Chapter 2

Fundamentals of Polymer Nanocomposite Technology

E. Manias*, G. Polizos, H. Nakajima†, M.J. Heidecker
Materials Science & Engineering department,
Penn State University, University Park, PA 16802

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*Corresponding Author; email: manias@psu.edu, fax: +1-814-865-2917, tel: +1-814-863-2980.
†Permanent address: Sumitomo Chemical Co. Ltd., Petrochemicals Res Lab, Sodegaura, JAPAN
2.1 Introduction

The term “nanocomposite” is widely employed to describe an extremely broad range of materials, where one of the components has a dimension in the sub-micron scale. A better –and far more restrictive– definition would require that a true nanocomposite should be a **fundamentally new material** (hybrid) in which the nanometer scale component or structure gives rise to **intrinsically new properties**, which are not present in the respective macroscopic composites or the pure components. This latter definition necessitates that the nanostructure has dimensions smaller than a characteristic scale that underlies a physical property of the material. For example, for the electronic properties of a conductor or semi-conductor this scale would relate to the de Broglie wavelength of the electron (ranging from a few nanometers for a metal to hundreds of nanometers for a semiconductor), for the mechanical properties of a polymer it would relate to the size of the polymer coil or crystal (again ranging from a few nanometers to hundreds of nanometers), and for the thermodynamic properties of a polymer glass it would relate to the cooperativity length (a few nanometers).

In this chapter we shall restrict our discussion even further, focussing on one sub-class of polymer/inorganic nanocomposites, where the polymers are typically thermoplastics and the inorganic component is a high aspect-ratio nanoscale filler. Particular emphasis will be given to principles that apply to pseudo-two-dimensional layered inorganic fillers (such as 2:1 alumino-silicates\(^1-9\), from where most of our examples will be derived, and layered double hydroxides\(^10\)), and to a smaller extent also to pseudo-one-dimensional fillers (such as carbon nanotubes\(^11\)). In these systems, concurrent improvements across multiple properties are typically achieved –with simultaneous enhancement of the mechanical, thermal, and thermomechanical response– in addition to ‘new’ properties –such as improved barrier, flammability, and biodegradability behaviors– compared to the unfilled polymer. Consequently, the resulting nanocomposite material is better described by the term “hybrid” (denoting the large scale changes in multiple material characters) rather than polymer “composite” (a term traditionally associated with an incremental improvement of one or two key properties\(^12-14\)).

For these nanocomposite systems, the fundamentally new properties typically originate from the change of the polymer nature in the vicinity of the filler, such as polymers adsorbed on the filler surfaces or confined in between fillers and, as such, they depend strongly on the effective surface area of the fillers –i.e., the surface area of a single filler when completely dispersed or the surface area of the typical filler cluster. Thus, good dispersions of fillers would result in a true ‘nanocomposite’ at rather low filler loadings, close to the percolation threshold of these high aspect ratio (cf. below 3 vol.% for typical layered-silicates\(^15\) or 1 vol.% for single-walled nanotubes\(^16\)). On the other hand, in absence of dispersion, neither the nanometer scale geometry of these fillers nor their ultra-high surface area is exploited, and the resulting composite falls into the class of conventional composites despite the nanometer size of the individual inorganic fillers.

In the case of nanometer-thin layered inorganic fillers, it has been long known that polymers can effectively disperse clay minerals, when those are appropriately
modified\textsuperscript{1,2}. The field has recently gained a large momentum, mainly due to two major findings that pioneered the revival of these materials: Firstly, the report of a nylon-6/montmorillonite material from Unitika and Toyota researchers\textsuperscript{17,18}, where very moderate inorganic loadings resulted in concurrent and remarkable enhancements of thermal and mechanical properties. Secondly, Giannelis \textit{et al.} found that it is possible to melt-mix polymers with clays without the use of organic solvents\textsuperscript{19}. Since then, the high promise for industrial applications has motivated vigorous research, which revealed concurrent dramatic enhancements in polymers by the dispersion of various nanometer-thin inorganic layered fillers\textsuperscript{10,20–23}. Where the property enhancements originate from the nanocomposite structure, these improvements are generally applicable across a wide range of polymers\textsuperscript{6,10}.

In contrast, carbon nanotubes were discovered much more recently, first observed by Iijima\textsuperscript{24}, and since then they have been the focus of considerable research activity. This pseudo-one-dimensional form of carbon has remarkable physical and mechanical properties, such as structure-tunable electronic properties, ultra-high thermal conductivity, and unmatched mechanical properties (e.g., stiffness, strength and resilience). These characteristics, combined with recent advances enabling a ‘high volume’ production of multi- and single-walled nanotubes, offer tremendous opportunities for the development of ultra-high performance nanotube-reinforced nanocomposite materials\textsuperscript{11}.

At this point, we should also mention that this chapter is not intended to provide an extensive review of the polymer nanocomposites field—the reader interested in such reviews can refer to a number of related books\textsuperscript{1–5}, numerous compilations of relevant symposia and conference proceedings, or recent review articles\textsuperscript{6–8,10,11}. This chapter is rather an attempt towards a brief eclectic overview of topics highlighting the fundamentals that underlie the materials discussed in the rest of this book.

\section{2.2 Fundamentals of Polymer Nanocomposites}

\subsection*{2.2.1 Thermodynamics of nanoscale Filler Dispersion}

As for polymer blends, the ‘thermodynamics of mixing’ for polymers and nanofillers can be described through a balance of entropic and enthalpic factors, which determines whether a pristine or organically-modified filler will be dispersed in a polymer\textsuperscript{25–27}. Especially for nanoparticles, favorable thermodynamics of mixing are essential since these ultra-small particles are held together with very high apparent attractive forces (\textit{vide infra} eq. 2.3) when immersed in liquid or polymeric media, and purely mechanical methods of mixing are not expected to be effective. Moreover, nanofillers—given the extensive amount of surface area that imposes entropic penalties for adsorbed, physisorbed or intercalated macromolecules—their dispersion necessitates sufficiently favorable enthalpic contributions to overcome the entropic penalties.

For example, following the interfacial tension formalization of van Oss-Chaudhury-Good\textsuperscript{28}, we consider two flat filler—e.g. layered-silicate ($s$)– layers separated by an organic layer—e.g. alkyl surfactant film ($a$) or an intercalated polymer film. In this
<table>
<thead>
<tr>
<th>Material</th>
<th>$\gamma_{LW}^i$</th>
<th>$\gamma^+_i$</th>
<th>$\gamma^-_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>21.8</td>
<td>25.5</td>
<td>25.5</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>26</td>
<td>0.7</td>
<td>36</td>
</tr>
<tr>
<td>Alkane ($C_{12}-C_{18}$)</td>
<td>26</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>26</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>33</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>42</td>
<td>0</td>
<td>1.1</td>
</tr>
<tr>
<td>PMMA</td>
<td>40.6</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>Carbon nanotube</td>
<td>18.4</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>PET</td>
<td>43.5</td>
<td>0.01</td>
<td>6.8</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>36.4</td>
<td>0.02</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Figure 2.1: (left) Various surface tension components in (mJ/m$^2$) for materials discussed in the text; *from $\gamma^{AB} \approx 24$ mJ/m$^2$ assuming $\gamma^+/\gamma^- = 1$. (right) Adhesive pressure vs. interlayer thickness, as predicted by eq. 2.3, for two flat montmorillonite surfaces separated by an apolar organic films (e.g. an olefin). For small film thicknesses (<2.5-3nm) this continuum approach is not valid, rather the adhesive pressure has discontinuous stable maxima (much higher than the dashed line) which correspond to integer numbers of monomer layers.

The case, successive layers are held together with an adhesive energy:

$$\Delta F_{sas} = -2\gamma_{sa} = -2(\sqrt{\gamma_{s}^{LW}} - \sqrt{\gamma_{a}^{LW}})^2 - 4(\sqrt{\gamma_{s}^+} - \sqrt{\gamma_{a}^+})(\sqrt{\gamma_{s}^-} - \sqrt{\gamma_{a}^-})$$  \hspace{1cm} (2.1)

when assuming additivity of apolar (Lifschitz-van der Waals, LW) and polar (electron donor/acceptor, or Lewis acid/base, AB) interaction terms, and using standard geometric combination rules:

$$\gamma_{ij} = \gamma_{ij}^{LW} + \gamma_{ij}^{AB}, \text{ with } \left\{ \begin{array}{l}
\gamma_{ij}^{LW} \approx (\sqrt{\gamma_{i}^{LW}} - \sqrt{\gamma_{j}^{LW}})^2 \\
\gamma_{ij}^{AB} \approx 2(\sqrt{\gamma_{i}^+} - \sqrt{\gamma_{j}^+})(\sqrt{\gamma_{i}^-} - \sqrt{\gamma_{j}^-})
\end{array} \right. \hspace{1cm} (2.2)$$

The $i, j$ subscripts correspond to the various system components (layered-silicate $s$, alkyl surfactant film $a$, and polymer $p$) and the $LW, AB$ superscripts to the nature of interactions (apolar $LW$, and polar $AB$). These relations can be converted into the Hamaker constant formalization by setting $\gamma_{i}^{LW} = A_i/(24\pi l_o^2)$ with $l_o = 1.58\text{Å}$. In the case of a 2:1 alumino-silicates organically modified by alkyl surfactants, the attractive interaction energy of eq. 2.1 would correspond (fig. 2.1), to an adhesive pressure between the parallel flat surfaces of:

$$P = \frac{A}{6\pi d^3} = \frac{-12\pi l_o^2 \Delta F_{sas}}{6\pi d^3}$$  \hspace{1cm} (2.3)

where $d$ is the thickness of the organic interlayer film. Given that typical alkyl-
surfactant modifications –butyl to dioctadecyl– correspond to a surfactant layer thickness of 0.5-1 nm, the corresponding adhesive pressure between successive silicate layers is at least $10^5-10^4$ bar (cf. fig. 2.1). Thus, favorable enthalpic interactions are absolutely necessary for filler dispersion and nanocomposite formation.

Focusing on polymer nanocomposites based on organically-modified layered silicates, Vaia et al. published a tractable approach to calculate the entropic and enthalpic contributions to the free energy of mixing, and have used this to predict miscibility of polystyrene with alkyl-ammonium modified silicates (montmorillonite and fluorohectorite). According to this model the entropic contributions are unfavorable and rather small: Specifically, the conformational entropy penalty of polymer confinement is compensated by an increase in conformational freedom of the tethered surfactants upon dispersion for gallery increases of up to 0.7 nm, and adopts small unfavorable values for larger gallery increases (see fig. 4 of Vaia et al.). Consequently, small per-monomer favorable enthalpic interactions can drive dispersion of these nanofillers in the polymer, and promote the formation of a nanocomposite. These favorable enthalpic interactions are an *excess enthalpy*, akin to the $\chi$ parameter definition in the Flory-Huggins theory; for silicate $s$ modified by a surfactant $a$ and a polymer $p$, this excess enthalpic interaction per area can be approximated by $\Delta H \approx \epsilon_{ps} + \epsilon_{pa} - (\epsilon_{aa} + \epsilon_{as})$, where $\epsilon_{ij}$ is a measurement of the pairwise interaction between component $i$ and $j$ (which can be quantified through pairwise atomic interaction parameters, cohesive energy densities, solubility parameters, or interfacial tension (Hamaker constants) formulations). For most polymers and surfactants $\epsilon_{pa} - \epsilon_{aa} \ll \epsilon_{ps} - \epsilon_{as}$, and to a first approximation for polymer/surfactant-modified inorganic nanocomposites, *favorable enthalpy for mixing is achieved when the polymer/inorganic interactions are more favorable than the surfactant/inorganic interactions*.

Following our prior nomenclature, dispersion would dictate a negative interaction energy change (upon mixing), which corresponds to a positive interfacial tension difference $(\gamma_{as} - \gamma_{ps})$. For an apolar $(\gamma_{a}^\pm \approx 0)$ alkyl-surfactant (e.g. dodecane to nonadecane), $\gamma_{as}^{LW} \approx 26$ mJ/m$^2$ used to organically modify a typical silicate (e.g. montmorillonite, with $\gamma_{s}^{LW} \approx 66$ mJ/m$^2$, $\gamma_{s}^+ \approx 0.7$ mJ/m$^2$, and $\gamma_{s}^- \approx 36$ mJ/m$^2$), miscibility would be achieved with any polymer for which

$$\gamma_{total}^{excess} = (\sqrt{\gamma_{ps}^{LW}} - \sqrt{66})^2 + 2(\sqrt{\gamma_{ps}^+} - \sqrt{0.7})(\sqrt{\gamma_{ps}^-} - \sqrt{36}) - 9.1 \text{ mJ/m}^2 < 0 \quad (2.4)$$

This is satisfied for most polymers (e.g. table XIII-5 in van Oss’ book) except perfluorinated polymers and most of the polyolefins (polypropylene, polyisobutylene, etc). Or, miscibility is promoted for all apolar polymers $(\gamma_{p}^\pm \approx 0)$ with 26 mJ/m$^2$ $< \gamma_{p}^{LW} < 125$ mJ/m$^2$, and for polar polymers with $\gamma_{ps}^{LW} \approx 26$ mJ/m$^2$ and $\gamma_{ps}^{AB} < 0$ (i.e., as Vaia states, $\gamma_{p}^+ > 0.7$ mJ/m$^2$ and $\gamma_{p}^- < 36$ mJ/m$^2$, or $\gamma_{p}^+ < 0.7$ mJ/m$^2$ and $\gamma_{p}^- > 36$ mJ/m$^2$). Thus, for *most polymers* the commonly used organic modification by alkyl-cationic surfactants is *adequate to create sufficient excess enthalpy and promote nanocomposite formation* with montmorillonite.

In a different approach, a longer macromolecular “surfactant” –that would increase the layer separation to 5-10nm– necessitates much smaller favorable enthalpic interactions.
contributions since the adhesive pressure to be overcome is about a thousand times smaller. This last theoretical prediction has been verified for polypropylene in absence of excess enthalpic interactions (i.e., $\gamma_{PP}^{LW} = 26 \text{ mJ/m}^2 \cong \gamma_a^{LW}$ and $\gamma_{PP}^{\pm} = 0$, and eq. 2.4 yields $\gamma_{total}^{excess} \cong 0$), which in turn implies that for short surfactants the entropic penalties from the physisorbed PP will hinder spontaneous miscibility, whereas the entropic gains from longer surfactants would promote miscibility.

At this point, we would like to make three more comments:

1. It should be obvious that free energy calculations cannot be done on a per molecule basis, but rather the free energy of the system or the free energy per volume must be calculated. Thus, certain parameters that were omitted herein (such as the monomeric volumes of polymer and surfactant and the grafting density of the surfactant on the filler—in the case of silicates this would be proportional to the cation exchange capacity, CEC) must also enter the calculations. The above arguments (e.g., eq. 2.4) can be used when there is a substantial fraction of both polymer and surfactant in contact with the filler surface—e.g. in the case of 2:1 alumino-silicates $0.65 < \text{CEC} < 1.7 \text{ meq/g}$ (or equivalently, surfactant grafting densities of one surfactant per $2 < A < 0.8 \text{ nm}^2$), and still provide only approximate values/criteria. A more detailed discussion is provided elsewhere.

2. In the case of polypropylene (PP) the above approach yields a zero excess enthalpic interaction for an alkyl-modified silicate (since $29 \gamma_{PP}^{LW} = 25.7 \text{ mJ/m}^2 \cong \gamma_a^{LW}$ and $\gamma_{PP}^{\pm} \cong 0$, eq. 2.4 yields $\gamma_{total}^{excess} \cong 0$ ), which implies that the entropic factors, albeit small in magnitude, will hinder spontaneous miscibility.

3. Under the approximations and assumptions mentioned above and without considering any entropic contributions, the interfacial (adhesive) energy per area of a polymer and a silicate is given by:

$$\Delta F_{ps}^{total} = \Delta F_{ps}^{LW} + \Delta F_{ps}^{AB} = (\gamma_{ps}^{LW} - \gamma_p^{LW} - \gamma_s^{LW}) + (\gamma_{ps}^{AB} - \gamma_p^{AB} - \gamma_s^{AB})$$

(2.5)

and substituting $\gamma_{ps}^{LW}$ and $\gamma_{ps}^{AB}$ from eq. 2.2:

$$\Delta F_{ps}^{total} = -2\sqrt{\gamma_p^{LW}\gamma_s^{LW}} - 2(\sqrt{\gamma_p^{+}\gamma_s^{-}} + \sqrt{\gamma_p^{-}\gamma_s^{+}})$$

(2.6)

which for a strictly apolar polymer becomes $\Delta F_{ps}^{total} = -2\sqrt{\gamma_p^{LW}\gamma_s^{LW}}$

2.2.2 Synthetic Routes for Nanocomposite Formation

For traditional composite materials, high performance requires—in a first approach—the homogeneous and thermodynamically stable dispersion of the fillers in the polymer matrix. To this end, the two major hurdles to be overcome are (a) de-aggregation of the filler assemblies (clusters of fillers oftentimes containing tens, hundreds, or even millions of filler particles, associated with very strong inter-particle forces), and (b) achieving sufficiently ‘strong’ polymer/filler interfaces, required for good mechanical coupling between the matrix and the filler. Both these requirements are also necessary in polymer-based nanocomposites, and—depending on the nanofiller—there exist
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additional hurdles that need to be overcome towards nanocomposite formation; examples of such challenges include entropic effects of polymers in nanoscopic confinements between 2D fillers, as discussed in the previous section, de-aggregation of intertwined 1D filler clusters, as in carbon nanotube bundles or ropes, and overcoming the much faster kinetics –compared to colloidal micron sized fillers– of nanofiller reaggregation.

As for the thermodynamic consideration in the previous section, we attempt to highlight these challenges by describing in some detail the most common synthetic routes for nanocomposite formation employed for polymer/layered-inorganic hybrids. Examples will be mostly drawn from layered-silicates fillers, but the conclusions are general across most nanofillers, and one should be able to envision similar strategies for nanocomposite formation based on other types of nanofillers.

**Solution-aided Dispersion and ‘Brute Force’ melt processing.** In most cases, polymer/inorganic systems that do not possess favorable thermodynamics for nanocomposite formation, can be “trapped” in dispersed –even exfoliated– structures through solvent casting, sonication, or high shear-rate/high temperature extrusion. Such trapped structures are usually easy to achieve\(^1\), but in most cases are not thermodynamically stable nor amenable to further processing. For example, in fig. 2.2, the XRDs of precipitated PP/mmt hybrids from a co-suspension of polypropylene and o-mmt (organically-modified montmorillonite) in trichloro-benzene (similar structures can be obtained from ‘aggressive’ melt processing such as high \(\dot{\gamma}\) extrusion\(^{34-37}\), or dynamic packing injection molding\(^{38}\)). However, upon subsequent processing by compression molding (at 180°C/15 tons) of these “hybrids”, the polymer melts and the trapped hybrid structure relaxes towards the thermodynamically favorable state. If the o-mmt dispersion is not thermodynamically favorable the layers will collapse in low d-spacing parallel stacks (e.g. neat-PP/dimethyl-dioctadecyl-ammonium-mmt fig. 2.2 left) during the high temperature processing, leading to a conventionally-filled ‘macro’composite. However, when there exists favorable free energy for the o-mmt/polymer mixing, the exfoliated filler structures are retained (e.g. polypropylene (PP) containing maleic anhydride (MA) functional groups and dimethyl-dioctadecyl-ammonium-mmt fig. 2.2 right). Typically, this approach can yield stable dispersions only for polymers with strong specific interactions with mmt (e.g. polymers that hydrogen bond to the silicates, such as poly(vinyl alcohol)\(^{39}\), poly(urethanes)\(^{40,41}\), and polyamide-6\(^{42-44}\)) it is striking that only 0.5 mol% of MA can have the same effect in PP. As expected, mechanical shear markedly reduces the time necessary for the structure relaxation, and the structure of figure 2.2(b) is recovered after 8 min of mixing (extrusion at 180°C). In concert, trapped systems of neat-PP/2C18-mmt even after very moderate mixing (1-3 min at 180°C) result in an immiscible/intercalated structure with a wide XRD reflection extending from 1.8 to 2.7 \(nm\) in d-spacing. Along the same lines, when sonication is employed in polymer nanofiller co-suspensions –instead of aggressive melt-processing of the polymer with the nanofiller– similar trends can be observed and the a well-dispersed structure can be stable when favorable inter-

\(^1\)Easy or successful ‘brute force’ melt processing in the case of layered inorganic fillers is obviously limited to relatively small lateral size fillers, given the very strong adhesive forces between such particles (fig. 2.1)
actions are present, as for example in polystyrene/alkyl-ammonium montmorillonite systems.\textsuperscript{45} The sonication approach is, in general, a highly successful route for polymer nanocomposites based on carbon nanotubes, since the sonication can effectively disperse the nanotube bundles in the solvent and subsequently in the polymer matrix (\textit{vide infra}), and is commonly employed despite criticisms that sonication may cause tube break-down.

This approach is qualitatively similar to the “swelling agent” approach, as for example by Wolf \textit{et al.}\textsuperscript{46}. In such approaches an alkyl-ammonium-exchanged montmorillonite is intercalated by an organic “swelling agent”, such as ethylene glycol, naphtha or heptane (all with boiling points below the processing/extrusion temperature)\textsuperscript{46}. Subsequently, the swollen organo-modified clay is compounded with PP in a twin-screw extruder at 250°C. At this processing temperature, the swelling agent evaporates leading to the formation of a ‘nano’composite which is XRD silent. In principle, this is the same as the solution intercalation approach, where a solvent is employed to mix the o-mmt with the polymer, and a mostly-exfoliated structure is trapped upon evaporation of the solvent. For fillers that cannot be surface-modified by grafted surfactants (such as graphite) this “swelling agent” approach is probably the most effective route for achieving filler dispersions.

In all the above cases, and in absence of polymer cross-linking or favorable thermodynamics to retain the dispersion achieved (by solvent, mechanical shear/vibration, swelling agent, etc.) the fillers will re-aggregate upon further processing and all the high performance character due to nanoscale filler dispersion will be lost.
**Static Melt Intercalation.** This method involves the mechanical mixing of a polymer with an appropriately modified filler, and subsequent annealing above the softening temperature of the polymer\(^{19}\). This approach provides the best route to test with sensitivity the thermodynamic arguments detailed above, and yield well-defined systems for fundamental studies. However, due to the quiescent processing conditions (absence of external shear), which eliminate any mechanical contribution for the dispersion of the fillers, and the very slow intercalation/exfoliation kinetics\(^{47,48}\), such methods are typically very slow, thus having very limited applicability in industry.

We will only mention one example for this method, polypropylene (PP) in organically modified montmorillonite (o-mmt), so as to elucidate how the thermodynamics of mixing can be tested\(^{33,49}\). The “challenge” with PP is to design systems where the polymer/mmt interactions are more favorable than the surfactant/mmt interactions. As mentioned above, for an alkyl surfactant used as the organic modification in o-mmt, there is no excess enthalpy for mixing with PP (\(\gamma_{\text{total}}^{\text{excess}} \approx 0\)), or in other words the polymer/mmt interactions are equal to the surfactant/filler interactions. In agreement with the thermodynamic arguments presented above, minute amounts (0.5-1 mol.%) of randomly incorporated polar or polarizable (\(\gamma_{AB} \neq 0\)) functional groups, such as methyl-styrene, hydroxyl, and maleic anhydride, can promote the PP/o-mmt miscibility\(^{49}\) under static melt intercalation. Also, small blocks (1-5 mol.%) of methyl-methacrylate (PMMA) added to PP were shown to be sufficient to drive miscibility (in this case, \(\gamma_{PMMA}^{AB} = 0\) but \(\gamma_{PMMA}^{LW} \approx 40 > \gamma_{a}^{LW} \approx 26\) mJ/m\(^2\)), since the favorable thermodynamics for the PMMA can overcome the purely entropic barrier for the PP intercalation. Even in the extreme case, where the miscible block becomes as short as a single group, miscibility can still be achieved\(^{33}\), when this group possesses sufficiently strong interactions for the filler (as for example an ammonium group\(^{33}\)). On the other hand, if mixing is to be promoted for non-functionalized PP, a surfactant must be chosen with poorer interactions for the filler than the olefinic polymer (i.e., \(\gamma_{PP}^{AB} = 0\) and \(\gamma_{PP}^{LW} < \gamma_{FE}^{LW} \approx 26\) mJ/m\(^2\)), such surfactants are for instance fluorinated or semi-fluorinated alkyls (\(\gamma_{FE}^{LW} \approx 18\) mJ/m\(^2\)); this strategy has also been proven experimentally\(^{49}\).

**Melt Processing.** This is a very frequently used approach\(^{6,8,16}\), where the polymer and the -usually organically modified- filler are incorporated together in a traditional polymer processing method, most commonly extrusion or kneading, and less frequently injection molding. In concert with the principles of static melt intercalation, favorable thermodynamics for mixing are introduced by the design of functionalities on the polymer and by the choice of the organic modification for the fillers. In addition to any thermodynamic contributions, mechanical shear also provides a kinetic driving force for further dispersion of the fillers in the polymer matrix and also accelerates substantially the kinetics of filler dispersion. This latter effect is particularly important for polymers that possess very high attractions for the filler surfaces and can be kinetically arrested under static melt intercalation\(^{48}\). In many cases, end-users of polymer nanocomposites are hesitant to incorporate nanofillers directly (in the form of ultra-fine powders) in their current processing practices, and the concentrate or “master batch” two-step approach is preferred. In this case, first a
polymer nanocomposite (concentrate) is formulated at relatively high filler loadings of ca. 25wt.%, which can be processed and palletized to look like a normal polymer resin. This concentrate is subsequently diluted –let down– in a second step by pure polymer resin to the desired filler loading [cf. next].

**Master-Batch Approaches.** Beyond any industrial reservations for incorporating directly nanoparticles into the final stages of processing, there also exist in some cases scientifically justified reasons to follow the concentrate or “master-batch” approach. For example, in the first studies aiming to develop PP/o-mmt materials\(^{34–37,46,50}\), polypropylene oligomers modified with either maleic anhydride (MA) or hydroxyl groups (OH) were first mixed with octadecylammonium-exchanged montmorillonite creating a “master batch” at high filler loadings, which was subsequently blended with neat PP, usually assisted by strong mechanical shear in an extruder or mixer. In this way, the MA-polypropylene disperses the o-mmt, given the favorable thermodynamics, and in the second step PP and PP-g-MA are effectively at theta conditions and the extrusion is promoting mixing only due to entropic reasons (cf. morphologies of miscible polymer blends). Although at first glance, this approach may seem similar to the one denoted above as a “brute force”, in the master batch case there do exist favorable thermodynamics for mixing which, not only result in more effective dispersions, but also stabilize the dispersed nanocomposite structure. However, still the structure and the properties of the resulting hybrid materials depended strongly on the processing conditions and, e.g. in the case of PP, they range from very moderate dispersions and property improvements\(^{34,36,37,46,50}\), to good dispersions and better performing hybrids\(^{35}\). Obviously, a MA-polypropylene pretreatment with very low maleic anhydride content does not promote the nanocomposite formation\(^{36}\), and very high maleic anhydride content makes the “master batch” so robust that mmt does not mix further with neat PP\(^{34,37}\). Furthermore, the PP-g-MA can have marked effects on the PP crystallization, and consequently deteriorate the mechanical properties, especially when the PP-g-MA is of substantially lower molecular weight or isotacticity than the PP matrix, or contains high levels of branching. Therefore, it is frequently necessary to develop several variants of a master batch [based on functional polymers with varied characteristics, e.g. in the case of PP with various molecular weights of PP-g-MA, or in the case of polyethylene (PE) with various polymer microstructures (LDPE, LLDPE, HDPE, etc)] depending on the specific characteristics of the polymer matrix that they are intended for.

**In-situ Polymerization schemes.** One of the cornerstone studies, and probably the single most important study in pioneering the revival of the polymer/layered silicate nanocomposites field, was the work by the Toyota group where they polymerized polyamide-6 in the presence of, and end-tethered on, the surfaces of montmorillonite layers\(^{17,18}\). Since then, the strategy of “in situ polymerization” of a monomer in a co-suspension with the inorganic filler has been successfully employed for a variety of polymers, with and without end-tethering the macromolecules on the filler surfaces, and through various polymerization reactions, for a variety of polymers and fillers (detailed examples are discussed in a recent review article\(^{8}\)). In most cases, nanocomposites formed by in situ polymerization result in structures that are kinetically trapped (cf. solution approach, above) in a well-dispersed structure. In
general, these structures do possess favorable thermodynamics to retain the filler dispersion upon subsequent processing (such as, compression or injection molding of the hybrid after polymerization), since this method requires that the monomer initially disperses sufficiently the inorganic particles. However, if more polymer is added in the subsequent processing step (cf. attempt to use the in situ polymerized hybrid as a “master batch”) in most cases there occurs a loss of the exfoliated structure achieved during the in situ polymerization step and typically a less dispersed structure is obtained. For example, attempts to dilute the polyamide-6/montmorillonite nanocomposite\textsuperscript{17} with pure polyamide-6, or the in situ poly(\(\epsilon\)-caprolactone)/montmorillonite hybrid\textsuperscript{51,52} with pure poly(\(\epsilon\)-caprolactone), result in collapse of the mostly-exfoliated in situ structure: Typically these well-dispersed \textit{in situ} structure becomes intercalated upon addition of the homopolymer, where the inorganic fillers adopt a parallel stacking with a polymer bilayer –intercalated layer about two monomers thin– in the interlayer gallery.

\textbf{Extension to Other Fillers}. These ideas can be extended to other high-aspect ratio fillers, when taking into account their idiomophies. The ideas can be transferred almost as stated above to other 2D and pseudo-2D layered fillers (e.g. LDH\textsuperscript{10} or graphite), when addressing their differences from layered-aluminosilicates; for example, LDH would require anionic surfactants, whereas graphite is not amenable to grafted modifications and an intercalated swelling agent is needed (cf. master-batch or solution approaches above).

For 1D nanofillers however, there are important differences that may necessitate different choices for their nanocomposite formation. For example, in the case of carbon nanotubes, polymer-matrix nanocomposites can be fabricated using almost all the previously discussed schemes, but the effectiveness and importance of these schemes are very different than in the case of polymer/layered-inorganic nanocomposites. Dispersion of nanotubes is hindered not only by their high affinity for one-another, but also by their ability to intertwine with one-another forming ‘bundles’ or ‘ropes’. These often large agglomerations are typically formed during the synthesis of the nanotubes (especially for single walled carbon nanotubes), which need to be well unbundled before attempting dispersion in a polymer matrix. At the same time, the reactive bonding of surfactants on the nanotube surfaces, although possible via multiple chemistries\textsuperscript{53,54}, most often deteriorates their remarkable physical properties (more so for single walled carbon nanotubes compared to multi walled), and in particular their thermal and electron conductivities, as well as their stiffness and strength\textsuperscript{5}.

After these thoughts, and following the above discussion for polymer/silicate nanocomposites, it seems obvious that the nanocomposite formation schemes that depend on favorable thermodynamics (e.g. melt blending) or ‘brute-force’ mechanical mixing are of limited use here, whereas the solution mixing and the \textit{in situ} polymerization schemes should be much more effective\textsuperscript{11,56}. In fact, the most common approach for

\textsuperscript{5}This does not automatically imply that the respective nanocomposites are also characterized by deteriorated properties. For example, where good dispersions and/or covalent bonding between the polymer matrix and the functionalized nanotubes occurs, the nanocomposite can have very good mechanical property enhancements\textsuperscript{55}.}
polymer/nanotube composite formation involves firstly unbundling in solvent—most often aided by sonication and physisorbed surfactants, and centrifugal separation—the nanotube aggregates, and subsequently a solution-aided dispersion in a polymer matrix. These solution-aided dispersions can effectively ‘trap’ the nanotubes in a well-dispersed morphology after solvent evaporation. Alternatively, instead of employing a physisorbed surfactant and two steps of solution dispersion, nanocomposites can also be formed in a one-step solution process (much like the polymer/silicate counterparts, by co-dissolving the ‘host’ polymers and nanotubes in a common solvent), as for example with poly(vinyl alcohol) and polystyrene. For the same reason, i.e., employing ‘solvent’ to unbundle the nanotubes, in situ polymerization has also been proven as an effective method for producing a well-dispersed nanocomposites. A characteristic example of this approach is the polymerization of PMMA in the presence of solution-dispersed nanotubes, leading to high molecular weight polymers and very good nanocomposite morphologies.

Finally, unlike polymer/layered-silicate nanocomposites, melt processing is far less common for nanotube reinforced nanocomposites. Melt processing is reliant upon mechanical shear and thermodynamics to unbundle the nanotubes, and further disperse them in a polymer matrix. Since neither of these two processes is expected to be very effective for ordinary polymers and nanotubes, typically the nanocomposites produced in this fashion have significant filler aggregation and comparably poor performance; e.g. high-density polyethylene, polypropylene, and polyamide-6/acrylonitrile-butadiene-styrene (ABS) have been melt-processed with nanotubes. Since direct melt processing is inherently ineffective in dispersing nanotubes into polymers, melt processing will probably remain limited in practice, except for those systems that polymer/nanotube “master-batches” can be developed at reasonable costs and with good nanotube dispersions.

2.2.3 Dispersion Characterization, techniques and limitations

Due to its easiness and its availability simple Bragg-reflection powder X-Ray Diffraction (XRD) is most commonly used to probe the nanocomposite structure, especially for polymer/layered-inorganic filler hybrids where the $d_{001}$ basal reflection is indicative of filler-filler separation. However, the XRD can only detect the distance of periodically stacked layers; disordered (bunched together but not parallel stacked) or exfoliated layers are not detected, and some times large $d$-spacings (higher than 50 nm) are not detectable by powder XRD. In general, for medium (ca. 1 μm) lateral size platelets, such as those in natural clays, even with favorable thermodynamics for nanocomposite formation, the structure is characterized by a coexistence of exfoliated, intercalated and disordered layers. Thus, a silent XRD may hide a large number of disordered tactoids, whereas an XRD with an intercalated peak does not reveal the extent of exfoliation. In both cases, the nanocomposite properties are commonly affected dramatically by structures that are not manifested in the XRD, and thus XRD can be highly misleading when employed as a single tool for quantifying nanocomposite structure or even filler dispersion. Although detailed quantitative analysis of such XRD data in the low $2\theta$ range, coupled with careful sample preparation
and use of model reference samples, can yield substantially more information about
the nanocomposite structure\textsuperscript{66}, still powder XRD is insufficient to capture and char-
acterize the nanocomposite structure. Furthermore, when the polymer/ inorganic
nanocomposites are based on materials that are not two-dimensional in geometry –
and thus do not have basal spacings, as for example carbon nanotubes and spherical
or ellipsoidal nanoparticles– then XRD is completely incapable of even a first-order
qualitative determination of dispersion or structure.

Small angle X-Ray scattering (SAXS) is probably the most informative widely-
available technique to characterize the nanocomposite structure. The main hurdle
with this method is to quantitatively convert the information collected in the k-space
into parameters that describe the real space morphology of the hybrids. As an exam-
ple, for polymer layered-inorganic fillers there have been proposed simple\textsuperscript{67} and more
realistic\textsuperscript{68} models of discoid scatters in organic matrices, that can be used to interpret
scattering data into real space parameters for such nanocomposites. In a simple ap-
proach\textsuperscript{67}, average descriptors of the structure can be obtained after relatively simple
analysis of the scattering data, which are of some value for quantifying the hybrid
structure. A more complete description of structure necessitates much more careful
design and implementation of scattering studies, and more tedious analysis\textsuperscript{68}. Even
where the models for the specific structures have been developed and the methods for
the experimental approach and the analysis have been outlined, as for example in the
case of layered inorganic nanoparticles\textsuperscript{68}, the amount of work involved to implement
such approaches in real polymer nanocomposite systems has proven as a barrier for
the widespread use of SAXS as a common morphology characterization practice.

Transmission electron microscopy (TEM) is also widely employed –in its simplest
bright-field mode– as a tool for directly visualizing the nanocomposite structure of
polymer nanocomposites. This is possible because there is a sufficient contrast for the
transmitted electrons between the polymer matrix and most fillers (inorganic parti-
cles, carbon in nanotubes or graphite, and almost all oxides) without any polymer
“staining”. In the extreme case, high resolution TEM\textsuperscript{69} can even provide a qualitative
picture of the inorganic filler crystal structure, or can be combined with point electron
diffraction to interrogate crystal structures at specific filler or polymer regions. Al-
though TEM does not suffer from the same shortcomings as XRD, since it can directly
visualize nanoscale fillers without a need for a parallel stacking, it does have other lim-
itations: Firstly, it is very painstaking to obtain quantitative information about any
of the characteristic parameters that describe the nanocomposite morphology. Such
information can only be derived from image analyses of many and independent TEM
images, so as to ensemble with some statistical importance the typical structures in
the composite. Secondly, since TEM is essentially a projection method, it is diffi-
cult to characterize structures normal to the large surface area of fillers; for example,
almost all TEM published for polymer/layered silicate nanocomposites show images
with the silicates positioned edge-on on the image, since layers parallel or oblique to
the sample surface project as extended dark areas in the TEM image. Despite these
limitations, we believe that informative TEM should –at a minimum– complement
XRD or other morphology studies, even only to qualitative capture the hierarchical
structures of the hybrid at various length scales. Probably the additional information
of TEM is crucial when accompanying featureless XRD structures: such as silent –no basal reflections– polymer/layered nanofiller nanocomposites (which in most cases are wrongfully interpreted as exfoliated structures), polymer nanotube hybrids, and polymer nanoparticulate composites.

Finally, morphological information can also be obtained indirectly from methods that reflect the composite morphology into other macroscopic properties. Within the focus of this book two examples of such methods can be mentioned, rheological measurements and cone calorimetry flammability methods. Both methods can sensitively detect well dispersed nanofillers in a polymer matrix, and can discriminate from the respective ‘conventional’ composites based on the same polymer and fillers but without nanometer scale dispersion of the latter. We shall not provide any further details on this, we just point the interested reader to the following chapters concerning the cone calorimetry approach, and to a few representative references for the rheology\textsuperscript{7,16,70}.

In summary, in lieu of providing a recipe for the characterization of the nanocomposite morphology we will illustrate the limitations of the above characterization techniques by schematically drawing an example of the plethora of parameters needed to describe the morphology of a polymer/layered-silicate nanocomposite (figure 2.3). Even in this case, that can be actually interrogated by XRD characterization, only the distribution of basal (layer-layer distances within parallelly stacked clusters) spacings can be obtained by XRD. SAXS can in addition provide some of the additional
parameters\textsuperscript{67}, such as mean number of layers per stack and “projected” lateral dimension of layers, while through more realistic models and analysis\textsuperscript{68} approximate values can only obtained for the rest of the important parameters (figure 2.3). In almost all cases, a representative set of TEM structure observations should also be obtained –in addition to diffraction/scattering characterization– which should provide the qualitative description of structure, albeit any shortcomings in quantitatively determining the various morphological parameters (due to the local only observation of morphologies, even by numerous TEM images).

2.3 Effects of nanofillers on Materials Properties

2.3.1 Effects on Polymer Crystallization

Polymer Specific Effects. It is expected that the incorporation of nanoparticles in a semi-crystalline polymer matrix would substantially affect the crystallization behavior of the polymer. Depending on the polymer/filler interactions there can develop three general behaviors:

(a) Development of new crystal structures: Where there exist strong specific interactions between the filler and the polymer, a new crystal structure develops in the vicinity of the filler, which is often not the same as the crystal structure of the unfilled polymer under normal crystallization conditions. The best example of such a behavior is the case of polyamide-6/ montmorillonite nanocomposites in which the $\gamma$-crystal phase of polyamide is promoted next to the fillers\textsuperscript{42–44}. This behavior originates from the strong hydrogen bonding of the amide groups with the silicate (SiO$_x$) surfaces, and is, for the same reason, also observed in poly(vinyl alcohol)/mmt nanocomposites\textsuperscript{39,71}. A less frequent case, where new crystal structures are promoted by nanoscale fillers, also exists for polymers that develop non-bulk crystal phases when the polymer chains are aligned parallel to filler’s solid surfaces –two examples of such nanocomposites are PVDF\textsuperscript{72} and syndiotactic-polystyrene (sPS)\textsuperscript{73}. In all these cases, where the inorganic surfaces promote growth of a different crystal phase, the nanocomposite mechanical and thermal properties can be enhanced through this mechanism, when the surface-nucleated crystalline phase has better mechanical and thermal characteristics than the bulk crystal phase. Fillers with large surface area maximize these filler-induced enhancements of the material properties; a dramatic manifestation of such a response is found in polyamide-6/montmorillonite nanocomposites.

(b) Polymer amorphized by filler: In very few cases, such as poly(ethylene oxide) (PEO)/ Na$^+$ montmorillonite nanocomposites, the polymer/Na$^+$ interactions are favorable to mixing but not conducive to crystallinity\textsuperscript{74}. Specifically, crystallization of PEO nanocomposites based on alkali-cation bearing fillers, is found to be inhibited, exhibiting a decrease of spherulite growth rate and crystallization temperature. Although the overall crystallization rate increases with silicate loading as a result of extra nucleation sites which occur in the bulk PEO matrix (\textit{i.e.} far from the silicate surfaces), PEO is highly amorphized near the montmorillonite surfaces. This behavior is attributed to the specific way that PEO interacts with Na$^+$ montmorillonite,
where strong coordination of PEO to the surface Na\(^+\) cations promotes non-crystalline (ether crown) PEO conformations.

**c) Heterogeneous nucleation by fillers:** For the vast majority of polymers, the effect of nanofillers on polymer crystallization relate only to crystal nucleation by the fillers (which typically increases proportionally to the number of individual filler clusters), and to changes in the kinetics of crystallization (which are typically characterized by a 2-4 fold decrease in the linear growth rate of crystallization). In these cases, and for filler loading below ca.10wt.%, the equilibrium melting temperature \(T_m\) is not affected by the nanocomposite formation. For example, as shown in figure 2.4, the \(T_m\) of PP-g-MA, PET, and PEO nanocomposites and the respective bulk polymers were estimated based on Hoffman-Weeks plots, and it is shown that moderate (below 10 wt.%) mmt addition does not change the \(T_m\) values \[T_m\text{(PP-g-MA)} = 183.8^\circ C, T_m\text{(PET)} = 260.1^\circ C, T_m\text{(PEO)} = 69.7^\circ C\]. These results are consistent with the literature reported before\(^8\) and allow for comparing the crystallization kinetics of neat polymers and their nanocomposites at the same isothermal crystallization temperature. To further elucidate the effect of mmt on the crystallization kinetics of these polymers, isothermal crystallization measurements were carried out with DSC, and complemented by direct imaging of the crystallites (cross-polarization optical microscopy and AFM) for systems crystallized under the same conditions (figure 2.4). Initially (crystals grow in 3-D and the crystallites have not yet impinged), crystallization kinetics can be expressed by the following equation:

\[
V_c^f = \frac{4}{3} \pi \rho_n G_R^2 t^3
\]

where, \(V_c^f\) is the total crystal volume (crystallinity), \(\rho_n\) is the nuclei density, \(G_R\) is the linear crystal growth rate, and \(t\) is the crystallization time. When \(V_c^f\) is 0.5, the corresponding crystallization time \(t\) is defined as the “half time” of crystallization \(t_{1/2}\), and denotes the time necessary to reach 50% of the total enthalpy of crystallization under isothermal DSC conditions (figure 2.4). When the nuclei density, \(\rho_n\), is measured by CPOM (cross polarized optical microscopy) and/or AFM (atomic force microscopy), the crystal linear growth rate \(G_R\) can be estimated. The half times of crystallization \(t_{1/2}\) for various isothermal crystallization temperatures \(T_{iso}\) for neat polymers and their nanocomposites. As expected, the overall crystallization rate increases with the clay addition in the polymer, as denoted by the decrease of \(t_{1/2}\) upon addition of the nanofillers (this effect is rather small for PP-g-MA). However, accounting for the nuclei density increase in the nanocomposites (for PP-g-MA, the \(\rho_n\) increased ca. 6-8 fold at 5-10wt% o-mmt content, for PET it increased more than 500 fold at 3-6wt% o-mmt, and for PEO 20-50 fold for 5-10wt% mmt) the linear crystal growth is slowed down due to the introduction of clay across all systems. Despite the qualitative differences between PEO, PP, and PET crystallization when reinforced by mmt, and despite the quantitative differences in \(t_{1/2}\), when the increase of nuclei density is accounted for, all systems show a \(G_R\) decrease of 0.25-0.5 upon mmt addition (for PP the nanocomposite \(G_R\) is 0.5 of the bulk polymer value, for PET is 0.25, and for PEO is 0.33 of the respective bulk polymers). This agreement between such different systems strongly indicates that the geometric constraints associated with
Figure 2.4: (Left) Hoffman-Weeks plots of neat polymers and their nanocomposites; the $T_M^0$ of the polymers is not affected by the nanocomposite formation. (Right) half time of crystallization for the same neat polymers and their nanocomposites; the overall crystallization rate is reduced for PET and PEO upon incorporation of an inorganic nanofiller, and is not affected for the PP-g-MA. When accounting for changes in the nuclei density with filler incorporation, the linear growth rates $G_R$ are slowed down in all systems shown. For both panels: PP-g-MA [top], PET [middle], PEO [bottom].
Figure 2.5: Differential Scanning Calorimetry comparison of unfilled polymers and their respective nanocomposites with montmorillonite layered-silicates. (top) Heating DSC scans: the crystalline melting point is markedly unaffected by the addition of the fillers since the polymer crystal structure (e.g. the crystal unit cell) is not affected by the filler. A notable exception are those polymers where a new crystal structure is promoted near the filler surface, such as PVA, syndiotactic-PS, and polyamide [not shown here]. (bottom) Cooling DSC scans: the crystallization point is strongly affected by the fillers, bearing traces of heterogeneous nucleation (PP, sPS, PVA), crystallization of new crystal structures (PVA), or hindering of crystallization near a filler (PEO).

the dispersion of mmt fillers is determining the effect (decrease) on the linear crystal growth rate in these systems, rather than the polymer/mmt interactions. In this latter case, one would expect a qualitatively different effect in PET/PP compared to PEO, and also substantial quantitative differences between PET and PP as well. All these effects manifest themselves in differential scanning calorimetry (DSC) studies, especially when the behavior of the neat –unfilled– polymer is compared against the respective nanocomposite (fig. 2.5).

General Effects across Polymers. Despite the variety of the nanofiller effects
on polymer crystallinity, which originate from the various polymer/filler interactions, there also exist important common effects on the crystallinity due to the nanocomposite structure. The most important of these general effects is probably a general reduction in size of the polymer crystallites upon nanocomposite formation. For example in figure 2.6 we compare the spherulites observed for unfilled polymers and their respective 3 wt.% montmorillonite nanocomposites. Independent of how the fillers affect the nucleation and/or the kinetics of crystallization, there is in all cases a substantial decrease of the spherulitic size. This behavior originates from the discontinuity of space caused by the inorganic fillers, which forces spherulites to have sizes comparable with the filler-filler separation, independent of the bulk polymer spherulite size. This effect is also independent of whether crystallization in the nanocomposite is nucleated homogeneously (PEO) or heterogeneously (PP, sPS), and of whether the filler hinder crystallization (PEO), promote new crystal structures (sPS), or simply act as heterogeneous nucleating agents (PP).

**Effects of 1D nanofillers.** Like layered-inorganic fillers, carbon nanotubes influence polymer crystallization when incorporated as filler in the polymer matrix, however these effects do not have as wide a variety as the layered-silicates discussed above. In the vast majority of reports, carbon nanotubes act simply as heterogeneous nucleating agents in crystallizable polymer systems\textsuperscript{11,56,64,75–78}. For example, polypropylene crystallization in the presence of nanotubes shows increased crystallization temperature and rate of crystallization with the introduction of varying concentra-
tions of nanotubes\textsuperscript{79,80}, with no change in the crystalline structure or the melting point. Furthermore, the PP crystallite size decreases in presence of nanotubes\textsuperscript{64,75,76}, in agreement with the general behavior observed in polymer/layered-inorganic nanocomposites.

When nanotubes interact strongly with the host polymer, as for example with conjugated and ferroelectric polymers, and in these cases polymer crystallization is altered, developing higher-order structures and increased degrees of crystallinity\textsuperscript{79,80}. However, crystallization effects discussed above for layered-silicates due to polymer coordination with alkali cations (for PEO) and due to extensive hydrogen bonding (for amides) are, as expected, absent in nanotube reinforced nanocomposites. Namely, PEO does not have any amorphous regions near nanotubes, and it follows bulk-like crystallization, with the overall percent crystallinity, crystallization point, and melting point remaining unaffected, even at loadings of 7 wt. % nanotubes\textsuperscript{81}. Similarly, polyamide-6 and polyamide-12 matrices reinforced with nanotubes exhibit crystallization similar to that of the unfilled polymer\textsuperscript{78,82}.

Finally, the 1D geometry of nanotubes provides exciting opportunities for controlled nucleation and growth of single crystals along individual fibers, as for example with polyamide-6,6 and polyethylene crystallized from solution, allowing for control of crystallite periodicity and molecular level architecture\textsuperscript{83}. This unique capability of nanotubes, can conceivably lead to special types of ‘functionalization’ of individual nanotubes, that can be exploited to improve interactions (\textit{vide infra} better interfacial coupling) and control dispersion in selected polymer matrices.
2.3.2 Effects on Mechanical Properties

Most of the polymer/clay nanocomposites studies report tensile properties, as a function of mmt content ($\phi_{\text{mmt}}$). As a typical example, in fig. 2.7 we compare tensile moduli from various studies of neat-PP/o-mmt and MA-functionalized-PP/o-mmt nanocomposites. The characteristic behavior for polymer/layered-inorganic nanocomposite materials\textsuperscript{6,8} is observed: Namely, there is a sharp increase of the Young’s modulus for very small inorganic loadings ($\phi_{\text{o-mmt}} < 4\text{wt\%}$) followed by a much slower increase beyond $\phi_{\text{o-mmt}} \approx 5\text{wt\%}$. With increasing $\phi_{\text{mmt}}$, the yield stress does not change markedly compared to the neat-polymer value, and there is a small only decrease in the maximum strain at break. PP systems conventionally filled –no nanometer level dispersion– by the same fillers (e.g. 2C18-mmt) do not exhibit as large increases in their tensile modulus (figure 2.7a).

This mechanical reinforcement is expected and not too exciting at first glance, especially considering that the montmorillonite filler platelets have a very high intrinsic stiffness (tensile modulus of 140-180GPa). However, there are some points that can

![Figure 2.7](image-url)

Figure 2.7: Tensile moduli (relative to bulk value) for various PP/mmt nanocomposites. (a) neat-PP hybrids: with f-mmt (■\textsuperscript{49}), C18-mmt (▽\textsuperscript{35}), and 2C18-mmt (○\textsuperscript{49}). In absence of favorable thermodynamics, the dispersion and thus the mechanical properties are a strong function of the processing conditions. (b) PP-g-MA/2C18-mmt melt-processed nanocomposite(■\textsuperscript{49}), and PP hybrids formed via various PP-g-MA pretreated o-mmt master batches: C18-mmt (▶\textsuperscript{34}), C18-mmt (○, △\textsuperscript{35}). Given the well defined thermodynamics of mixing there is small variation of dispersion and mechanical properties across different systems and various research groups. Slight changes in the thermodynamics, e.g. when a different surfactant is employed C8-mmt (▽, □\textsuperscript{35}), do result in moduli changes.
be made: The tensile results obtained from thermodynamically stable hybrids are not affected by processing conditions (since the nanocomposite structure remains the same) whereas, in absence of favorable PP/o-mmt thermodynamics, the structure and the tensile properties vary strongly with the processing conditions (fig. 2.7b). Similar improvements in mechanical properties can also be achieved by other layered particulate fillers, however, much higher filler loadings are required (e.g. by loading 30-60 wt% of talc or mica\textsuperscript{14}), since such particles are not well dispersed and the effective filler surface area is orders of magnitude smaller. Finally, for PP/o-mmt the relative improvement of the moduli compared to the unfilled polymer is rather small (barely reaching 60% for PP and 100% for PP-g-MA), whereas in other systems such as elastomers or polyethylene improvements of 400% to 1200% can be achieved by the same o-mmt fillers. The origin of this behavior is traced to two effects: (i) The relatively poor interaction of the polyolefins with o-mmt (\textit{cf.} eq. 2.6, \textit{vide infra} interfacial adhesion energy of \( \sim 83\text{mJ/m}^2 \), see also §11.2 in\textsuperscript{32}). As the polymer/inorganic adhesion is improved –e.g. when MA functional groups are added to the polymer– the stresses are much more effectively transferred from the polymer matrix to the inorganic filler, and thus a higher increase in the Young’s modulus is achieved (fig. 2.7b). (ii) The relatively high modulus of the original polymer (for the PP reported, 0.6-1.3 GPa). This latter effect becomes clearer when this behavior is contrasted to nanocomposites formed by the same filler in a ‘softer’ matrix, such as elastomers or PE that have tensile moduli in the range of 0.1-0.3 GPa.

As further evidence of the last two points, we also show the tensile moduli of polyamide/mmt systems (figure 2.8a), where substantial improvements of the me-
Mechanical properties can be achieved, despite the relatively high stiffness of the polymer matrix, due to the very effective stress transfer from the polymer to the filler, mediated by strong hydrogen bonding. In the case of polyamide-6/mmt nanocomposites, independent of the original polyamide-6 matrix characteristics and independent of whether the hybrids were formed by in-situ polymerization or melt blending\textsuperscript{17,18,42–44,84}, there seems to be a considerable agreement on the achieved enhancement in tensile modulus that spans research groups, methods, and materials. We postulate that due to the strong interfacial adhesion—every amide group of the polymer can hydrogen bond to the silicate surface—the interfacial strength and maximum interfacial shear stress are dictated by the polymer/mmt interactions and overwhelm all other parameters that relate to processing and dispersion, polymer matrix characteristics, and/or stiffness of the filler.

### Theoretical Insights in the Mechanical Properties

Even from the very brief discussion of the previous paragraph, it becomes obvious that the \textit{a priori} prediction of the mechanical properties of polymer/inorganic nanocomposites is rather involved, and to date the design of such nanocomposites is based on mostly Edisonian approaches. Theoretical models developed for the prediction of mechanical properties of conventional composites, such as the Halpin-Tsai\textsuperscript{86} and the Mori-Tanaka\textsuperscript{87} models, fail in their ‘straight forward’ application to nanocomposite systems. There are numerous physical phenomena that need to be included in such models so as to better describe the mechanical behavior of polymer-matrix nanocomposite materials. Again drawing examples from the polymer[layered-silicate nanocomposites, recent theoretical models have been developed attempting to capture the behavior of these materials, by accounting for the high aspect ratio of the fillers. For example, there is a recent effort\textsuperscript{88}, which modifies the Halpin-Tsai model to account for buckling of filler platelets, incomplete dispersion, and non biaxial in-plane filler orientation; despite its additional complexity and improvements, still this modified Halpin-Tsai model does not seem highly successful in predicting mechanical properties of polymer[layered-silicate nanocomposites for a wide range of polymer matrices\textsuperscript{88}. The main shortcoming in the previous approach is attributed\textsuperscript{89} to the insufficient modeling of a ‘constraint region’ of polymeric material surrounding the nanoscopic filler; this interfacial polymer is expected to differ in properties and morphology from the bulk polymer matrix, as has been observed experimentally. However, accounting for such a ‘constrained region’, as for example by introducing appropriate modifications\textsuperscript{89,90} in the Mori-Tanaka model, still has a limited predictive power when applied across various polymer matrices and necessitates the adjustment of the model’s parameters for each nanocomposite system\textsuperscript{90}. Even in the most focussed approach, when a mechanical model is developed to describe a single polymer/inorganic nanocomposite\textsuperscript{91}—while accounting for the imperfect interfacial coupling, and the effective aspect ratio and filler volume fraction due to varied dispersion with filler loading—such a model necessitates the calculation of an interfacial strength parameter (in this case an interfacial shear stress, which was calculated\textsuperscript{91} to be 2-8MPa for the PDMS/mmt system).
These theoretical endeavors, despite any shortcomings and approximations, offer valuable insights in important design parameters for the mechanical performance of polymer nanocomposites. Specifically:

- Mechanical properties are determined by the effective filler aspect ratio and effective filler volume fraction, when incomplete dispersion is accounted for\(^{88,91}\) (rather than on the absolute filler loading and the aspect ratio of the individual fillers).
- Filler-specific mechanisms of deformation and fracture can have a considerable contribution to the mechanical properties of their nanocomposite\(^{88}\).
- The correct enumeration of the interfacial strength is crucial for the correct estimation of the composite’s mechanical properties\(^{90,91}\), and its small value –compared to the modulus of the filler– can dramatically limit the filler’s reinforcing effectiveness.

In particular for the last item, this interfacial strength at the polymer/filler interface can only be experimentally measured directly in very few cases; for example, carbon nanotubes have been pulled out from a polymer (polyethylene-butene) matrix by AFM, yielding interfacial strengths\(^{92,93}\) of 10-90MPa, depending on the nanotube radius. These experimental interfacial strength values correlate well with interfacial forces calculations\(^{30}\), such as those described earlier (eq. 2.6). Thus, one may expect that the same approach used for predicting miscibility of polymers and layered-fillers may be helpful in estimating the polymer/filler interfacial strength. Given the continuum character and the assumptions behind such calculations, and also the very approximate numbers available for the surface tension components of the materials involved, this approach can only provide a first-order estimation of the interfacial strength for polymer and various nanofillers. Albeit its uncertainty, this ‘theoretical’ value of the polymer/filler interfacial strength may be an important design element for the mechanical properties of nanocomposites, especially since it is very difficult to envision approaches able to determine this property experimentally.

Some examples of the application of eq. 2.6 for polymer/layered-inorganic nanocomposites could be:

- For polypropylene/montmorillonite interfaces –ignoring all necessary functionalizations for PP– would yield an interfacial adhesive energy of \(\sim 83 \text{ mJ/m}^2\) corresponding to an interfacial strength of \(\sim 10 \text{ MPa} \) (cf. 3-7 MPa from tensile measurements\(^{49}\));
- For PDMS/montmorillonite the same approach yields an interfacial energy of \(\sim 91 \text{ mJ/m}^2\), or an interfacial strength of \(\sim 11 \text{ MPa} \) (cf. 2-8 MPa from theoretical models\(^{91}\));
- For polyamide/montmorillonite nanocomposites –and ignoring all crystalline phase changes that may be caused by the silicate fillers\(^{42-44}\)– an adhesive interfacial adhesion of \(\sim 107 \text{ mJ/m}^2\) corresponding to an interfacial strength of \(\sim 14 \text{ MPa} \); and
- For carbon nanotube/polyethylene yields an interfacial energy of \(\sim 49 \text{ mJ/m}^2\) (cf. 47 mJ/m\(^2\) from AFM experiments\(^{92}\)) or an interfacial strength\(^{4}\) of \(\sim 6.2\)

\(^{4}\)Equation 2.6 is independent of geometry, however when estimating an interfacial strength the
MPa (cf. 20-40 MPa from multi-walled nanotubes\textsuperscript{93}, and 2 MPa from computer simulations\textsuperscript{94}).

The above observations, to the extent that they are valid, bear significant implications for the possibilities of mechanical property improvement via nanocomposite formation. Specifically, (1) given the nature of a polymer (i.e., $\gamma_{LW}$ and $\gamma_{\pm}$) the maximum mechanical reinforcement by a completely dispersed nanofiller will be limited by the polymer/filler interfacial strength. For example, in the case of PE and PP ($\gamma_{LW} \approx 26$ mJ/m\textsuperscript{2} and $\gamma_{\pm}=0$) and layered-silicates, there would be a common limit of about 2-4 MPa for the maximum tensile modulus that can be achieved through nanocomposite formation. This is in agreement with experimental studies for these systems, which show a similar absolute value for the maximum tensile modulus obtained by PE and PP (albeit reflected in much bigger relative improvements of 400-1200\% for the softer LDPE, compared to 60-100\% for the stiffer i-PP [fig. 2.7]).

(2) The addition of a small number of functional groups, e.g. addition of maleic-anhydride groups in PP, would only increase moderately the interfacial adhesion, and would similarly increase the tensile moduli to a moderate only extent [fig. 2.7b].

(3) The addition of large numbers of strongly interacting (with the filler) groups along the chain, such as H-bonding groups densely across the polymer backbone, would result in larger relative improvements in mechanical properties [fig. 2.8], but still below the upper limits set by the calculated interfacial adhesions (the use of the polyamide-6 as an example in this case is questionable, given the promotion of the $\gamma$-phase crystal for the nanocomposites\textsuperscript{42–44}; however, the favorable comparison of the polyamide-6 behavior with the behavior of the urethane/urea systems may \textit{a posteriori} justify this choice).

(4) Finally, although chemical bonding of the polymer to the filler may seem as the ultimate route to reinforce the polymer-filler interface, if such covalent bonds are not introduced densely across the length of the polymer, they will result in a limited only interfacial reinforcement, and a respectively moderate improvement in the mechanical properties. This has been shown in cross-linked systems with reactive –via the cross linking groups– dispersion of silicate layered fillers\textsuperscript{95}. 

\textsuperscript{93} filler geometry –contact geometry– must be considered –for example see\textsuperscript{32} (§11.1) or\textsuperscript{29} (§VI.1). The value provided for the nanotube/polyethylene here (6.2 MPa) is based on the interaction of two semi-infinite flat surfaces. Calculation for a cylinder in contact with a semi-infinite flat surface yields an interfacial strength of 4.6 MPa, whereas the interaction between a cylinder emerged in a polymer should be somewhere in between these two values.
2.3.3 Effects on Barrier Properties

The permeability of small penetrant molecules through an organic matrix is determined by the solubility and diffusivity of the small molecule in this matrix, as well as by the mean square displacement (total traveled path length) divided by the sample thickness. In principle, the addition of a filler in the polymer matrix is expected to affect the solubility and diffusivity of a penetrant molecule, especially in the vicinity of the filler — i.e., in the filler polymer interfacial region and at least one polymer $R_g$ away from the filler surface. Also, it is expected that fillers will affect the path tortuosity (mean square displacement of penetrant versus film thickness) directly, when penetrants are forced to travel around impermeable fillers, and indirectly, when fillers induce polymer chain alignment or alignment and modification of polymer crystallites.

Theoretical approaches on the barrier properties of nanocomposites, treat fillers as impermeable non-overlapping particles and assume no permeability changes in the polymer matrix. Effectively, this means that the permeability of the composite will be smaller than the permeability of the matrix — unfilled polymer — by a factor equal to path tortuosity in the composite (simply assuming that the penetrant path does not cross any filler particles). This path tortuosity was calculated by Nielsen for completely aligned filler particles (all fillers have their larger surface parallel to the film surfaces, but there is no order in the filler center of mass), and its contribution to the composite permeability was derived to be:

$$\frac{P_{\text{comp}}}{P_{\text{poly}}} = \frac{1 - \phi}{1 + a\phi}$$  

with $a$ being the filler aspect ratio (for square fillers of length/width $L$ and thickness $W$, $a=L/2W$) and $\phi$ the volume fraction of the filler. Recently, Bharadwaj modified this equation to account for non-aligned fillers, by introducing an order parameter $S$ for the filler orientation:

$$\frac{P_{\text{comp}}}{P_{\text{poly}}} = \frac{1 - \phi}{1 + a\phi S^2(S + 1/2)}$$  

with $S = \frac{1}{2} (3\cos^2\theta - 1) = \begin{cases} 1 & \parallel \text{surface} \\ 0 & \text{random} \\ -\frac{1}{2} & \perp \text{surface} \end{cases}$  

which reduces to the Nielsen equation for perfectly aligned fillers ($S=1$). In a more detailed approach, Friedrickson and Bicerano derived the same path tortuosity effects for circular fillers (radius $R$ and thickness $2W$), obtaining:

$$\frac{P_{\text{comp}}}{P_{\text{poly}}} = \frac{1}{4} \left( \frac{1}{1 + a\phi\beta_1} + \frac{1}{1 + a\phi\beta_2} \right)^2$$  

with $\begin{cases} \beta_1 = (\pi/\ln a)(2 - \sqrt{2})/4 \\ \beta_2 = (\pi/\ln a)(2 + \sqrt{2})/4 \end{cases}$  

The first mechanism, associated with chain alignment and the related diffusive anisotropy of small-molecule within aligned chains, bears a relatively weak effect on permeability, whereas the second mechanism, associated with crystallite alignment and changes in the crystal morphologies, causes rather strong changes in permeability and is commonly employed in strain-hardened semi-crystalline polymers for barrier applications.
Figure 2.9: Comparison of theoretical models quantifying the effect of path tortuosity on the permeability of a composite: Nielsen model\(^9\) (eq. 2.8), Friedrickson-Bicerano\(^9\) (eq. 2.10), and modified\(^9\) Nielsen and Cussler-Aris (eq. 2.11).

which can cover a wider \(\phi\) range –from dilute to semi dilute– than the ‘modified Nielsen’ and ‘modified Cussler-Aris’ relations (as presented in this same work\(^9\), modified to address circular fillers):

\[
\frac{P_{\text{comp}}}{P_{\text{poly}}} = \frac{1}{1 + a \phi \pi / \ln a} \quad \text{(modified Nielsen)} \quad \frac{1}{1 + (a \phi \pi / (4 \ln a))^2} \quad \text{(modified Cussler-Aris)} \quad (2.11)
\]

Nevertheless, eq. 2.10 generally gives results similar to the Nielsen approach (eq. 2.8), when a geometric correction of \(\sqrt{\pi}/2\) is applied to the filler aspect ratio (i.e., comparing equal area fillers, square for Nielsen and circular for Friedrickson-Bicerano). The comparison of the theoretical models is illustrated in figure 2.9. Given that all models –except for the Cussler-Aris– give similar behavior for the range of parameters relevant to polymer/layered-inorganic nanocomposites (10 < \(a\) < 1000 and \(\phi\) ≤ 15 vol.%) we henceforth use the much simpler Nielsen model, including the addition of the orientation term (eq. 2.8 and eq. 2.9). According to this model, the obvious expectations can be quantified: higher aspect ratio fillers provide substantial lower permeabilities for a given filler volume fraction (fig. 2.10a), and aligned fillers are much more effective barriers for a given aspect ratio and filler loading (fig. 2.10c). Additionally, some not-so-obvious conclusions can also be drawn:

- Beyond the filler aspect ratio, the composite permeability is also controlled by the filler volume fraction and/or by filler alignment [e.g. eq. 2.9]: Thus, low aspect ratio fillers can be as effective as higher aspect ratio fillers, though at slightly higher loadings. For example, for aligned fillers –fig. 2.10a– a completely exfoliated montmorillonite (\(a=500\)) at \(\phi=2\) vol.%, has comparable permeability with a partially exfoliated montmorillonite (\(a=200\)) at \(\phi \sim=3\%\), or a mostly-
Figure 2.10: Theoretical predictions based on path tortuosity [eq. 2.9], as a function of: (a) filler aspect ratio $a=1$ to 1000; (b) filler aspect ratio and alignment, $S=1$: perfect smectic alignment /dashed lines, $S=0$: random orientation /solid lines; (c) filler aspect ratio for a constant volume fraction $\phi_V=5\%$. (d) Comparison of the same theoretical predictions –parameters as indicated– with experimental values for water vapor permeabilities in various polymer/ montmorillonite nanocomposites$^{39-41}$.

intercalated montmorillonite ($a=100$) at $\phi \sim 5\%$. This observation has important implications in designing a barrier nanocomposite: for the same example, instead of completely exfoliating a given filler –a task that is usually difficult to achieve– the same filler in a partially-exfoliated or mostly-intercalated morphology could achieve the same barrier performance at slightly higher filler loadings.

- Perfectly aligned fillers result in similar permeabilities with randomly oriented fillers of higher aspect ratio and/or higher loading. For example, fig. 2.10b, for a $a=300$ filler, perfect alignment at $\phi=1.5\%$ results in the same barrier
performance as the same filler when randomly oriented at $\phi \sim 4.3\%$; and for a $a=500$ filler, perfect alignment at 1.5 vol.% is comparable in permeability with a 4.5 vol.% composite with random filler orientation. Along the same lines, a perfectly aligned filler nanocomposite with $a=300$ at $\phi=1\%$ has similar barrier performance as $a=500$ at 2\%. This observation provides also important guidance on how to avoid the difficult task of perfectly aligning the fillers parallel to the film surface (fig. 2.10c).

- The effect of filler orientation on permeability is decreasing in importance with higher filler aspect ratio (fig. 2.10c). For example, permeability improvement for $a=1000$ is only 5\% better with perfect alignment ($S=1$) compared to a random orientation ($S=0$), and for $a=500$ this difference is about 10\%.

Additionally, the favorable comparison of these theoretical predictions with experimental data (fig. 2.10d) gives some credibility to the conclusions above. In figure 2.10d we plot experimental water vapor permeabilities of various solvent cast nanocomposite films. The experimental behavior follows well the theoretical trend, and is enclosed between the response of exfoliated systems—especially for low filler loadings— and the one of intercalated systems—for moderate and higher loadings. This reflects the same “effective filler aspect ratio” discussed before in the mechanical properties. This agreement persists for all systems that have good filler dispersion—as achieved by solvent casting—and disappears for the same polymer and filler when dispersion is poor (cf. PDMS/dimethyl-dialkyl-montmorillonite with intercalated vs. exfoliated composite structures). Finally, this agreement is rather independent of polymer and filler hydrophillicity—ranging from very hydrophillic poly(vinyl alcohol) reinforced by Na$^+$ montmorillonite, to moderate poly(urethane-co-ureas), to rather hydrophobic poly(dimethyl siloxane) and dialkyl-modified montmorillonite. This agreement is also independent of polymer crystallinity—ranging from semi-crystalline poly(vinyl alcohol) with filler-induced crystallinity effects, to segmented semi-crystalline poly(urethane-co-ureas), to amorphous poly(dimethyl siloxane). Thus, it seems that the path tortuosity effects may in fact overwhelm other important parameters, such as permeant solubility changes** and polymer crystallinity effects, when it comes to predicting permeability changes upon nanocomposite formation.

**We should point out that barrier or permeability properties relate to the rate of a permeant molecule diffusion through a polymer or a nanocomposite material, and cannot be extended to make predictions for ultimate water uptake—or more general solvent uptake. If water or solvent uptake is of interest an independent experiment is needed and required, and for this property the changes in solubility upon nanocomposite formation will be the determining factor.
2.4 Future Outlook

Nanocomposites in the sense of hybrid materials with novel properties, beyond the realm of unfilled polymers and conventional composites, bear high promise for enabling new uses and applications of polymer materials. In the simplest approach they can expand the window of applications of a given polymer, and in the best case they can enable the use of polymer-matrix composites in applications where metal or ceramic materials are currently used. One of the first untapped challenges in the field is to go beyond the simple dispersion of fillers, and move towards the development of methods to create well-defined 3D morphologies of nanofillers: morphologies that contain highly aligned fillers, house-of-cards structures, edge-connected (star-like) formations, alternating 2D and 1D fillers.

The highest benefit of the hybrid character of nanocomposites comes from overcoming the property tradeoffs associated with conventional composites: For example, nanocomposites can improve the stiffness without sacrificing toughness, can enhance barrier without sacrificing transparency, can bestow flame retardancy without sacrificing mechanical properties, can simultaneously enhance mechanical performance and biodegradability. When such behaviors are synergistically enhanced with effects from other additives or fillers, they can effectively push the envelope of the current state of the art. Such approaches will develop particularly exciting systems where synergistic combinations of multiple nano- and macro- fillers are properly combined in a multi-filler composite material.

The field, although it currently engages an overwhelming number of research groups, desperately needs well-designed scientifically-based studies to explore the fundamentals of these materials. Since the barriers of entering the field are really low (no need for special equipment or expensive materials, studies can be published even when reproducing results from previous works or making minor incremental advances) the temptation is high to simply mix polymers with off-the-shelf nanofillers and just report X-ray diffraction and mechanical measurements. The real potential of these materials however will remain untapped until the nanoscale mechanisms responsible for macroscopic properties are unveiled, and are further exploited to make radically new materials. New horizons need to be explored, especially outside the “comfort zone” of traditional polymer or materials scientists. If one considers the numerous examples of biological organic/inorganic nanostructures with unparalleled performances and combination of properties that transcend any synthetic material, one can only start to imagine the limitless possibilities of this field.

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Bibliography


