SELECTIVE DISPERSION OF NANOFILLERS IN PET/PC BLENDS, TAILORED BY THERMODYNAMICS OF MIXING AND MELT-PROCESSING CONDITIONS

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Introduction

Polymer/layered-silicate nanocomposites are probably the most widely studied class of nanostructures, since they combine very interesting fundamental science[1] and opportunities for applications, as attested by a number of commercialized products. The success of these materials in applications is due to remarkable concurrent improvements possible at low filler loading levels (<5wt. % nanofillers) in thermo-mechanical properties.[2,3] and the rise of new/novel behaviors that are genuine 'nano' enhancements: barrier, optical/UV, and flame retardancy.

In a first approach, high performance and genuinely 'nano' characters necessitates a good dispersion of these nanofillers. In particular, the dispersion of high-aspect ratio fillers (such as clay or synthetic layered-silicates, and nanotubes) has been directly linked to several of the most impressive property enhancements. As with traditional and microscale composites, the filler dispersion in nanocomposites is realized through strategies that combines appropriate processing approaches and favorable thermodynamics of mixing (through modification of the filler surfaces). In nanocomposites, the importance of the latter (mixing/interfacial thermodynamics) can substantially overwhelm the processing conditions, given the high surface area of the fillers (more interfacial surface) and their smaller size (less sensitive to shear rates and flow). There exist a couple of theoretical models that can guide how to modify/functionalize the nanofillers so as to achieve dispersion in a given matrix, e.g. for montmorillonite layered-silicates the surface tension formalization by Vaia *et.al* [4] based on the van Oss-Chaudhury-Good theory. Where the entropic contributions are small, dispersion can be achieved when there exist favorable excess enthalpic contributions, *i.e.* when the polymer/filler interactions are greater than the corresponding surfactant/filler interactions[4]. For multi-component systems, e.g. immiscible PET/PC blends, one can envision to move beyond simple dispersion and to design strategies that afford the opportunity to *selectively reinforce only one of the polymer phases*, or even design nanofillers that can *promote compatibilized structures of the phases*.

In this work we have used theoretical insights to guide us in designing appropriate organic modification for montmorillonites, that (1) selectively disperse in the PET phase only, and (2) promote some miscibility of PET with PC without marked transesterification, resulting in new nanostructures with novel mechanical performance.

Experimental

Materials. A high molecular weight, high intrinsic viscosity (0.95dl/g, Mn=35,000) PET from Voridian and a high molecular weight, high viscosity PC from Bayer MaterialScience (Mn=32,000 per GPC with PS standard~~s~~), were used to prepare the polymer blends. Na+-montmorillonite silicates were purchased from Southern Clay Products (Cloisite) and Nanocor (Nanomer), and were modified by various cationic surfactants, which were either commercially-available (Aldrich), or were synthesized in our lab[5].

PET/PC/o-mmt Nanocomposite. Nanocomposites of the PET/PC blends were prepared via melt-blending (twin-screw extrusion followed by injection molding) in two ways: (a) a 'one-shot' extrusion, in which all three components (PET + PC + o-mmt) were fed and extruded simultaneously, and (b) a 'masterbatch' two-step approach, where o-mmt was pre-dispersed in one of the two polymers and was subsequently let-down by PET and PC.

Characterization The morphology of the nanocomposite blends was analyzed via TEM on a JEOL 1200 EXII microscope operated with an accelerating voltage of 80kV and equipped with a Tietz F224 digital camera.

Results and Discussion

Thermodynamic arguments can suggest suitable surfactants that can be used to modify mmt so that it can disperse in PET and/or PC[4,6]. Given that PET and PC have different interactions with mmt, *any* of these "common" surfactants (which posses favorable thermodynamics of mixing with both PET and PC) would exhibit a *higher thermodynamic energy gain* for one of these two phases (e.g. PET) compared to the energy gain when dispersed in the other phase (e.g. PC). So although such a surfactant would promote dispersion in either PET or PC homopolymers, when introduced in the PET/PC blend it would have a tendency to preferentially disperse in one of these two phases, and this tendency is increased as the *difference* in two energies of mixing (PET/o-mmt and PC/o-mmt) is increased. Moreover, given the ultra-high accessible surface area per individual filler particle ($\sim 750 m^2/g$) this tendency can result in a complete segregation (selective dispersion) in one of the two phases even when the excess-energy difference per mer is infinitesimally small between the two phases.

As a test of this argument, in **Figure 1** we show three TEM images at a low magnification of three PET/PC nanocomposites with different PET/PC ratios, which were prepared by an 'one shot' extrusion of PET, PC, and o-mmt. The surfactant used as the mmt organic modification, yields good dispersion in PET and in PC alone (experimentally confirmed, not shown here)[5,7], but is predicted by theoretical arguments to have a slightly higher *mixing energy gain per mer* with PET (compared to when in PC). As can be seen in fig.1 this o-mmt selectively disperses in the PET phase, a morphology that persists even when PET becomes the minority phase (**Figure 1c**). The PC is present in unfilled, well-dispersed, droplet-like morphologies with distinct phase boundaries.

Even more impressively, if the same o-mmt is premixed (masterbatched) with the thermodynamically less-favored PC phase (we made a PC/15% o-mmt) and this masterbatch is subsequently let-down by (extruded-with) PET plus PC towards a final 25/75 PET/PC blend, the o-mmt 'leaves' the PC phase and selectively disperses in the minority PET phase. In this case (**Figure 2**) we observe similar morphologies as before, *i.e.* no difference is observed between the 'one-shot' and 'PC-masterbatched' samples for all compositions studied (only one shown here, Figure 2). This denotes a remarkable "triumph of the thermodynamics over the processing" in this system, especially when considering that complete segregation to PET takes place even for the 25/75 PET/PC, with o-mmt premixed in PC, and with PC being of higher viscosity than PET at the processing conditions (*cf.* extrusion and injection molding T = 553 and 573K).

Pushing this thermodynamic argument even further, if one could design an organic modification that has (a) moderate, poor, or no dispersion in PET and in PC *and* (b) PET/o-mmt and PC/o-mmt interactions per mer are smaller than the $\chi^{PET/PC}$ parameter, then the o-mmt the PET and PC would prefer to physisorb on the o-mmt rather than forming PET/PC interfaces; thus, such a o-mmt filler would promote miscibility of the PET/PC blend (*cf.* hydrophobic attraction in colloidal solutions). Along these lines, a second surfactant was used as an organic modification for mmt, which showed to promote PET/PC miscibility (**Figure 3**). As can be seen by comparing the TEM images of figs. 1 and 3, the o-mmt modified with this second surfactant were well dispersed in both PET and PC phases. Furthermore, a more "compatibilized" PET/PC phase morphology (without distinct phase boundaries) was developed, in sharp contrast with the selective o-mmt dispersion observed in figs. 1 and 2. As before, the masterbatch approach was also utilized (by forming a concentrate of PET/o-mmt prior to being let-down with PET and PC); here, again, the same "compatibilized" morphologies, similar to those seen in Figure 3, were obtained (not shown here), providing further indications that thermodynamics overwhelm the system response and processing conditions play a substantially less important role.

Extensive characterization of the PET/PC/o-mmt nanocomposites using FTIR and Raman spectroscopy showed that the compatibilization seen in Figure 3 is mostly physical without *additional* transesterification being introduced/catalyzed by the nanofillers. Differential scanning calorimetry (DSC) was used to measure the transesterification extent, changes in both Tg, and PET crystallization behavior (which was altered in Tm, morphology, and kinetics). Finally, mechanical characterization showed that these materials exhibit 'genuine nano' behavior, manifested by improvements in modulus with simultaneous improvements in enlogation-at-break and toughness [5].

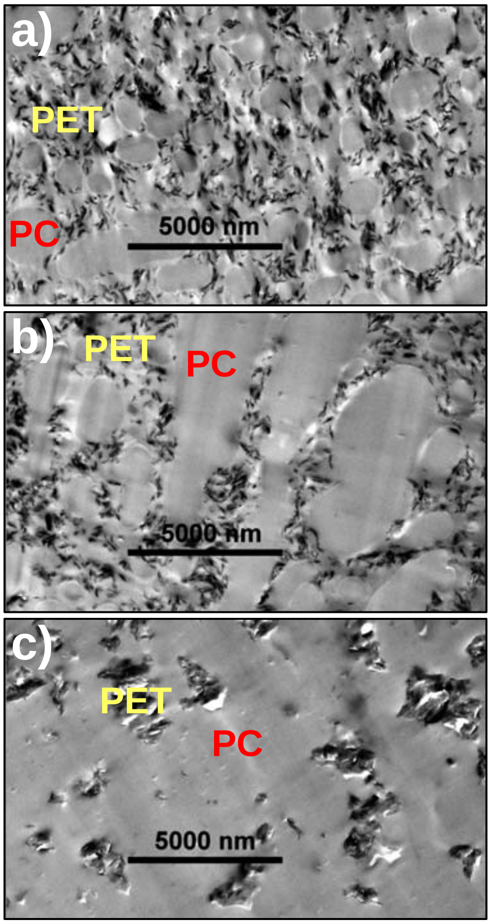

Figure 1. Low magnification TEM images of ‘one-shot’ PET/PC/3 wt%mmt nanocomposite blends. The organic modification of the mmt promotes good dispersion in both PET and in PC, and is designed to drive strong selectivity of the filler (o-mmt) in the PET phase of PET/PC blends: (a) 75PET-25PC-3% mmt, (b) 50PET-50PC-3% mmt, and (c) 25PET-75PC-3% mmt.

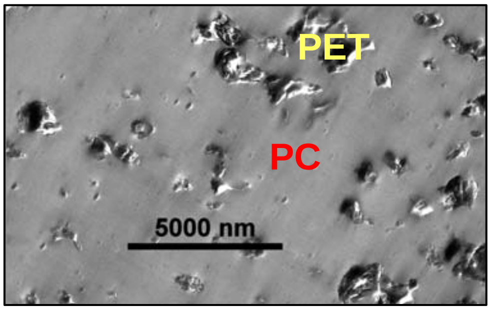

Figure 2. Low magnification TEM image of the same system as in Figure 1c above, but processed from a PC/15% o-mmt masterbatch/concentrate, which was let-down with appropriate quantities of PET and PC to yield a 25PET/75PC/3 wt% mmt nanocomposite blend.

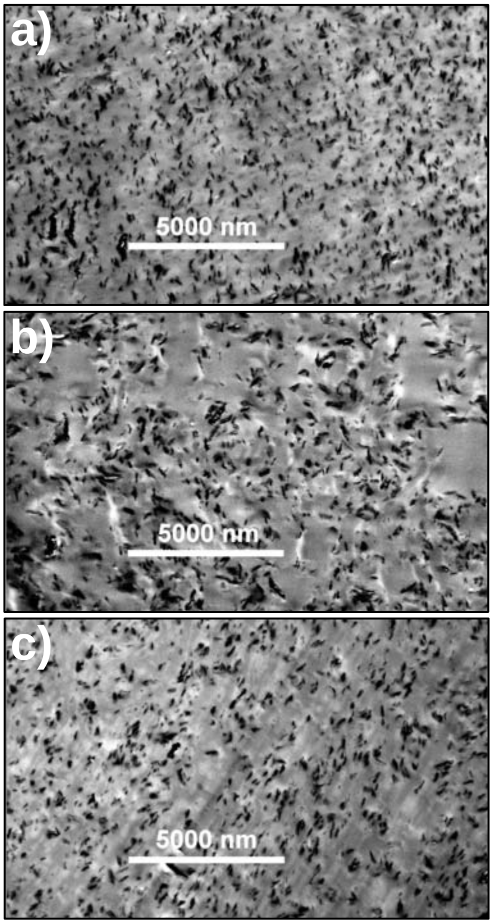

Figure 3. Low magnification TEM images of ‘one-shot’ PET/PC/3 wt% mmt nanocomposite blends. The organic modification of the mmt promotes good dispersion in both PET and in PC, and is designed to drive compatibilization of the PET and PC phases: (a) 75PET-25PC-3% mmt, (b) 50PET-50PC-3% mmt, and (c) 25PET/75PC/3% mmt.

Conclusions

The nanocomposite formation of immiscible PET/PC blends with organically-modified montmorillonite was studied, and the nanofillers were designed to (a) selectively disperse only in the PET phase, and (b) promote physical mixing (“compatibilization”) of the PET/PC blends. Dispersion was controlled by tailoring the thermodynamics of mixing between the fillers and the two polymers (which was experimentally realized through design of appropriate surfactant chemistries used for filler modification). Further, we showed that the desired composite structure can be obtained even when the organically-modified fillers are premixed (masterbatched) in the ‘unfavorable’ polymer. This behavior, *i.e.* the composite structure is markedly independent of processing conditions, indicates that, for these systems, the thermodynamics of dispersion overwhelmingly determine the resulting structure and the processing choices become of secondary importance. Further characterization was used to quantify the extent of transesterification, Tg changes, and PET crystallization.

Acknowledgements. Financial support for this project was provided by Bayer MaterialScience. MJH gratefully acknoledges an ES&F fellowship from PSU-ARL.

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