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Novel Organic Modification of Clay Particles for Nanocomposite Formation

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Summary

Understanding the governing thermodynamics of miscibility between polymers and organically modified clays or silicates is of great importance in designing materials with desired miscibility/exfoliation and thus with desired materials properties. Along these lines, our current opinion on how to select appropriate organic modifications for layered inorganic fillers is provided, with the emphasis on two polymer classes: apolar polymers, e.g. polypropylene, and high temperature polymers, e.g. syndiotactic polystyrene. A comparative discussion of previous theoretical models and of our experimental findings on the miscibility, aims to unveil the guiding principles in selecting appropriate organic modifications for inorganic fillers, so as to achieve dispersion in thermoplastic matrices.

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Introduction

Traditionally the commercial importance of modifying the polymer properties has been driving an intense investigation of polymeric composites reinforced by additives: particulates, fibers, and layered inorganic fillers [1, 2]. More recently, special emphasis and very vivid research has been focused on nanometer-thin layered aluminosilicate inorganic fillers, such as clays, talc, and mica [3, 4]. Although it has been long known that polymers can be mixed with appropriately modified clay minerals and synthetic clays [5, 6], the field of polymer/clay nanocomposites has gained a very large momentum recently. Two major findings pioneered the revival of these materials: (i) the report of a nylon-6/montmorillonite material from Toyota research [7], where very moderate inorganic loadings resulted in *concurrent* and *remarkable* enhancements of thermal and mechanical properties; (ii) the report of Giannelis *et al* that it is possible to melt-mix polymers with clays without the use of organic solvents [8]. Since then, the high promise for industrial applications has motivated vigorous research, which revealed concurrent dramatic enhancements of many materials properties by the nano-dispersion of inorganic layered fillers [3, 9–16].

Although there exist many different natural and synthetic clays, dispersible in various polymers, in this paper we shall draw examples from montmorillonite (mmt). Montmorillonite is a naturally occurring 2:1 phyllosilicate, which has the same layered and crystalline structure as talc and mica but a different layer charge [5, 6]. The mmt crystal lattice consists of $1nm$ thin layers, with a central octahedral sheet of alumina fused between two external silica tetrahedral sheets (in such a way, so that the oxygens from the octahedral sheet also belong to the silica tetrahedra). Isomorphic substitution within the layers (for example, Al^{+3} replaced by Mg^{+2} or Fe^{+2}) generates a negative charge –defined through the *charge exchange capacity* (CEC)– and for mmt is typically 0.9-1.2 meq/g depending on the mineral origin. These layers organize themselves in a parallel fashion to form stacks with a regular van der Walls gap in between them, called *interlayer* or *gallery*. In their pristine form their excess negative charge is balanced by cations (Na^+, Li^+, Ca^{+2}) which exist hydrated in the interlayer. Obviously, in this pristine state mmt is only miscible with hydrophilic polymers, such as poly(ethylene-oxide) and poly(vinyl-alcohol) [14, 17]. In order to render mmt miscible with other polymers it is required to exchange the alkali counterions with cationic-organic surfactants, such as alkyl-ammoniums [3, 4].

In this paper we focus on two specific cases of designing/choosing organic modifications for layered silicates, that have been proven particularly challenging to address: the case of apolar polymers and the case of high softening temperature polymers.

Nanocomposite Miscibility

Thermodynamics of Mixing. In general, an interplay of entropic and enthalpic factors determines the outcome of whether an organically modified mmt (o-mmt) will be dispersed –intercalated or exfoliated– in a polymer [18–20]. Dispersion of mmt in a polymer requires sufficiently favorable enthalpic contributions to overcome any entropic penalties [1]. Favorable enthalpy of mixing for the polymer/o-mmt is achieved when the polymer/mmt interactions are more favorable compared to the surfactant/mmt interactions [18–20]. For most polar or polarizable polymers, an alkyl-ammonium surfactant (the most commonly used organic modification) is adequate to offer sufficient *excess enthalpy* [2] and promote the nanocomposite formation.

The use of alkyl-ammoniums is limited in the case of apolar polymers, e.g. polyolefins [21], because, in this case, the polymer-clay interactions are as poor as the surfactant alkyl-clay interactions; thus, the system is in "theta" conditions of mixing and the entropic barriers can prevent any dispersion of the inorganic fillers in such polymers. The use of alkyl-ammoniums is also limited in the case of high softening temperature thermoplastics, although due to a completely different reason: the thermal stability of the ammonium group –which is necessary to end-tether the organic surfactant on the anionic surfaces– is very poor above *ca.*240°C. Here we report surfactant alternatives for these two cases of materials.

Miscibility Strategies for Apolar Polymers

As mentioned before, the challenge with apolar polymers and alkyl-ammonium modified clays is due to the absence of any *excess* favorable interactions in the polymer-filler compared to the alkyl-filler.

Polymer Functionalization. One solution is to make block-copolymers with polymers that are miscible with alkyl-ammonium clays, e.g. polystyrene or poly(methyl methacrylate). In this case, only small blocks (1-5 mol%) are needed [21], but despite their small size these blocks can change the polymer properties. Moreover, the application barriers for implementing block-copolymer synthetic strategies in industrial settings is, in many cases, quite substantial, especially for commodity polymers such as polyethylene and polypropylene (PP). One way around this problem is the addition of functional groups *randomly* across the polymer. Very small amounts –e.g. 0.5-2 mol%– of polar or polarizable groups placed randomly across the polymer are sufficient to promote miscibility (fig. 1). For example, in the case of polypropylene just 0.5 mol% of functional groups (methyl-styrene, maleic anhydrite, or 3,hydroxyl-butylene-styrene) is sufficient to promote miscibility with alkyl-ammonium clays [21, table 1]. At such levels the functional groups do not change in any measurable extent the polymer characteristics (crystallinity, melting point, etc). However, the changes needed in the synthetic industrial practices to synthesize functionalized polymers can become an impedance to this strategy becoming a general commercial practice. This additional synthetic effort to functionalize the polymers is probably straight-forward in the

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[1] confinement of the polymer inside the interlayers results in a decrease in the conformational entropy of the polymer chains. However, this entropic penalty of polymer confinement may be compensated in part by the increased conformational freedom of the tethered surfactant chains, that are located in a less confined environment as the layers separate [18–20]

[2] excess enthalpy in the sense of polymer/mmt interactions being more favorable than the alkyl-surfactant/mmt interactions

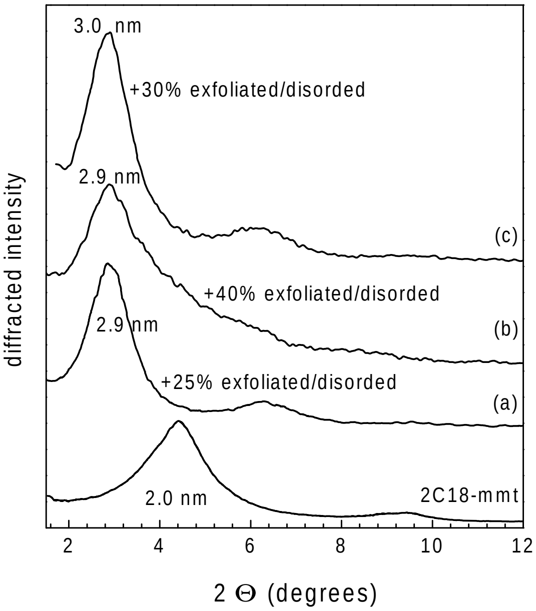

Figure 1: *X-Ray diffraction of three different functionalized polypropylenes (PP) with 6 wt% of dimethyl-dioctadecyl-ammonium montmorillonites (o-mmt). PP/o-mmt nanocomposites with different functionalizations [1 mol% methyl-styrene (a); 0.5 mol% maleic-anhydrite-styrene (b); and 0.5 mol% hydroxy-propyl-styrene (c)] show very similar XRD, albeit containing different levels of exfoliated layers (as enumerated by TEM analysis). Figure from [21].*

case of polyethylene, but can actually be quite demanding in the case of polypropylene [21]. **Exfoliated structures by "trapping" filler layers apart**. In many cases, polymer/clay systems that do not have favorable thermodynamics for nanocomposite formation, can be "trapped" in exfoliated structures (through solvent casting, or high shear-rate/high temperature extrusion). Such trapped structures are usually easy to achieve, but in most cases are not thermodynamically stable nor amiable to further processing. For example, in fig. 2, we show the XRDs of precipitated PP/mmt hybrids from a co-suspension of polypropylene and o-mmt in trichloro-benzene (similar structures can be obtained from high $\dot{\gamma}$ extrusion [22–25]). Subsequently, we process these "hybrids" by compression molding (at 180°C/15 tons). This allows for the polymer to melt and the trapped hybrid structure to relax. If the o-mmt dispersion is not thermodynamically favored the layers will collapse in low d-spacing parallel stacks (e.g. neat-PP/dimethyl- dioctadecyl-ammonium-mmt fig. 2 left) during the high temperature processing, leading to a conventionally-filled 'macro'composite. However, if the there exists a favorable free energy of the o-mmt/polymer mixing, the exfoliated structure may be retained (e.g. PP-MA/dimethyl-dioctadecyl-ammonium-mmt fig. 2 right). 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) [14], poly(urethanes) [15, 16], and nylon-6) 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 1(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

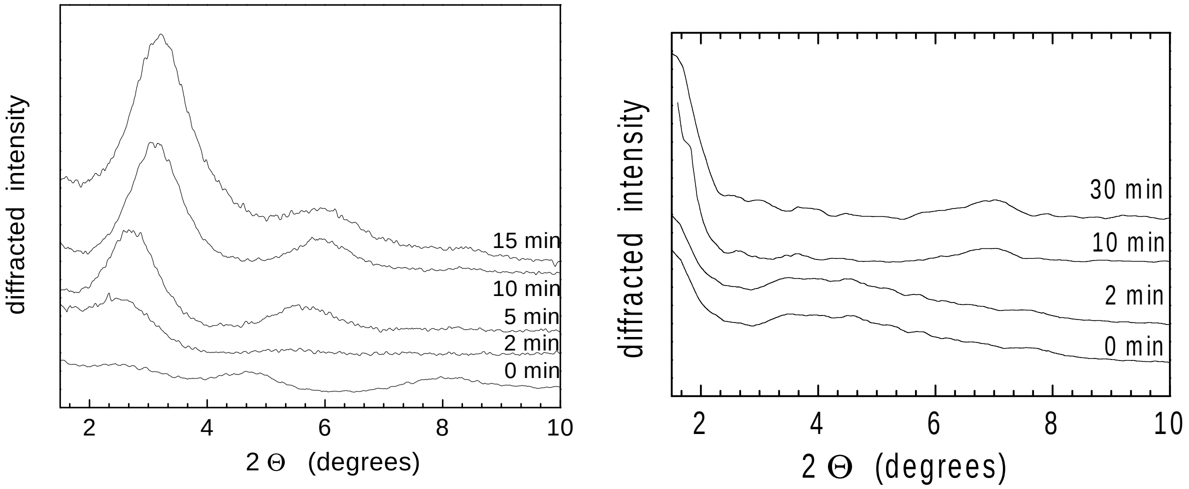

Figure 2: *The structure stability of neat-PP/2C18-mmt (left) and PP-MA/2C18-mmt (right) 'nano'composites, that were initially (0 min) trapped apart. XRD studies of compression molded samples are shown. For the neat-PP, 2C18-mmt very fast collapses to intercalated/immiscible tactoids, whereas for the MA-functionalized PP, the trapped exfoliated structure is maintained even under prolonged annealing. This suggests that the MA groups have sufficiently strong interactions with the mmt to prevent the polymer from sliding away from the inorganic layers.*

(1-3 min at 180°C) result in an immiscible/intercalated structure with a wide XRD reflection extending from 1.8 to 2.7nm in d-spacing.

At this point, we should note that this approach is qualitatively similar to the "swelling agent" approach, as for example by Wolf et al. [26]. 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) [26]. 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 our solution intercalation experiment, where a solvent is employed to mix the o-mmt with the polymer, and an exfoliated structure is trapped when evaporating the solvent.

Master Batch approaches. The combination of the above two strategies do actually lead to a commercially viable route for nanocomposite synthesis [22–27]. Namely, polypropylene oligomers modified with either maleic anhydride (MA) or hydroxyl groups (OH) can be first mixed with *high loadings* of octadecyl-ammonium-exchanged montmorillonite creating a "*master batch*", which is subsequently blended with –diluted by– neat PP, usually assisted by strong mechanical shear in an extruder or mixer. In this way, the PP polymer and the MA-polypropylene pretreated o-mmt are effectively at theta conditions, and the extrusion only promotes 'entropic' mixing aided by mechanical shear. As a result, the structure and

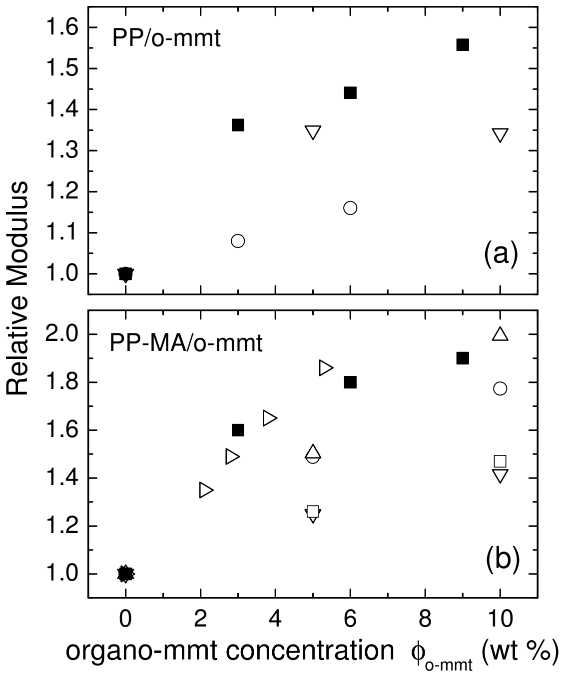

Figure 3: *Relative Young's moduli of various PP nanocomposites, each normalized by the Young's modulus of the respective PP. (a) neat-PP hybrids: with f-mmt (■, [21]), C18-mmt (▽, [23]), and 2C18-mmt (○, [21]). (b) PP-r-MA/2C18-mmt nanocomposite (■, [21]), and PP hybrids with various PP-MA pretreated o-mmt: C18-mmt (▷, [22]), C18-mmt (○, △, [23]), and C8-mmt (▽, □, [23]).*

the properties of the resulting hybrid materials depended strongly on the processing conditions and ranged from very moderate dispersions and property improvements [22, 24–27], to good dispersions and better performing hybrids [23] [fig. 3]. Obviously, a MA-polypropylene pretreatment with very low maleic anhydride content does not promote the nanocomposite formation [24], and very high maleic anhydride content made the "master batch" so robust that mmt does not mix further with neat PP [22, 25]. Finally, it is still unknown –despite the commercialization of these systems– whether subsequent processing of the PP mixture with PP-MA/o-mmt master batch retains the nanocomposite structure, or whether the PP separates out from the PP-MA/o-mmt domains [fig. 2].

Fluoro-Organic Functionalization of Clay Fillers. Finally, a way to render the polymer/mmt interactions more thermodynamically favorable than the surfactant/mmt interactions can be achieved by introducing organic modification in the mmt which is thermodynamically less favorable than the olefinic polypropylene; such a modification can be a semi-fluorinated surfactant [21]. Expectedly, an o-mmt that is completely modified by fluorinated organic surfactants would be very difficult to obtain (since the ultra-low surface tension surfactants will not exchange the alkali counterions under normal exchange conditions). Instead, a mixture of hydrogenated- and fluorinated-alkyl surfactants was employed: Specifically, we first exchanged all the native mmt cations by octadecyl-ammoniums, and subsequently we introduced a second semifluorinated alkyl-trichloro-silane surfactant (CF_3-$(CF_2)_5$-$(CH_2)_2$-Si-Cl_3). This second surfactant is tethered to the mmt surface through a reaction of the trichlorosilane groups with hydroxyls in the cleavage plane of the mmt [21]. The resulting o-mmt contain octadecyl-ammoniums at full CEC, and approximately 60% additional semi-fluorinated surfactants (as quantified by TGA analysis). The XRD of the

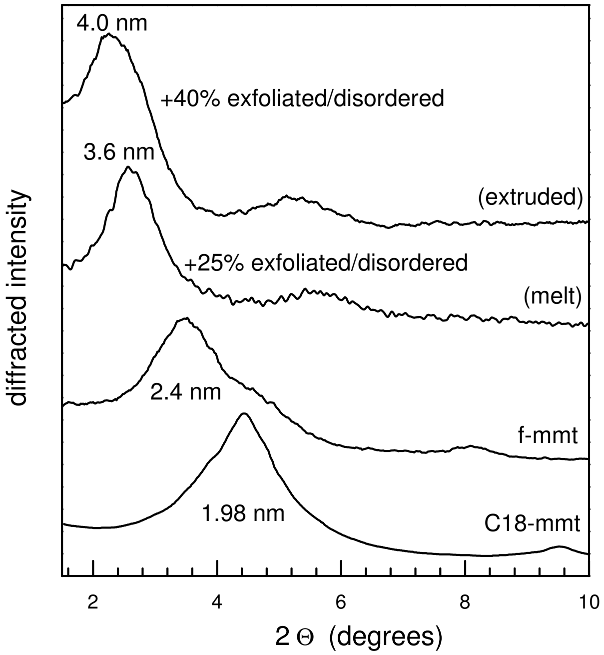

Figure 4: *X-Ray diffraction patterns of octadecyl-ammonium modified montmorillonite (C18-mmt) and C18-mmt modified by trichloro-(1,1,2,2H-perfluoro octyl)-silane (f-mmt). Also the XRD of nanocomposites made with f-mmt and unfunctionalized PP ($\bar{M}_w$=580000), via melt-intercalation processing (melt) and through extrusion in a twin-screw extruder (extruded). The levels of exfoliation in the extruded and melt-intercalated nanocomposites were quantified by analysis of multiple TEM images. Figure from [21].*

initial C18-mmt and the subsequent fluoro-organic mmt (f-mmt) are shown in figure 4. In the same figure, we also show the XRD of unfunctionalized-PP/f-mmt nanocomposites, which were formed by melt-intercalation and by extrusion. The hybrid formed by static melt-intercalation (i.e. by just annealing a physical mixture of polymer and f-mmt) reveals that there exist favorable thermodynamics for the nanocomposite formation [figure 4(melt)]. Moreover, the usage of mechanical shear [figure 4(extruded)] promotes further dispersion and exfoliation of the f-mmt layers.

Miscibility Strategies for high-Temperature Polymers

In many cases, although the thermodynamics of mixing between a specific polymer and organically modified silicates/clays are well known, and alkyl-ammonium based silicates are readily available commercially, the poor thermal stability of the ammonium group limits the ability to melt-process miscible nanocomposites. Examples of such cases include syndiotactic polystyrene (s-PS) and poly(ethylene terephthalate) (PET). Namely, numerous systematic studies [19, 28] of atactic polystyrene (PS) provide detailed information for the necessary organic modification for silicates (montmorillonite, hectorite, etc) so as to become miscible (intercalated/exfoliated) with styrene-based polymers. Along the same lines, it is also well-known how to modify silicates of varied CEC to render them miscible with esters and phenolics, thus, there exists an accurate guide on how to design silicate organic modifications for PET and s-PS.

Imidazolium-based organic modifications and neat s-PS. The necessary characteristics of the surfactants to be used for the organic modification of 2:1 layered silicates, as

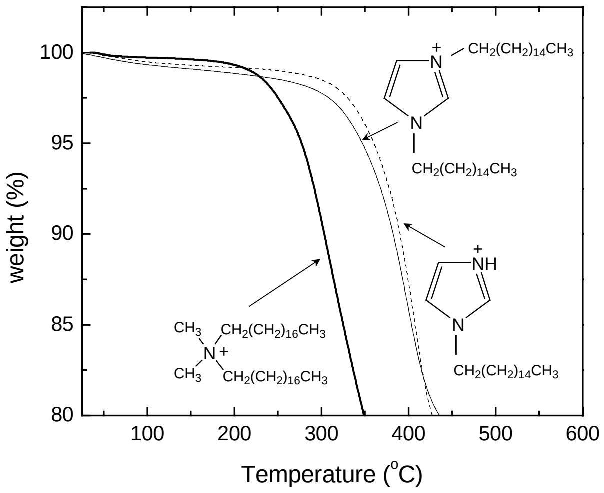

Figure 5: *Comparative TGA studies of the thermal stability of organically modified montmorillonites: Three o-mmts exchanged by dimethyl-dioctadecyl-ammonium, hexadecyl-imidazolium, and dihexadecyl-imidazolium are shown. Following their bulk behavior, the imidazolium-based surfactants exhibit substantially higher thermal stability than the ammonium-based one when used as mmt organic modifiers. All TGA scans were carried out under N_2 at 10 deg/min; figure from [29].*

for example mmt, is the cationic head –which will ionically attach to the negatively charged layers– and a hydrophobic tail –which will satisfy the thermodynamics of mixing with a specific polymer. The low thermal stability of the ammoniums limis these surfactants' usage for high-temperature polymers which need to be processed at temperature above *ca.*240°C, such as s-PS (Tm = 270°C) or PET (Tm = 265°C). The replacement of the ammonium by more thermally stable cationic groups, such as phosphonium or imidazolium, while keeping the organic tails at the appropriate size and hydrophobicity, will result in maintaining favorable thermodynamics for the dispersion and, at the same time, enable higher temperatures for melt-blending. For example in fig. 5 we compare the thermal stability of organo-montmorillonites based on a di-octadecyl quad-ammonium and two on imidazolium surfactants (an imidazolium with one hexadecyl alkyl, and an imidazolium with two hexadecyls). From these TGA results, it is very obvious that the imidazoliums extend substantially the range of temperature for the organo-mmt. Specifically, the alkyl-ammonium modified mmt exhibits strong thermal decomposition of the surfactant above *ca.*220°C, whereas the imidazoliums are stable up to about 340°C –independent of one or two alkyls. This improvement allows for the melt-processing of high temperature polymers –such as PET and s-PS– at temperatures close to 300°C. The PET case is described in details elsewhere [30], here we use s-PS to prove the same feasibility:

In figure 6 we show the XRD of s-PS with mono- and di- alkyl imidazoliums. Namely, in order to demonstrate the miscibility of these o-mmt with s-PS, we used di-hexadecyl-imidazolium (fig. 6a) and hexadecyl-imidazolium (fig. 6b) modified montmorillonites, which were melt-blended with s-PS at 270°C under static conditions[3]. Even in absence of any shear, miscible s-PS/imm-mmt nanocomposites are obtained for both imidazolium surfactants. Furthermore, upon nanocomposite formation the imm-mmt fillers enhance the thermal stability

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[3] melt processing under higher temperatures and/or under strong shear provides qualitatively the same miscible structures, however, the static melt intercalation reported here is the best proof for the existence of favorable thermodynamics of mixing

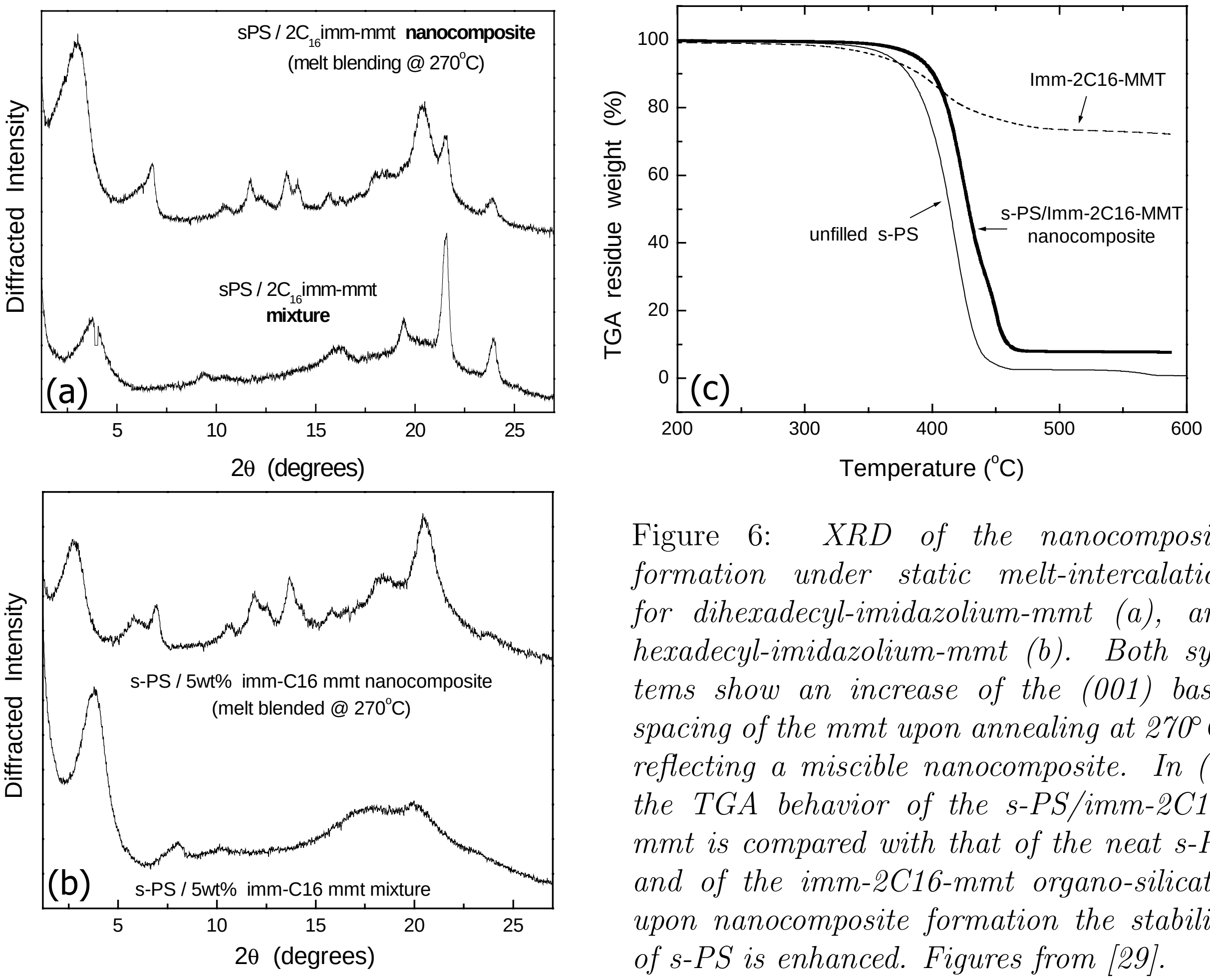

Figure 6: *XRD of the nanocomposite formation under static melt-intercalation for dihexadecyl-imidazolium-mmt (a), and hexadecyl-imidazolium-mmt (b). Both systems show an increase of the (001) basal spacing of the mmt upon annealing at 270° C, reflecting a miscible nanocomposite. In (c) the TGA behavior of the s-PS/imm-2C16-mmt is compared with that of the neat s-PS and of the imm-2C16-mmt organo-silicate: upon nanocomposite formation the stability of s-PS is enhanced. Figures from [29].*

of s-PS by about 40-50°C, as is the general case with stable polymer/mmt nanocomposites that have nanometer dispersion of the fillers [13].

The same strategy, involving imidazolium surfactants can be used for the melt-processing of PET/imm-mmt nanocomposites as detailed elsewhere [30]. In addition to the higher thermal stability of the imidazolium surfactants, which allows for the melt-processing of PET imm-mmt nanocomposites, imidazoliums have a second benefit for PET: Namely, the aromatic imidazoliums render the mmt surface much more hydrophobic than the ammonium-modified mmt surfaces, thus reducing substantially the water content in imm-mmt compared to water in ammonium-mmt. Since PET decomposes strongly in the presence of humidity, the more hydrophobic imidazolium-mmts cause much less PET decomposition compared to the ammonium-mmts [30].

Use of Na^+-montmorillonite and s-PS-*block*-PEO. Because of its favorable interactions with the Na^+ and Li^+ on the silicate surfaces, polyethylene oxide (PEO) blocks can be incorporated in s-PS (e.g. as an s-PS-b-PEO diblock copolymer) so as to promote silicate/ s-PS miscibility, where the PEO block is long enough to overcome any thermodynamic barriers of s-PS insertion in Na^+/Li^+ silicates. The PEO can replace the water from within the mont-

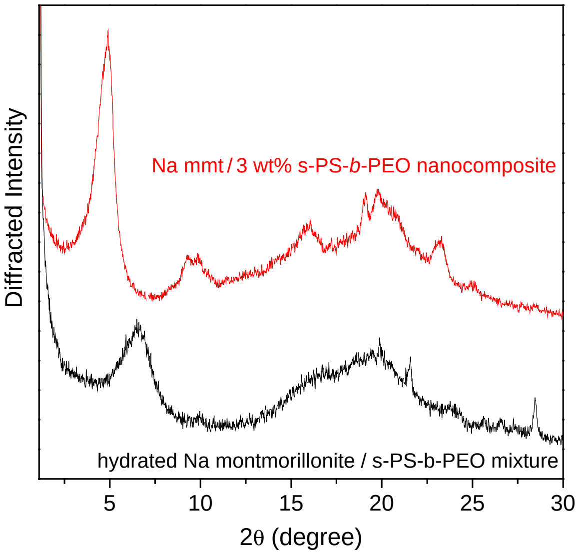

Figure 7: *X-Ray diffraction patterns of* s-PS-*block*-PEO *and* Na^+ *montmorillonite, as a mixture and after nanocomposite formation. Figure from [29].*

morillonite layers, and coordinate to the native cations (Na^+, Li^+, etc.) that reside ontop of the silicate surface. Typically, only very short "compatibilizer" blocks are necessary for this approach to prepare polymer/clay nanocomposite (e.g. 5 mol% for PP-b-PMMA (Mw = 150,000), or 3 mol% for PP-b-PEO (Mw = 200,000) [21]) and consequently the crystallinity and the melting point of the polymer are not markedly affected. We here synthesized an s-PS-b-PEO (s-PS block: Mn=110,000 g/mol, PEO block: Mn=10,000 g/mol) to demonstrate miscibility with Na^+ montmorillonite. s-PS-b-PEO/Na^+ mmt nanocomposites were prepared from solution (same method as in [14]). Figure 7 shows the (001) peak of montmorillonite shifting from $2\theta = 7.05°$ to $4.86°$, (*i.e*, the d-spacing increases form 1.25 to 1.82 *nm*), indicating the intercalated structure formed in the s-PS/clay nanocomposite. DSC studies show the crystallinity and the melting temperature of the s-PS block in the nanocomposite do not change compared with the neat polymer. Therefore, using functional diblock copolymer is an effective alternative route to prepare polymer/clay nanocomposite without the use of organic cationic surfactants. Although ethylene-oxide is more thermally stable than most amines, given the very high melting point of s-PS it is still problematic to envision extensive melt-processing of these s-PS-b-PEO polymers with Na^+/Li^+ silicates, but this may be a viable strategy for other polymers with lower softening temperature (Tm or Tg) than s-PS.

Conclusions

Guided by simple thermodynamic arguments, we reviewed various general synthetic routes to PP/organo-mmt nanocomposite formation aiming to overcome the thermodynamic challenge of mixing an apolar polymer with organically-modified inorganic layers. Using polypropylene (PP) as an example, two general approaches with demonstrated feasibility were reviewed: (i) the first one implements "ordinary" organic modifications for the mmt and functionalized polypropylene polymers, or a premixed functionalized-PP clay "master batch" that is subsequently diluted by neat PP; (ii) alternatively, neat/unfunctionalized polypropylene can disperse mmt modified by a mixture of hydrogenated and semi-fluorinated surfactants. In both cases, polymer/o-mmt nanocomposites can be formed by melt-intercalation (i.e. unassisted by mechanical shear or organic solvents). Moreover, in both cases the resulting hybrid structures contain intercalated mmt tactoids in coexistence with exfoliated/disordered mmt layers [21]. We should mention that the second approach (employing f-mmt) is generally applicable for non-polar polymers, such as polycarbonates, polyolefins, and polydienes.

In the case of high softening temperature polymers, such as PET or syndiotactic polystyrene, where the thermodynamics of mixing are well known, the challenge is to achieve an organic modification that can survive the high temperatures of processing needed for the melt-blending of their nanocomposites. In such cases, general strategies involve (a) the usage of imidazolium based surfactants –rather than ammonium-based ones– for the silicate modification, or (b) the use pristine silicates (e.g. Na^+, Li^+ silicates) to be dispersed in polymers that are modified by a short block of PEO. Nanometer dispersion can be achieved in both cases, thus providing concurrent materials properties enhancements that are typical of the nanocomposite formation. The approach employing imidazolium-based surfactants is generally applicable to polymers processes up to 320°C.

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Experimental

Synthesis of 1-hexadecylimidazolium iodide (Imm-C16). 0.5 g (7.35 mmol) of imidazole (Aldrich 43,615-1, CAS 288-32-4) was placed in a 100 mL flask with reflux condenser. 50mL THF was added to the flask to completely dissolve the imidazole. Then 2.59 g (7.35 mmol) of 1-iodohexadecane (Aldrich 23,827-9, CAS 544-77-4) was dropwise added to the flask while stirring and heated to 45-55°C. The reaction lasted for approximately 12 hours. Complete consumption of imidazole was demonstrated by the disappearance of the peak at the chemical shift of about 11.8ppm in NMR assigned to the hydrogen connected to the nitrogen of the ring. The solution was dried to remove the THF and obtain yellow solid. 20mL of hexane was used to wash the solid (repeated three times). The complete removal of unreacted 1-iodohexadecane can be verified by the absence of the peak of 3.28 ppm attributed to the CH2 adjacent to the iodium in the 1-iodohexadecane. The resulted solid was protonated in 30 mL hydrochloric acid / methanol solution (1wt%) for an hour, and then dried in vacuum to get a yellow solid. The yield was 2.3 g (74%). NMR characterization did not detect any dihexadecylimidazolium.

Synthesis of 1,3-dihexadecylimidazolium iodide (Imm-2C16). 0.5 g (7.35 mmol) of imidazole (Aldrich, CAS 288-32-4) was placed in a 100 mL flask with reflux condenser. 50mL THF was added to the flask to completely dissolve the imidazole. Then 7.77 g (3 times of the moles of imidazole) of 1-iodohexadecane (Aldrich, CAS 544-77-4) was dropwise added to the flask while stirring. The solution was heated to reflux at high temperature (the solution was boiling, $T>66°C$) for approximately 48 hours. After the removal of THF, the resulted purple yellow solid was washed with large quantities of pentane to remove the unreacted 1-iodohexadecane. The solid was then dried in vacuum, yielding 2.8 g of product (34% of yield). NMR characterization did not detect any hexadecylimidazolium content.