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Limitations of mechanical improvement for high-stiffness polymers layered-inorganic nanocomposites

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Abstract

Nanometer-thin inorganic fillers are currently being explored for the improvement of the mechanical properties of various polymers. Although the nanocomposite structure offers generally applicable principles for such enhancements across polymers, there exist realistic limitations for the extent of improvement that can be achieved. Simple theoretical arguments quantifying the relevant dependencies are discussed. A comparative discussion, across several polymers reinforced by the same layered inorganic fillers, aims in revealing these limitations and tracing their molecular origins to the polymer/filler interactions and the filler characteristics.

Introduction

In this conference proceeding we discuss the implications of simple theoretical arguments on the limitations of possible improvements in the mechanical properties of polymer/inorganic nanocomposites; a more detailed discussion –including extensive comparisons with experimental studies can be found elsewhere [1, ch.2].

The term “nanocomposite” is commonly employed to describe an extremely broad range of materials, where one of the components has a dimension in the sub-micron scale. A more accurate –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). Here, we restrict our discussion even further, focussing on a subclass of polymer/inorganic nanocomposites, where the inorganic component is a high aspect-ratio, pseudo-two-dimensional nanoscale filler (such as 2:1 alumino-silicates). 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 between fillers [2].

Here, we first briefly describe the thermodynamic arguments for polymer/layered-filler miscibility, and we shall subsequently attempt to use the same thermodynamic considerations to describe the strength at the polymer-filler interface.

Thermodynamic Arguments

Central to our discussion of the mechanical properties of nanocomposites will be the strength of interactions at the polymer-filler interface. These same interactions also define whether a miscible (true) nanocomposite can be achieved, based on favorable thermodynamics of mixing. Thus, we shall first discuss thermodynamic arguments for mixing, and subsequently extend the same arguments to describe the polymer-filler interface strength.

Miscibility and Nanocomposite Formation 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 matrix [3–5]. 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 [3]. According to this model the entropic contributions are unfavorable but rather small, and here, as a first approximation, are ignored. 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 χ parameter definition in the Flory-Huggins theory, and can be quantified through pairwise atomic interaction parameters, cohesive energy densities, solubility parameters, or interfacial tension (Hamaker constants) formulations [6, 7]. Since for most polymers and surfactants the polymer/polymer, polymer/surfactant, and surfactant/surfactant interactions are all of comparable magnitude, enthalpic contributions are mostly associated with the competitive adsorption of polymer and surfactant on the filler, and *favorable enthalpy of mixing is achieved when the polymer/filler interactions are more favorable than the surfactant/filler interactions.* Such favorable enthalpic interactions are very important if miscibility is to be driven by thermodynamics, since parallel stacked layers separated by *ca.*1 nm of organic surfactant are held together by very high forces (fig. 1, *vide infra* eq. 3). For example, following the interfacial tension formalization of van Oss-Chaudhury-Good [8] as modified by Vaia [4], for a layered-silicate (s) modified by a surfactant (a) successive layers are held together with an adhesive energy:

$$\Delta F_{sas} = -2\gamma_{sa} = -2(\sqrt{\gamma_s^{LW}} - \sqrt{\gamma_a^{LW}})^2 - 4(\sqrt{\gamma_s^+} - \sqrt{\gamma_a^+})(\sqrt{\gamma_s^-} - \sqrt{\gamma_a^-}) \tag{1}$$

when assuming additivity of apolar (Lifschitz-van der Waals, LW) and polar (electron donor/acceptor, or Lewis acid/base, AB) interaction terms [8], and using standard geometric combination rules:

$$\gamma_{ij} = \gamma_{ij}^{LW} + \gamma_{ij}^{AB}, \text{ with} \begin{cases} \gamma_{ij}^{LW} \cong (\sqrt{\gamma_i^{LW}} - \sqrt{\gamma_j^{LW}})^2 \\ \gamma_{ij}^{AB} \cong 2(\sqrt{\gamma_i^+} - \sqrt{\gamma_j^+})(\sqrt{\gamma_i^-} - \sqrt{\gamma_j^-}) \end{cases} \tag{2}$$

These relations can be converted into the Hamaker constant formalization by setting $\gamma_i^{LW} = A_i/(24\pi l_o^2)$ with $l_o = 1.58\mathring{A}$. In the case of a 2:1 alumino-silicates organically modified by alkyl surfactants, the attractive interaction energy of eq. 1 would correspond (fig. 1), to an adhesive *pressure* between the parallel flat surfaces of:

$$P = \frac{A}{6\pi\ d^3} = \frac{-12\pi l_o^2 \Delta F_{sas}}{6\pi\ d^3} \tag{3}$$

material	γ^{LW}	γ^{+}	γ^{-}	ref.
water	21.8	25.5	25.5	[7]
montmorillonite	66	0.7	36	[4]
alkane (C_{12}-C_{18})	26	0	0	[7]
polypropylene	26	0	0	[7]
polyethylene	33	0	0	[7]
polystyrene	42	0	1.1	[7]
PMMA	40.6	0	12	[7]
carbon nanotube*	18.4	12	12	[9]
PET	43.5	0.01	6.8	[10]
nylon 6,6	36.4	0.02	21.6	[7]

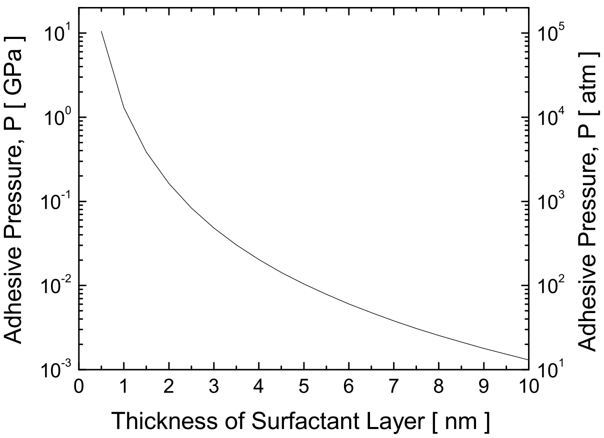

Figure 1: (left) Various surface tension components in (mJ/m^2) for materials discussed in the text; *from $\gamma^{AB} \cong 24$ mJ/m^2 assuming γ^+/γ^-=1. (right) Adhesive pressure *vs.* surfactant layer thickness, as predicted by eq. 3, for two flat montmorillonite surfaces bearing alkyl-surfactants.

where d is the thickness of the organic (surfactant) layer.

Given that typical alkyl-surfactant modifications (*cf.* butyl to dioctadecyl) correspond to a surfactant layer thickness of 0.5-2 nm, the corresponding adhesive pressure between successive silicate layers is 10^5-10^3 atm (*cf.* fig. 1). Thus, favorable enthalpic interactions are absolutely necessary for nanocomposite formation; *i.e.*, a negative free energy change (upon mixing) is needed, which corresponds to a negative interfacial tension difference ($\gamma^{total}_{excess} = \gamma_{ps} - \gamma_{as}$; competitive adsorption of polymer p and surfactant a on the filler surface s [11]). For example, a typical silicate (e.g. montmorillonite [4]: $\gamma_s^{LW} \cong 66$ mJ/m^2, $\gamma_s^+ \cong 0.7$ mJ/m^2, and $\gamma_s^- \cong 36$ mJ/m^2) organically modified by alkyl-surfactants (e.g. dodecane to nonadecane [7]: $\gamma_a^{LW} \cong 26$ mJ/m^2 and $\gamma_a^\pm \cong 0$) would be miscible with any polymer for which:

$$\gamma^{total}_{excess} = (\sqrt{\gamma_p^{LW}} - \sqrt{66})^2 + 2(\sqrt{\gamma_p^+} - \sqrt{0.7})(\sqrt{\gamma_p^-} - \sqrt{36}) - 9.1 \text{ mJ/m}^2 < 0 \qquad (4)$$

This is satisfied for most polymers [e.g. table XIII-5 in 7]) except perfluorinated polymers and polyolefins (polypropylene, polyisobutylene, etc). Thus, *for most polymers* the commonly used *alkyl-surfactant* organic modification *is adequate in creating sufficient excess enthalpy and promoting nanocomposite formation* with montmorillonite –and similar layered-silicates. In a different approach [5], a longer macromolecular "surfactant" –that would increase the layer separation to 5-10nm– necessitates much smaller favorable enthalpic contributions since the adhesive pressure to be overcome is 10^3 times smaller. This last theoretical prediction has been verified for polypropylene (PP) [12] there is no excess enthalpic interaction (*i.e.*, $\gamma_{\mathrm{PP}}^{LW} = 26$ mJ/m$^2 \cong \gamma_a^{LW}$ and $\gamma_{\mathrm{PP}}^\pm = 0$, and eq. 4 yields $\gamma^{total}_{excess} \cong 0$) which 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 [5].

Implications on Mechanical Properties The *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 conventional composites' mechanical properties, such as the Halpin-Tsai

[13] and the Mori-Tanaka [14] 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. Recent theoretical models have been developed attempting to better capture the mechanical behavior of polymer/layered-silicate nanocomposites, by accounting for the high aspect ratio of the fillers. For example, there is a recent effort [15], 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, this modified Halpin-Tsai model still does not seem highly successful in predicting mechanical properties of polymer/layered-silicate nanocomposites for a wide range of polymer matrices [15]. The main shortcoming in that approach is attributed [16] 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 in [16, 17] where appropriate modifications were introduced in 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 [17]. Even in the most focussed approach, when a mechanical model is developed to describe a single polymer/inorganic nanocomposite [18] –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 [18] to be 2-8MPa for the PDMS/mmt system, *cf.* mmt elastic modulus $\sim 10^5$MPa).

These theoretical endeavors, despite any shortcomings and approximations, offer valuable insights into important design parameters that control 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 [15, 18], 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 the respective nanocomposites [15].
- The correct enumeration of the interfacial strength is crucial for the correct estimation of the composite's mechanical properties [17, 18], and its small value –compared to the modulus of the filler– can dramatically limit the filler's reinforcing effectiveness.

Under the approximations and assumptions mentioned in the previous section (esp. ignoring the enthalpic contributions from the surfactant and all entropic contributions) the interfacial adhesive energy per area of a polymer and a silicate is given by [8]:

$$\Delta F_{ps}^{total} = \Delta F_{ps}^{LW} + \Delta F_{ps}^{AB} = (\gamma_{ps}^{LW} - \gamma_{p}^{LW} - \gamma_{s}^{LW}) + (\gamma_{ps}^{AB} - \gamma_{p}^{AB} - \gamma_{s}^{AB}) \tag{5}$$

and substituting γ_{ps}^{LW} and γ_{ps}^{AB} from eq. 2 gives:

$$\Delta F_{ps}^{total} = -2\sqrt{\gamma_p^{LW}\gamma_s^{LW}} - 2\left(\sqrt{\gamma_p^{+}\gamma_s^{-}} + \sqrt{\gamma_p^{-}\gamma_s^{+}} \right) \tag{6}$$

As noted before, this equation is based on severe approximations, and can only be expected to provide the order of magnitude of the interfacial adhesive forces. In the case of strictly apolar polymers some of these approxiamtions vanish and eq. 6 becomes $\Delta F_{ps}^{total} = -2\sqrt{\gamma_p^{LW}\gamma_s^{LW}}$

Checking the validity of the above approach –and the corresponding predictive power of eq. 6, if any– requires knowledge of the polymer-filler interfacial energy (or strength). The interfacial strength of the polymer-filler interface can be measured experimentally directly only in very few cases; for example, carbon nanotubes have been pulled out from a polymer (polyethylene-butene) matrix by AFM, yielding interfacial strengths [19, 20] of 10-90MPa, depending on the nanotube radius. These experimental interfacial strength values correlate well with interfacial forces calculations [9], such as those described earlier (*cf.* eq. 6). Such calculations may yield a first-order estimation of the interfacial strength for polymer and nanofillers, especially in the absence of experimental approaches for determining this adhesion directly for the majority of the relevant layered-inorganic particles.

Some examples of the application of eq. 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 ∼83 mJ/m^2 corresponding to an interfacial strength of ∼10 MPa (*cf.* 3-7 MPa from tensile measurements [21]);
- For PDMS/montmorillonite the same approach yields an interfacial energy of ∼91 mJ/m^2, or an interfacial strength of ∼11 MPa (*cf.* 2-8 MPa from theoretical models [18]);
- For nylon/montmorillonite nanocomposites –and ignoring all crystalline phase changes that may be caused by the silicate fillers [22]– an adhesive interfacial adhesion of ∼107 mJ/m^2 corresponding to an interfacial strength of ∼14 MPa; and
- For carbon nanotube/polyethylene yields an interfacial energy of ∼49 mJ/m^2 (*cf.* 47 mJ/m^2 from AFM experiments [19]) or an interfacial strength[1] of ∼6.2 MPa (*cf.* 20-40 MPa from multi-walled nanotubes [20], and 2 MPa from computer simulations [23]).

Concluding Remarks

The above approach, despite its approximations, bears significant implications for the possibilities and extent of improvement of the mechanical properties of polymers via nanocomposite formation. Specifically,

(1) given the nature of a polymer (*i.e.*, γ^{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 ($\gamma^{LW} \cong 26$ mJ/m^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 300-500% for the softer LDPE, compared to 60-100% for the stiffer i-PP [fig. 2]).

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

(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

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[1] Equation 6 is independent of geometry, however when estimating an interfacial strength the filler geometry –contact geometry– must be considered –for example see [6, §11.1] or [7, §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.

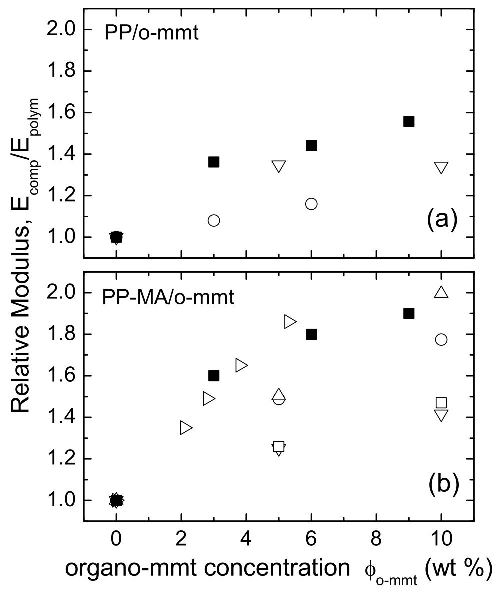

Figure 2: Relative tensile moduli for various PP/mmt nanocomposites. (a) neat-PP hybrids: with f-mmt (■ [21]), C18-mmt (▽ [24]), and 2C18-mmt (○ [21]). In absence of favorable thermodynamics, dispersion and mechanical properties depend on processing. (b) PP-MA/alkyl-mmt nanocomposites (2C18-mmt: ■ [21], C18-mmt: ▷ [25]; ○, △ [24]). Given the better defined thermodynamics of mixing there is smaller variation in dispersion and mechanical properties across different systems and research groups. Slight changes in the thermodynamics, e.g. when a shorter surfactant is employed (C8-mmt: ▽, □ [24]), result in measurable moduli changes.

relative improvements in mechanical properties [fig. 3], but still below the upper limits set by the calculated interfacial adhesions (the use of the nylon-6 as an example in this case is questionable, given the promotion of the γ-phase crystal for the nanocomposites [22]; however, the favorable comparison of the nylon-6 behavior with the behavior of the urethane/urea systems may *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 [30].

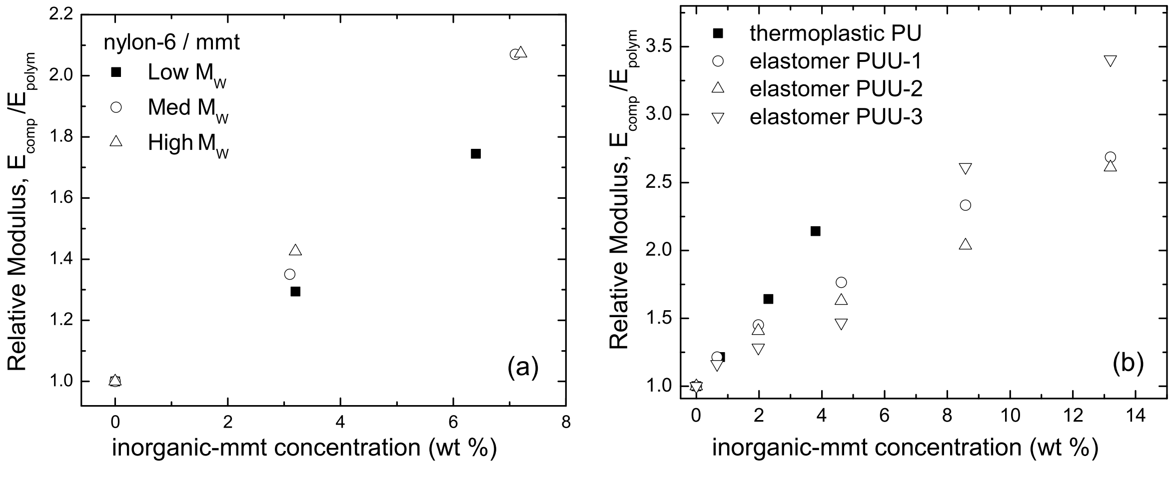

Figure 3: Relative tensile moduli for (a) nylon-6/mmt nanocomposites[26], with low, medium, and high M_W nylon-6 matrix. (b) polyurethane and polyurethane copolymers/mmt nanocomposites (■ [27], ▽ [28], ○ △ [29]).

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