hard segment ratios. *Polymer* **2001**, *42*, 3213–3221. [\[CrossRef\]](#)
222. Yao, K.J.; Song, M.; Hourston, D.J.; Luo, D.Z. Polymer/layered clay nanocomposites: 2. Polyurethane nanocomposites. *Polymer* **2002**, *43*, 1017–1020. [\[CrossRef\]](#)
223. Xu, R.; Manias, E.; Snyder, A.J.; Runt, J. Low permeability biomedical polyurethane nanocomposites. *J. Biomed. Mater. Res. A* **2003**, *64*, 114–119. [\[CrossRef\]](#) [\[PubMed\]](#)
224. Xu, R.; Manias, E.; Snyder, A.J.; Runt, J. New biomedical poly(urethane urea)-layered silicate nanocomposites. *Macromolecules* **2001**, *34*, 337–339. [\[CrossRef\]](#)
225. Lan, T.; Kaviratna, P.D.; Pinnavaia, T.J. On the nature of polyimide–clay hybrid composites. *Chem. Mater.* **1994**, *6*, 573–575. [\[CrossRef\]](#)
226. Yano, K.; Usuki, A.; Okada, A. Synthesis and properties of polyimide–clay hybrid films. *J. Polym. Sci. Part A Polym. Chem.* **1997**, *35*, 2289–2294. [\[CrossRef\]](#)
227. Zhu, Z.-K.; Yang, Y.; Yin, J.; Wang, X.Y.; Ke, Y.C.; Qi, Z.N. Preparation and properties of organosoluble montmorillonite/polyimide hybrid materials. *J. Appl. Polym. Sci.* **1999**, *73*, 2063. [\[CrossRef\]](#)
228. Yang, Y.; Zhu, Z.K.; Yin, J.; Wang, X.Y.; Qi, Z.E. Preparation and properties of hybrids of organo-soluble polyimide and montmorillonite with various chemical surface modification methods. *Polymer* **1999**, *40*, 4407–4414. [\[CrossRef\]](#)
229. Tyan, H.L.; Wei, K.H.; Hsieh, T.E. Mechanical properties of clay–polyimide (BTDA-ODA) nanocomposites via ODA modified organoclay. *J. Polym. Sci. Part B Polym. Phys.* **2000**, *38*, 2873. [\[CrossRef\]](#)
230. Gu, A.; Chang, F.C. A novel preparation of polyimide/clay hybrid films with low coefficient of thermal expansion. *J. Appl. Polym. Sci.* **2001**, *79*, 289–294. [\[CrossRef\]](#)
231. Gu, A.; Kuo, S.W.; Chang, F.C. Syntheses and properties of PI/clay hybrids. *J. Appl. Polym. Sci.* **2001**, *79*, 1902–1910. [\[CrossRef\]](#)
232. Hsiao, S.H.; Liou, G.S.; Chang, L.M. Synthesis and properties of organosoluble polyimide/clay hybrids. *J. Appl. Polym. Sci.* **2001**, *80*, 2067–2072. [\[CrossRef\]](#)
233. Tyan, H.L.; Leu, C.M.; Wei, K.H. Effect of reactivity of organics modified montmorillonite on the thermal and mechanical properties of montmorillonite/polyimide nanocomposites. *Chem. Mater.* **2001**, *13*, 222–226. [\[CrossRef\]](#)
234. Huang, J.C.; Zhu, Z.K.; Ma, X.D.; Qian, X.F.; Yin, J. Preparation and properties of montmorillonite/organo-soluble polyimide hybrid materials prepared by a one-step approach. *J. Mater. Sci.* **2001**, *36*, 871. [\[CrossRef\]](#)
235. Agag, T.; Koga, T.; Takeichi, T. Studies on thermal and mechanical properties of polyimide–clay nanocomposites. *Polymer* **2001**, *42*, 3399–3408. [\[CrossRef\]](#)
236. Morgan, A.B.; Gilman, J.W.; Jackson, C.L. Characterization of the dispersion of clay in a polyetherimide nanocomposite. *Macromolecules* **2001**, *34*, 2735–2738. [\[CrossRef\]](#)
237. Leu, C.M.; Wu, Z.W.; Wei, K.H. Synthesis and properties of covalently bonded layered silicates/polyimide (BTDA-ODA) nanocomposites. *Chem. Mater.* **2001**, *14*, 3016–3021. [\[CrossRef\]](#)
238. Magaraphan, R.; Lilayuthalert, W.; Sirivat, A.; Schwank, J.W. Preparation, structure, properties and thermal behavior of rigid-rod polyimide/montmorillonite nanocomposites. *Compos. Sci. Technol.* **2001**, *61*, 1253–1264. [\[CrossRef\]](#)
239. Delozier, D.M.; Orwoll, R.A.; Cahoon, J.F.; Ladislav, J.S.; Smith, J.G., Jr.; Connell, J.W. Polyimide nanocomposites prepared from high-temperature reduced charge organoclays. *Polymer* **2003**, *44*, 2231–2241. [\[CrossRef\]](#)
240. Liang, Z.-M.; Yin, J.; Xu, H.-J. Polyimide/montmorillonite nanocomposites based on thermally stable, rigid-rod aromatic amine modifiers. *Polymer* **2003**, *44*, 1391–1399. [\[CrossRef\]](#)
241. Tyan, H.L.; Liu, Y.C.; Wei, K.H. Enhancement of imidization of poly(amic acid) through poly(amic acid)/organoclay nanocomposites. *Polymer* **1999**, *40*, 4877–4886. [\[CrossRef\]](#)
242. Kim, J.; Ahmed, R.; Lee, S.J. Synthesis and linear viscoelastic behavior of poly(amic acid)–organoclay hybrid. *J. Appl. Polym. Sci.* **2001**, *80*, 592–603. [\[CrossRef\]](#)
243. Sur, G.S.; Sun, H.L.; Lyu, S.G.; Mark, J.E. Synthesis, structure, mechanical properties, and thermal stability of some polysulfone/organoclay nanocomposites. *Polymer* **2001**, *42*, 9783–9789. [\[CrossRef\]](#)
244. Lee, J.; Takekkoshi, T.; Giannelis, E.P. Fire retardant polyetherimide nanocomposites. *Mater. Res. Soc. Symp. Proc.* **1997**, *457*, 513–518. [\[CrossRef\]](#)
245. Huang, J.C.; Zhu, Z.K.; Qian, X.F.; Sun, Y.Y. Poly(etherimide)/montmorillonite nanocomposites prepared by melt intercalation: Morphology, solvent resistance properties and thermal properties. *Polymer* **2001**, *42*, 873–877. [\[CrossRef\]](#)
246. Vora, R.H.; Pallathadka, P.K.; Goh, S.H.; Chung, T.-S.; Lim, Y.X.; Bang, T.K. Preparation and characterization of 4,4'-bis(4-aminophenoxy)diphenyl sulphone based fluoropoly(etherimide)/organo-modified clay. *Macromol. Mater. Eng.* **2003**, *288*, 337–356. [\[CrossRef\]](#)
247. Kurokawa, Y.; Yasuda, H.; Oya, A. Preparation of nanocomposites of polypropylene and smectite. *J. Mater. Sci. Lett.* **1996**, *15*, 1481–1487. [\[CrossRef\]](#)
248. Furuichi, N.; Kurokawa, Y.; Fujita, K.; Oya, A.; Yasuda, H.; Kiso, M. Preparation and properties of polypropylene reinforced by smectite. *J. Mater. Sci.* **1996**, *31*, 4307–4310. [\[CrossRef\]](#)

249. Tudor, J.; Willington, L.; O'Hare, D.; Royan, B. Intercalation of catalytically active metal complexes in phyllosilicates and their application as propene polymerization catalyst. *Chem. Commun.* **1996**, *17*, 2031–2032. [\[CrossRef\]](#)
250. Kurokawa, Y.; Yasuda, H.; Kashiwagi, M.; Oya, A. Structure and properties of a montmorillonite/polypropylene nanocomposite. *J. Mater. Sci. Lett.* **1997**, *16*, 1670–1672. [\[CrossRef\]](#)
251. Nyden, M.R.; Gilman, J.W. Molecular dynamics simulations of the thermal degradation of nano-confined polypropylene. *Comput. Theor. Polym. Sci.* **1997**, *7*, 191–198. [\[CrossRef\]](#)
252. Kato, M.; Usuki, A.; Okada, A. Synthesis of polypropylene oligomer–clay intercalation compounds. *J. Appl. Polym. Sci.* **1997**, *66*, 1781–1785. [\[CrossRef\]](#)
253. Usuki, A.; Kato, M.; Okada, A.; Kurauchi, T. Synthesis of polypropylene–clay hybrid. *J. Appl. Polym. Sci.* **1997**, *63*, 137–138. [\[CrossRef\]](#)
254. Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; Okada, A. Preparation and mechanical properties of polypropylene–clay hybrids. *Macromolecules* **1997**, *30*, 6333–6338. [\[CrossRef\]](#)
255. Hasegawa, N.; Kawasumi, M.; Kato, M.; Usuki, A.; Okada, A. Preparation and mechanical properties of polypropylene–clay hybrids using a maleic anhydride-modified polypropylene oligomer. *J. Appl. Polym. Sci.* **1998**, *67*, 87–92. [\[CrossRef\]](#)
256. Oya, A. Polypropylene–clay nanocomposites. In *Polymer–Clay Nanocomposites*; Pinnavaia, T.J., Beall, G.W., Eds.; John Wiley and Sons: London, UK, 2000; pp. 151–172.
257. Hasegawa, N.; Okamoto, H.; Kato, M.; Usuki, A. Preparation and mechanical properties of polypropylene–clay hybrids based on modified polypropylene and organophilic clay. *J. Appl. Polym. Sci.* **2000**, *78*, 1918–1922. [\[CrossRef\]](#)
258. Oya, A.; Kurokawa, Y.; Yasuda, H. Factors controlling mechanical properties of clay mineral/polypropylene nanocomposites. *J. Mater. Sci.* **2000**, *35*, 1045–1050. [\[CrossRef\]](#)
259. Lee, J.W.; Lim, Y.T.; Park, O.O. Thermal characteristics of organoclay and their effects upon the formation of polypropylene/organoclay nanocomposites. *Polym. Bull.* **2000**, *45*, 191–198. [\[CrossRef\]](#)
260. Zhang, Q.; Fu, Q.; Jiang, L.; Lei, Y. Preparation and properties of polypropylene/montmorillonite layered nanocomposites. *Polym. Int.* **2000**, *49*, 1561–1564. [\[CrossRef\]](#)
261. Garces, J.M.; Moll, D.J.; Bicerano, J.; Fibiger, R.; McLeod, D.G. Polymeric nanocomposites for automotive applications. *Adv. Mater.* **2000**, *12*, 1835–1839. [\[CrossRef\]](#)
262. Hasegawa, N.; Okamoto, H.; Kawasumi, M.; Kato, M.; Tsukigase, A.; Usuki, A. Polyolefin–clay hybrids based on modified polyolefins and organoclay. *Macromol. Mater. Eng.* **2000**, *281*, 76–79. [\[CrossRef\]](#)
263. Hambir, S.; Bulakh, N.; Kodgire, P.; Kalgaonkar, R.; Jog, J.P. PP/clay nanocomposites: A study of crystallization and dynamic mechanical behavior. *J. Polym. Sci. Part B Polym. Phys.* **2001**, *39*, 446–450. [\[CrossRef\]](#)
264. Zanetti, M.; Camino, G.; Reichert, P.; Mulhaupt, R. Thermal behaviour of poly(propylene) layered silicate nanocomposites. *Macromol. Rapid Commun.* **2001**, *22*, 176–180. [\[CrossRef\]](#)
265. Galgali, G.; Ramesh, C.; Lele, A. A rheological study on the kinetics of hybrid formation in propylene nanocomposites. *Macromolecules* **2001**, *34*, 852–858. [\[CrossRef\]](#)
266. Solomon, M.J.; Almusallam, A.S.; Seefeldt, K.F.; Somwangthanaroj, A.; Varadan, P. Rheology of polypropylene/clay hybrid materials. *Macromolecules* **2001**, *34*, 1864–1872. [\[CrossRef\]](#)
267. Gloaguen, J.M.; Lefebvre, J.M. Plastic deformation behavior of thermoplastic/clay nanocomposites. *Polymer* **2001**, *42*, 5841–5847. [\[CrossRef\]](#)
268. Garcia-Martinez, J.M.; Laguna, O.; Areso, S.; Collar, E.P. Polypropylene/mica composites modified by succinic anhydride-grafted atactic polypropylene: A thermal and mechanical study under dynamic conditions. *J. Appl. Polym. Sci.* **2001**, *81*, 625–636. [\[CrossRef\]](#)
269. Reichert, P.; Hoffman, B.; Bock, T.; Thomann, R.; Mulhaupt, R.; Friedrich, C. Morphological stability of polypropylene nanocomposites. *Macromol. Rapid Commun.* **2001**, *22*, 519–523. [\[CrossRef\]](#)
270. Nam, P.H.; Maiti, P.; Okamoto, M.; Kotaka, T.; Hasegawa, N.; Usuki, A. A hierarchical structure and properties of intercalated polypropylene/clay nanocomposites. *Polymer* **2001**, *42*, 9633–9640. [\[CrossRef\]](#)
271. Liu, X.; Wu, Q. PP/clay nanocomposites prepared by grafting-melt intercalation. *Polymer* **2001**, *42*, 10013–10019. [\[CrossRef\]](#)
272. Manias, E. A direct-blending approach for polypropylene/clay nanocomposites enhances properties. *Mater. Res. Soc. Bull.* **2001**, *26*, 862–863.
273. Okamoto, M.; Nam, P.H.; Maiti, P.; Kotaka, T.; Hasegawa, N.; Usuki, A. A house-of-cards structure in polypropylene/clay nanocomposites under elongational flow. *Nano. Lett.* **2001**, *1*, 295–298. [\[CrossRef\]](#)
274. Okamoto, M.; Nam, P.H.; Maiti, M.; Kotaka, T.; Nakayama, T.; Takada, M.; Ohshima, M.; Usuki, A.; Hasegawa, N.; Okamoto, H. Biaxial flow-induced alignment of silicate layers in polypropylene/clay nanocomposite foam. *Nano. Lett.* **2001**, *1*, 503–505. [\[CrossRef\]](#)
275. Sun, T.; Garces, J.M. High-performance polypropylene–clay nanocomposites by in-situ polymerization with metallocene/clay catalysts. *Adv. Mater.* **2002**, *14*, 128–130. [\[CrossRef\]](#)
276. Maiti, P.; Nam, P.H.; Okamoto, M.; Kotaka, T.; Hasegawa, N.; Usuki, A. Influence of crystallization on intercalation, morphology, and mechanical properties of propylene/clay nanocomposites. *Macromolecules* **2002**, *35*, 2042–2049. [\[CrossRef\]](#)
277. Maiti, P.; Nam, P.H.; Okamoto, M.; Kotaka, T.; Hasegawa, N.; Usuki, A. The effect of crystallization on the structure and morphology of polypropylene/clay nanocomposites. *Polym. Eng. Sci.* **2002**, *42*, 1864–1871. [\[CrossRef\]](#)

278. Nam, P.H.; Maiti, P.; Okamoto, M.; Kotaka, T.; Nakayama, T.; Takada, M.; Ohshima, M.; Usuki, A.; Hasegawa, N.; Okamoto, H. Foam processing and cellular structure of polypropylene/clay nanocomposites. *Polym. Eng. Sci.* **2002**, *42*, 1907–1918. [\[CrossRef\]](#)
279. Hambir, S.; Bulakh, N.; Jog, J.P. Propylene/clay nanocomposites: Effect of compatibilizer on the thermal, crystallization and dynamic mechanical behavior. *Polym. Eng. Sci.* **2002**, *42*, 1800–1807. [\[CrossRef\]](#)
280. Kaempfer, D.; Thomann, R.; Mulhaupt, R. Melt compounding of syndiotactic polypropylene nanocomposites containing organophilic layered silicates and in situ formed core/shell nanoparticles. *Polymer* **2002**, *43*, 2909–2916. [\[CrossRef\]](#)
281. Lele, A.; Mackley, M.; Galgali, G.; Ramesh, C. In situ rheo-Xray investigation of flow-induced orientation in layered silicate-syndiotactic polypropylene nanocomposite melt. *J. Rheol.* **2002**, *46*, 1091–1110. [\[CrossRef\]](#)
282. Zhang, Q.; Wang, Y.; Fu, Q. Shear-induced change of exfoliation and orientation in polypropylene/montmorillonite nanocomposites. *J. Polym. Sci. Part B Polym. Phys.* **2003**, *41*, 1–10. [\[CrossRef\]](#)
283. Somwangthanaaroj, A.; Lee, E.C.; Solomon, M.J. Early stage quiescent and flow-induced crystallization of intercalated polypropylene nanocomposites by time-resolved light scattering. *Macromolecules* **2003**, *36*, 2333–2342. [\[CrossRef\]](#)
284. Morgan, A.B.; Harris, J.D. Effects of organoclay soxhlet extraction on mechanical properties, flammability properties and organoclay dispersion of polypropylene nanocomposites. *Polymer* **2003**, *44*, 2113–2120. [\[CrossRef\]](#)
285. Jeon, H.G.; Jung, H.T.; Lee, S.W.; Hudson, S.D. Morphology of polymer silicate nanocomposites. High density polyethylene and a nitrile. *Polym. Bull.* **1998**, *41*, 107–113. [\[CrossRef\]](#)
286. Heinemann, J.; Reichert, P.; Thomson, R.; Mulhaupt, R. Polyolefin nanocomposites formed by melt compounding and transition metal catalyzed ethane homo- and copolymerization in the presence of layered silicates. *Macromol. Rapid Commun.* **1999**, *20*, 423–430. [\[CrossRef\]](#)
287. Privalko, V.P.; Calleja, F.J.B.; Sukhorukov, D.I.; Privalko, E.G.; Walter, R.; Friedrich, K. Composition-dependent properties of polyethylene/Kaolin composites. Part II. Thermoelastic behavior of blow-molded samples. *J. Mater. Sci.* **1999**, *34*, 497–508. [\[CrossRef\]](#)
288. Bergman, J.S.; Chen, H.; Giannelis, E.P.; Thomas, M.G.; Coates, G.W. Synthesis and characterization of polyolefin-silicate nanocomposites: A catalyst intercalation and in situ polymerization approach. *J. Chem. Soc. Chem. Commun.* **1999**, *21*, 2179–2180. [\[CrossRef\]](#)
289. Rong, J.; Jing, J.; Li, H.; Sheng, M. A polyethylene nanocomposite prepared via in-situ polymerization. *Macromol. Rapid Commun.* **2001**, *22*, 329–334. [\[CrossRef\]](#)
290. Wang, K.H.; Choi, M.H.; Koo, C.M.; Choi, Y.S.; Chung, I.J. Synthesis and characterization of maleated polyethylene/clay nanocomposites. *Polymer* **2001**, *42*, 9819–9826. [\[CrossRef\]](#)
291. Alexandre, M.; Dubois, P.; Sun, T.; Graces, J.M.; Jerome, R. Polyethylene-layered silicate nanocomposites prepared by the polymerization-filling technique: Synthesis and mechanical properties. *Polymer* **2002**, *43*, 2123–2132. [\[CrossRef\]](#)
292. Gopakumar, T.G.; Lee, J.A.; Kontopoulou, M.; Parent, J.S. Influence of clay exfoliation on the physical properties of montmorillonite/polyethylene composites. *Polymer* **2002**, *43*, 5483–5491. [\[CrossRef\]](#)
293. Jin, Y.-H.; Park, H.-J.; Im, S.-S.; Kwak, S.-Y.; Kwak, S. Polyethylene/clay nanocomposite by in situ exfoliation of montmorillonite during Ziegler–Natta polymerization of ethylene. *Macromol. Rapid. Commun.* **2001**, *23*, 135–140. [\[CrossRef\]](#)
294. Bafna, A.; Beaucage, G.; Mirabella, F.; Mehta, S. 3D hierarchical orientation in polymer–clay nanocomposite films. *Polymer* **2003**, *44*, 1103–1115. [\[CrossRef\]](#)
295. Osman, M.A.; Seyfang, G.; Suter, U.W. Two-dimensional melting of alkane monolayers ionically bonded to mica. *J. Phys. Chem. B* **2000**, *104*, 4433–4439. [\[CrossRef\]](#)
296. Zanetti, M.; Camino, G.; Thomann, R.; Mulhaupt, R. Synthesis and thermal behavior of layered silicate-EVA nanocomposites. *Polymer* **2001**, *42*, 4501–4507. [\[CrossRef\]](#)
297. Usuki, A.; Tukigase, A.; Kato, M. Preparation and properties of EPMD–clay hybrids. *Polymer* **2002**, *43*, 2185–2189. [\[CrossRef\]](#)
298. Wanjale, S.D.; Jog, J.P. Poly(1-butene)/clay nanocomposites: Preparation and properties. *J. Polym. Sci. Part B Polym. Phys.* **2003**, *41*, 1014–1021. [\[CrossRef\]](#)
299. Nazzal, A.I.; Street, G.B. Pyrrole-styrene graft copolymers. *J. Chem. Soc. Chem. Commun.* **1985**, *375*, 83–84. [\[CrossRef\]](#)
300. Sun, Y.; Ruckenstein, E. Polypyrrole-bearing conductive composite prepared by an inverted emulsion pathway involving nonionic surfactants. *Synth. Met.* **1995**, *72*, 261–267. [\[CrossRef\]](#)
301. Wang, L.; Brazis, P.; Rocci, M.; Kannewurf, C.R.; Kanatzidis, M.G. A new redox host for intercalative polymerization: Insertion of polyaniline into α -RuCl₃. *Chem. Mater.* **1999**, *10*, 3298–3300. [\[CrossRef\]](#)
302. Sinha Ray, S.; Biswas, M. Preparation and evaluation of composites from montmorillonite and some heterocyclic polymers: 3. A water dispersible nanocomposite from pyrrole–montmorillonite polymerization system. *Mater. Res. Bull.* **1998**, *35*, 1187–1194.
303. Kim, J.W.; Liu, F.; Choi, H.J.; Hong, S.H.; Joo, J. Intercalated polypyrrole/Na-montmorillonite nanocomposite via an inverted emulsion pathway method. *Polymer* **2003**, *44*, 289–293. [\[CrossRef\]](#)
304. Biswas, M.; Sinha Ray, S. Preparation and evaluation of composites from montmorillonite and some heterocyclic polymers 1, poly(N-vinylcarbazole)–montmorillonite system. *Polymer* **1998**, *39*, 6423–6428. [\[CrossRef\]](#)
305. Sinha Ray, S.; Biswas, M. Preparation and evaluation of composites from montmorillonite and some heterocyclic polymers, II. Nanocomposite from N-vinylcarbazole and ferric chloride impregnated montmorillonite polymerization system. *J. Appl. Polym. Sci.* **1999**, *73*, 2971–2976.

306. Kim, J.W.; Kim, S.G.; Choi, H.J.; Jhon, M.S. Synthesis and electrorheological properties of polyaniline–Na-montmorillonite suspensions. *Macromol. Rapid. Commun.* **1999**, *20*, 450–452. [\[CrossRef\]](#)
307. Biswas, M.; Sinha Ray, S. Water-dispersible nanocomposites of polyaniline and montmorillonite. *J. Appl. Polym. Sci.* **2000**, *77*, 2948–2956. [\[CrossRef\]](#)
308. Dai, L.; Wang, Q.; Wan, M. Direct observation of conformational transitions for polyaniline chains intercalated in clay particles upon secondary doping. *J. Mater. Sci. Lett.* **2000**, *19*, 1645–1647. [\[CrossRef\]](#)
309. Lee, D.; Lee, S.H.; Char, K.; Kim, J. Expansion distribution of basal spacing of the silicate layers in polyaniline/Na⁺-montmorillonite nanocomposites monitored with X-ray diffraction. *Macromol. Rapid. Commun.* **2000**, *21*, 1136–1139. [\[CrossRef\]](#)
310. Wu, Q.; Xue, Z.; Qi, Z.; Wang, F. Synthesis and characterization of PAN/clay nanocomposite with extended chain conformation of polyaniline. *Polymer* **2000**, *41*, 2029–2032. [\[CrossRef\]](#)
311. Uemura, S.; Yoshie, M.; Kobayashi, N.; Nakahira, T. Photopolymerization of aniline dimer by photocatalytic reaction of ruthenium trisbipyridyl in the interlayer of hectorite clay. *Polym. J.* **2000**, *32*, 987–990. [\[CrossRef\]](#)
312. Kim, B.H.; Jung, J.H.; Joo, J.; Kim, J.W.; Choi, H.J. Charge transport and structure of nanocomposites of polyaniline and inorganic clay. *J. Korean. Phys. Soc.* **2000**, *36*, 366–370.
313. Yeh, J.M.; Liou, S.J.; Lai, C.Y.; Wu, P.C.; Tsai, T.Y. Enhancement of corrosion protection effect in polyaniline via the formation of polyaniline–clay nanocomposite materials. *Chem. Mater.* **2001**, *13*, 1131–1136. [\[CrossRef\]](#)
314. Feng, B.; Su, Y.; Song, J.; Kong, K. Electropolymerization of polyaniline/montmorillonite nanocomposite. *J. Mater. Sci. Lett.* **2001**, *20*, 293–294. [\[CrossRef\]](#)
315. Kim, J.W.; Kim, S.G.; Choi, H.J.; Suh, M.S.; Shin, M.J.; Jhon, M.S. Synthesis and electrorheological characterization of polyaniline and Na⁺-montmorillonite clay nanocomposite. *Int. J. Mod. Phys.* **2001**, *15*, 657–664. [\[CrossRef\]](#)
316. Kim, B.H.; Jung, J.H.; Kim, J.W.; Choi, H.J.; Joo, J. Physical characterization of polyaniline–Na⁺-montmorillonite nanocomposite intercalated by emulsion polymerization. *Synth. Met.* **2001**, *117*, 115–118. [\[CrossRef\]](#)
317. Choi, H.J.; Kim, J.W.; Joo, J.; Kim, B.H. Synthesis and electrorheology of emulsion intercalated PANI–clay nanocomposite. *Synth. Met.* **2001**, *121*, 1325–1326. [\[CrossRef\]](#)
318. Cho, M.S.; Choi, H.J.; Kim, K.Y.; Ahn, W.S. Synthesis and characterization of polyaniline/mesoporous SBA-15 nanocomposite. *Macromol. Rapid Commun.* **2002**, *23*, 713–716. [\[CrossRef\]](#)
319. Kim, B.H.; Jung, J.H.; Hong, S.H.; Joo, J.; Epstein, A.J.; Mizoguchi, K.; Kim, J.W.; Choi, H.J. Nanocomposite of polyaniline and Na⁺-montmorillonite clay. *Macromolecules* **2002**, *35*, 1419–1423. [\[CrossRef\]](#)
320. Nascimento GMdo Constantino, V.R.L.; Temperini, M.L.A. Spectroscopic characterization of a new type of conducting polymer–clay nanocomposite. *Macromolecules* **2002**, *35*, 7535–7537. [\[CrossRef\]](#)
321. Winkler, B.; Dai, L.; Mau, A.W.-H. Organic–inorganic hybrid light-emitting composites: Poly(p-phenylene vinylene) intercalated clay nanoparticles. *J. Mater. Sci. Lett.* **1999**, *18*, 1539–1541. [\[CrossRef\]](#)
322. Wright, M.E.; Schorman, D.A.; Feher, F.J.; Jin, R.-Z. Characterization of clays by organic compounds. *Clay Miner.* **1981**, *16*, 1–21.
323. Kawasumi, M.; Hasegawa, N.; Usuki, A.; Okada, A. Nematic liquid crystal/clay mineral composites. *Mater. Sci. Eng. C* **1998**, *6*, 135–143. [\[CrossRef\]](#)
324. Vaia, R.A.; Giannelis, E.P. Liquid crystal polymer nanocomposites: Direct intercalation of thermotropic liquid crystalline polymers into layered silicates. *Polymer* **2001**, *42*, 1281–1285. [\[CrossRef\]](#)
325. Zhou, W.; Mark, J.E.; Unroe, M.R.; Arnold, F.E. Some clay nanocomposites based on a high temperature, high performance polymer. *J. Macromol. Sci. Pure Appl. Chem. A* **2001**, *38*, 1–9. [\[CrossRef\]](#)
326. Chang, J.H.; Seo, B.S.; Hwang, D.H. An exfoliation of organoclay in thermotropic liquid crystalline polyester nanocomposites. *Polymer* **2002**, *43*, 2969–2974. [\[CrossRef\]](#)
327. Plummer, C.J.G.; Garamszegi, L.; Leterrier, Y.; Rodler, T.M.; Manson, J.-A.E. Hyperbranched polymer-layered silicate nanocomposites. *Chem. Mater.* **2002**, *14*, 486–488. [\[CrossRef\]](#)
328. Ganguli, S.; Dean, D.; Jordan, K.; Price, G.; Vaia, R. Mechanical properties of intercalated cyanate ester-layered silicate nanocomposites. *Polymer* **2003**, *44*, 1315–1319. [\[CrossRef\]](#)
329. Young, S.K.; Mauritz, K.A. Nafion®/(organically modified silicate) nanocomposites via polymer in situ sol–gel reactions: Mechanical tensile properties. *J. Polym. Sci. Part B Polym. Phys.* **2002**, *40*, 2237–2247. [\[CrossRef\]](#)
330. Wright, M.E.; Schorman, D.A.; Feher, F.J.; Jin, R.-Z. Synthesis and thermal curing of aryl-ethyl-terminated coPOSS imide oligomers: New inorganic/organic hybrid resins. *Chem. Mater.* **2003**, *15*, 264–268. [\[CrossRef\]](#)
331. Ogata, N.; Jimenez, G.; Kawai, H.; Ogihara, T. Structure and thermal/mechanical properties of poly(L-lactide)–clay blend. *J. Polym. Sci. Part. B Polym. Phys.* **1997**, *35*, 389–396. [\[CrossRef\]](#)
332. Sinha Ray, S.; Maiti, P.; Okamoto, M.; Yamada, K.; Ueda, K. New polylactide/layered silicate nanocomposites. 1. Preparation, characterization and properties. *Macromolecules* **2002**, *35*, 3104–3110. [\[CrossRef\]](#)
333. Sinha Ray, S.; Okamoto, K.; Yamada, K.; Okamoto, M. Novel porous ceramic material via burning of polylactide/layered silicate nanocomposite. *Nano Lett.* **2002**, *2*, 423–426. [\[CrossRef\]](#)
334. Sinha Ray, S.; Yamada, K.; Okamoto, M.; Ueda, K. New polylactide/layered silicate nanocomposite: A novel biodegradable material. *Nano Lett.* **2002**, *2*, 1093–1096. [\[CrossRef\]](#)
335. Sinha Ray, S.; Yamada, K.; Ogami, A.; Okamoto, M.; Ueda, K. New polylactide layered silicate nanocomposite. Nanoscale control of multiple properties. *Macromol. Rapid Commun.* **2002**, *23*, 493–497.

336. Maiti, P.; Yamada, K.; Okamoto, M.; Ueda, K.; Okamoto, K. New polylactide/layered silicate nanocomposites. Role of organoclay. *Chem. Mater.* **2002**, *14*, 4654–4661. [\[CrossRef\]](#)
337. Pluta, M.; Caleski, A.; Alexandre, M.; Paul, M.-A.; Dubois, P. Polylactide/montmorillonite nanocomposites and microcomposites prepared by melt blending: Structure and some physical properties. *J. Appl. Polym. Sci.* **2002**, *79*, 1497–1506. [\[CrossRef\]](#)
338. Paul, M.-A.; Alexandre, M.; Degee, P.; Henrist, C.; Rulmont, A.; Dubois, P. New nanocomposite materials based on plasticized poly(L-lactide) and organo-modified montmorillonites: Thermal and morphological study. *Polymer* **2003**, *44*, 443–450. [\[CrossRef\]](#)
339. Chang, J.-H.; Uk-An, Y.; Sur, G.S. Poly(lactic acid) nanocomposites with various organoclays. I. Thermomechanical properties, morphology, and gas permeability. *J. Polym. Sci. Part B Polym. Phys.* **2003**, *41*, 94–103. [\[CrossRef\]](#)
340. Sinha Ray, S.; Yamada, K.; Okamoto, M.; Ueda, K. New polylactide/layered silicate nanocomposites. 2. Concurrent improvements of material properties, biodegradability and melt rheology. *Polymer* **2003**, *44*, 857–866. [\[CrossRef\]](#)
341. Sinha Ray, S.; Okamoto, K.; Maiti, P.; Okamoto, M. New poly(butylene succinate)/layered silicate nanocomposites. 1. Preparation, characterization, and mechanical properties. *J. Nanosci. Nanotechnol.* **2002**, *2*, 171–176.
342. Sinha Ray, S.; Okamoto, K.; Okamoto, M. Structure–property relationship in biodegradable poly(butylene succinate)/layered silicate nanocomposites. *Macromolecules* **2003**, *36*, 2355–2367. [\[CrossRef\]](#)
343. Gao, F. New poly(butylene succinate)/layered silicate nanocomposites. 2. Effect of organically modified layered silicates on morphology, materials properties, melt rheology, and biodegradability. *J. Polym. Sci. Part B* **2003**, *41*, 3160–3172.
344. Kornmann, X.; Berglund, L.A.; Sterete, J.; Giannelis, E.P. Nanocomposites based on montmorillonite and unsaturated polyester. *Polym. Eng. Sci.* **1998**, *38*, 1351–1358. [\[CrossRef\]](#)
345. Choi, H.J.; Kim, J.H.; Kim, J. Mechanical spectroscopy studies on biodegradable synthetic and biosynthetic aliphatic polyesters. *Macromol. Symp.* **1997**, *119*, 149–155. [\[CrossRef\]](#)
346. Park, S.H.; Choi, H.J.; Lim, S.T.; Shin, T.K.; Jhon, M.S. Viscoelasticity of biodegradable polymer blends of poly(3-hydroxybutyrate) and poly(ethylene oxide). *Polymer* **2001**, *42*, 5737–5742. [\[CrossRef\]](#)
347. Maiti, P.; Batt, C.A.; Giannelis, E.P. Renewable plastics: Synthesis and properties of PHB nanocomposites. *Polym. Mater. Sci. Eng.* **2003**, *88*, 58–59.
348. Lee, S.R.; Park, H.M.; Lim, H.L.; Kang, T.; Li, X.; Cho, W.J.; Ha, C.S. Microstructure, tensile properties, and biodegradability of aliphatic polyester/clay nanocomposites. *Polymer* **2002**, *43*, 2495–2500. [\[CrossRef\]](#)
349. Lepoittevin, B.; Pantoustier, N.; Alexander, M.; Calberg, C.; Jerome, R.; Dubois, P. Polyester layered silicate nanohybrids by controlled grafting polymerization. *J. Mater. Chem.* **2002**, *12*, 3528–3532. [\[CrossRef\]](#)
350. Bharadwaj, R.K.; Mehrabi, A.R.; Hamilton, C.; Murga, M.F.; Chavira, A.; Thompson, A.K. Structure–property relationships in cross-linked polyester–clay nanocomposites. *Polymer* **2002**, *43*, 3699–3705. [\[CrossRef\]](#)
351. Lim, S.T.; Hyun, Y.H.; Choi, H.J.; Jhon, M.S. Synthetic biodegradable aliphatic polyester/montmorillonite nanocomposites. *Chem. Mater.* **2002**, *14*, 1839–1844. [\[CrossRef\]](#)
352. Gao, F. Clay/Polyme Composites: The Story. *Mater. Today* **2004**, *7*, 50–55. [\[CrossRef\]](#)
353. Okamoto, M. Properties and Applications of Polyme Nanocomposites. *Seikei-Kakou* **2013**, *25*, 63–67.
354. Koo, J. (Ed.) *Fundamentals, Properties, and Applications of Polyme Nanocomposites*; Cambridge University Press: New York, NY USA, 2016; p. 697.

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