POLYOLEFIN NANOCOMPOSITES IN TPOS

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Abstract

The commercial promise of polyolefin nanoclay composites has been tied to the level of exfoliation of the nanoclay. This has been driven mostly by automotive demands for increasing performance of TPO materials.

The most common promise of nanocomposites in TPO applications is the impact/modulus balance while retaining low specific gravity. There are often many additional benefits that nanoclays can offer, such as controlled shrink and CLTE, improved surface appearance, and warp resistance, among others. However, different approaches may be required to achieve these benefits. The relevance of both the degree of exfoliation and the method of exfoliation will be discussed in this paper as related to the expected benefits. Comparisons will be made between existing TPO composites and current and potential nanocomposite TPO.

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Why are nanocomposites of value to the automotive industry today?

One of the primary benefits of nanoclay enhanced TPO's is the low specific gravity, when compared to traditional talc filled TPO's. This is important to note because it was not that long ago when a key driver in the automotive market was weight reduction. Over the past few years, however, that philosophy has changed. Weight reduction is still talked about, but primarily as a path to cost reductions. Could this philosophy be changing? All of us in the automotive industry must ask, will greater than $3.00/gallon gasoline drive consumers to demand more fuel efficient vehicles? Couple this with the fact that consumers are demanding vehicles with more overall content, which actually adds weight, and we realize that this is working against the overall fuel efficiency of today's vehicles. Looking forward, the opportunity for weight reduction favors materials that are lower in weight, but still provide the desired physical properties required for the specific application.

Probably the most discussed benefit of nanoclays is the impact/modulus balance. This balance is primarily focused in the area of thermoplastic polyolefins (TPOs), though there are many applications in various polyethylenes and nylons as well. It is important to note that TPO and conventional filler technology have improved dramatically in the last five years and approach the impact/modulus balance of nanocomposites. New fillers that only loosely bear the name "talc" are increasing the boundary on the impact/modulus balance. Still, the balance obtainable with nanocomposites is outstanding and the secondary benefits of nanocomposites still can not be achieved, even with the advances made by these competing technologies. This will be discussed in greater detail later in this paper.

Another touted benefit is the increase in heat distortion temperature (HDT) with the addition of nanoclay. While this is benefit is more pronounced in crystalline polyolefin systems, increases in the HDT by 10°C can readily be obtained in Nanoclay modified TPO formulations. While one could argue that 10°C is a relatively insignificant change our belief is that any improvement in the overall dimensional stability of the polymer system is a benefit. This improvement could open up more opportunities for TPO's or it could simplify the design required for certain applications already in these materials.

Continuing to address the benefits of improved dimensional stability, nanocomposites also provide isotropic shrink properties as well as reduced coefficient of liner thermal expansion (CLTE) properties. Both of these physical attributes are becoming increasingly important as OEM's continue to design for reduced dimensional tolerances, smaller nominal gaps and improved fit/finish to mating parts. For example, by adding 4% nanoclay to a reactor grade TPO, we are able to reduce the CLTE from 7.5×10^{-5} cm/cm/^{o}C to 6.2×10^{-5} cm/cm/^{o}C. By increasing the percentage to 8% nanoclay, it reduces further to 5.3×10^{-5} cm/cm/^{o}C or nearly 30%.

In summarizing the value of clay nanocomposite TPO's for automotive applications, there are several key physical attributes that continue to drive the development of new generations of these materials. Improved fuel economy and pollution reduction is driving the push to lighter weight materials. The demand for higher performance TPO's opens the door for these nanocomposite materials to replace metal for weight savings as well as the facilitating of part consolidations. These advancements of nanocomposite TPO systems also open the door to replace other engineering thermoplastics (ETP's) for improved processing as well as the overall recyclability of the vehicle. Furthermore, increasing styling requirements continue to push for materials with dimensional stability approaching that of metals.

While we have focused on developing fully compounded materials for the automotive market, there appears to be a benefit in being able to manipulate the physical properties of certain materials in an effort to "dial in" the properties needed. So, while there are a handful of fully compounded, nanocomposite materials on the market today, there are also, highly loaded nanoclay masterbatch materials, which provide the processor the ability to truly tailor an existing material to the requirements needed for the application right at the press. This could be anything from improving stiffness, to reducing warp to adjusting for shrinkage control. The benefits also include inventory and logistics due to the need for fewer resins. The balance of this paper addresses the relative importance of the exfoliation of the clay within the polymer matrix as well as the specific physical property enhancements of clay nanocomposite TPO's compared to competing technologies. These enhancements can theoretically be achieved by either a fully compounded or masterbatch approach.

The Relative Importance of Exfoliation versus End Application Requirements

The broadening field of nano-technology has in part been led by the ability to characterize nano structures, through various analytical techniques. In general, the value of nano-technology lies in the low loading required for property enhancements. These can be traditional enhancements, such as physical property improvements such as increased modulus, or unique property performance attributes such as anti-microbial or UV absorption phenomenon developed by certain nano materials. Organoclay based nano-technology usually focuses on the typical, and more broadly applicable, enhancement in standard physical properties, specifically those properties listed above.

In clay polymer nanocomposites, the importance of exfoliation is stressed as the key performance requirement to achieving "nano" enhanced properties. The nano enhancement is based upon the naturally occurring large aspect ratio of the individual platelets of the base montmorillonite. This is completely logical, in that typical physical property modulus indicate the greatest reinforcing effect with the largest aspect ratios. Typically, Halpin-Tsai or more simple Nielsen models are used to predict performance of the composite based on the individual modulus of the components and aspect ratio of the filler. Few models exist which incorporate the alignment and adhesion of the matrix to the filler. In most cases, these aspects are dealt with empirically.

These simple composite models and the hype around nanocomposites in general have lead to various studies on the method of exfoliating organoclays in polymer composites. Along with this goal has been the production of copious amounts of TEM and x-ray data. True exfoliation, as seen in materials like polyamide 6, have led to dramatic improvements in modulus, which has been correlated with the above mentioned dispersion techniques. In the case of polyamide 6, nanoclay composites can be made that require less than ½ the equivalent level of glass to reach the same modulus. In these cases, the nano "effect" is approaching the theoretical limit of models such as the Halpin-Tsai, especially when the materials are processed in a way to create excellent alignment of the fillers. However, one must remember that in many of the polyamide systems, the organoclay surfactant is chemically bonded to the backbone of the polyamide chain, and stress transfer is not an issue.

Polyolefins however are a different system, one that does not have the advantages of polyamide 6 in regard to their polymerization techniques, nor their polarity. Though several reactor based approaches are under study for polyolefins, no commercially available materials have been developed. The most common commercially viable route to polyolefin nanocomposites today is via melt compounding. Most of the studies around polyolefin nanocomposites focus on the aforementioned exfoliation. The most common techniques to determine this are; high resolution microscopy which examines a very localized morphology or x-ray to determine the bulk existence and qualitative level of ordered d-spacing in the clay. These techniques are very complimentary, however they do not often relate to true performance. Often the best properties in polyolefins are not achieved by maximizing exfoliation, but achieving the highest level of exfoliation while maintaining good adhesion and stress transfer from the matrix to the nanoclay filler.

To illustrate this effect, several nanocomposites were prepared with different compatibilization technologies in homopolymer PP, at a 6% level of organoclay. All samples were prepared by the same melt compounding method, however different chemical approaches were taken to increase the exfoliation of the clay. Materials were subsequently molded and physical properties were determined along with the corresponding d-spacing of the clay by X-ray. In no cases was complete exfoliation obtained, using no dispersion peak in the 2 theta spectra as the definition of complete exfoliation. The relative d-spacing versus the measured flexural modulus for each sample is shown in Figure 1. A dashed line represents the starting modulus of the material. Clearly, there is no direct correlation between the d-spacing of the material, and the resulting improvement in flexural modulus. In fact, materials that are 400 MPa lower in modulus can have the same d-spacing of approximately 3.6 nm, quite large in polyolefins. In addition, it is the author's experience that TEM is also not indicative of performance, in that the usual resolution required determining the true nature of the morphology does not lend itself to the overall bulk performance of the composite.

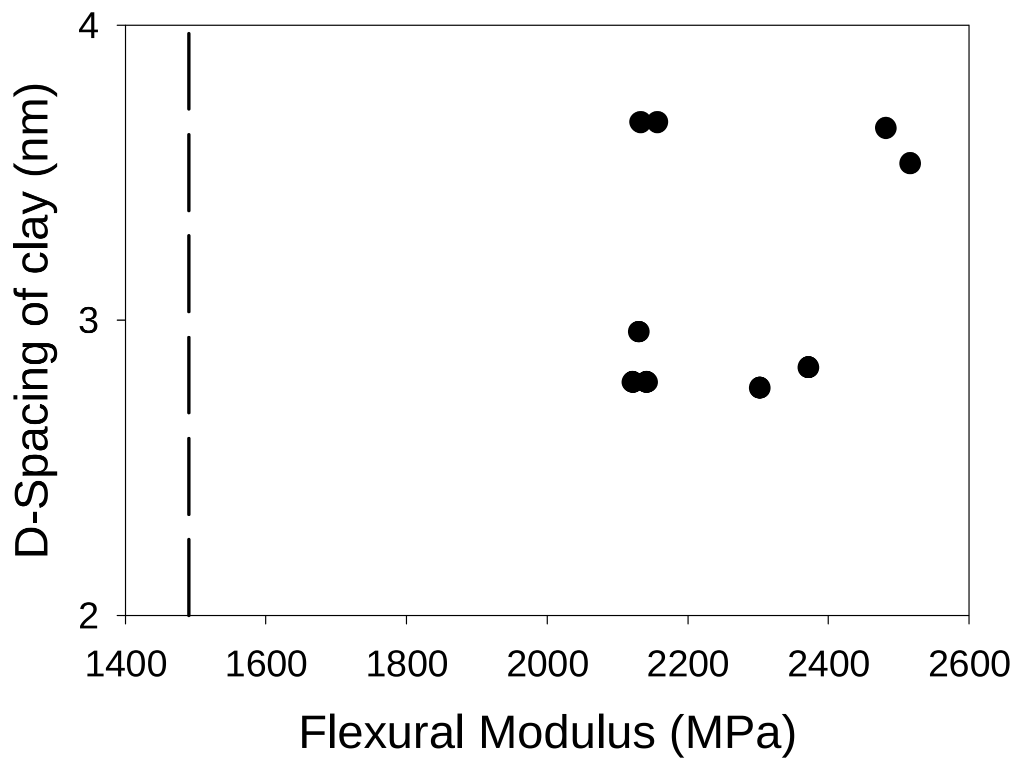

Figure 1 – The lack of correlation between analytical techniques of dispersion and the achieved physical performance.

It is clear from Figure 1 that the greatest challenge in achieving nano enhanced performance in polyolefins is not the directly the level of exfoliation. The manner of exfoliation is equally critical. Complete exfoliation in polyolefin materials is possible, and there are examples in the literature, however at the sacrifice of reinforcement. These materials may have applicability to barrier, but not automotive TPO applications. All things being equal, if one were able to maintain good adhesion and stress transfer to nano-particles, exfoliation would become the overriding factor in composite performance. Unfortunately, today most dispersion techniques are mutually exclusive, and do not focus on both exfoliation and stress transfer. The key to effective TPO formulations is maintaining this balance while improving exfoliation.

Achieving "Nano" performance in TPO formulations

The property performance map of filled and unfilled automotive TPO formulations has gone through quite an evolution in the past five years. These have mostly targeted the performance enhancements that have been touted as the benefit of nanoclays, such as the impact/modulus balance, CTLE, low specific gravity, and shrinkage to name a few. It should not go unnoticed that the bar has risen dramatically this half decade, perhaps more than the entire previous decade. It is possible the threat of nanocomposites have driven more innovation than the introduction of nanocomposites themselves in achieving these goals. However, the promise and theoretical expectation of polyolefin nanocomposites is still being developed, with much room to grow. Several key approaches and enhancements will be discussed, and compared with current materials.

The advent of microtalcs and other "engineered" minerals has led to a decrease in filler loading with substantial improvement in both impact and modulus. The relative difference in performance versus standard talcs of years past is significant, and approaches that of current nanocomposites. A relative comparison of the specific modulus and impact of "standard" talcs, microtalcs, and nanocomposites is compared in Figure 2 in a medium impact TPO.

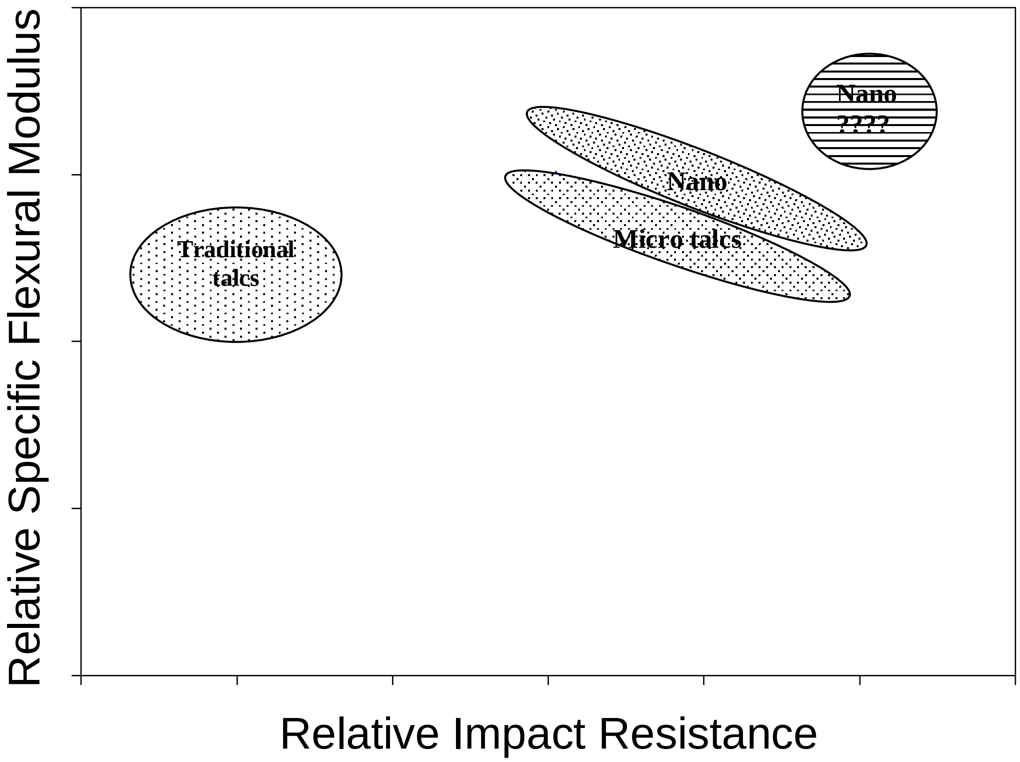

Figure 2 – Relative impact modulus balance of various "new" fillers used in TPO today. The realistic expected potential of organoclay nanocomposites is also represented.

The advent of microcomposites has come close to the performance of nanocomposites in regard to specific modulus/impact balance, and is approaching the existing performance on a direct modulus/impact balance. So, on a direct modulus/impact balance, microcomposites offer a cost effective alternative to nanocomposites when this is the only required design attribute. However, shrinkage, CLTE, surface appearance and other attributes distinguish the nanocomposites and are an excellent option when there are multiple end use requirements beyond the impact modulus balance. Furthermore, as the exfoliation and adhesion of the nanoclay systems is improved, and economies of scale are developed, nanocomposites still offer the potential to be a broad class replacement for microcomposites and other filled polyolefins. These improvements have gone from the invention stage to the innovation stage and should be expected by the industry in the near term.

Summary

Two key aspects of polymer nanocomposites were discussed, the relative importance of measuring exfoliation versus the end use requirements, and the current and near term potential of nanocomposites compared with current state of the art filled TPO materials. The de-emphasis on exfolation relative to performance does not indicate one should ignore dispersion of the nanocomposites. However, one should use exfolation as a secondary technique to determine the relative potential of a specific dispersion system relative to theoretical expectations. In general, there are various approaches to nanocomposites that induce very good dispersion or very good rigid bonding to the clay, but only recently have systems begun to address both aspects simultaneously. Also, the advent of microcomposites has led to very good TPO formulations, however the continual advance in nanocomposite technology is still progressing toward theoretical limits beyond the performance space of microcomposites.