APPLICATIONS OF NANOMER® IN NANOCOMPOSITES: FROM CONCEPT TO REALITY

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ABSTRACT

Nanomers® are surface modified montmorillonite minerals available for a range polymer resins from commodity polyolefins to specialty polyamides. Nano-effects have been demonstrated for resins in which Nanomers are added either during polymerization or by melt compounding. Montmorillonite's unique morphology contributes to improved strength and toughness, heat/dimensional stability, gas barrier and flame retardation. In addition to Nanomer product development, Nanocor has developed advanced processing technology to facilitate our customers' easy incorporation into resin systems. Downstream products using nanocomposite technology are now emerging at an accelerating pace. This presentation will focus on the benefits of nanocomposites with examples of their use in commercial products.

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Introduction

Nanomers® are surface modified montmorillonite minerals available for a range polymer resins from commodity polyolefins to specialty polyamides. Incorporation into these resins forms a nanocomposite plastic. Because Nanomers are used at low addition levels, significant property improvement is achieved with lighter part weight. Due to Nanomers platey morphology and propensity to accelerate polymer crystallization, gas barrier enhancement is a common feature. Depending on the specific resin, gas barrier can improve dramatically. Nanocomposite plastics are potent char formers, making them a valuable tool in creating improved fire retardant materials. In fluid resin systems Nanomer rheology is similar to that of fumed silica, and in addition to traditional property improvement, it carries the benefit of providing flow control when used in thermoset resin formulations.

Commercial nanocomposite plastics are emerging rapidly. These include nylon 6 and polypropylene for packaging and injection molded articles, semi-crystalline nylon for ultra-high barrier containers and fuel systems, epoxy electrocoat primers and high voltage insulation, unsaturated polyester for watercraft lay-ups and outdoor advertizing panels, and polyolefin fire retardant cable, electrical enclosures and housings.

This paper will illustrate the range of advantages for nanocomposite technology using four applications: packaging films, beverage containers, fire retardant electrical enclosures and fiber-reinforced boat accessories.

Nylon 6 Nanocomposites

Nylon 6 nanocomposites containing 2 wt% Nanomer are currently available from two commercial sources, Honeywell Engineered Polymers & Solutions and Bayer AG. Four percent loaded products are under development. Currently available products feature dry-as-molded (DAM) strength improvements of 30% and heat distortion increases double those of neat nylon. As loading increases, so too do strengths and HDT's.

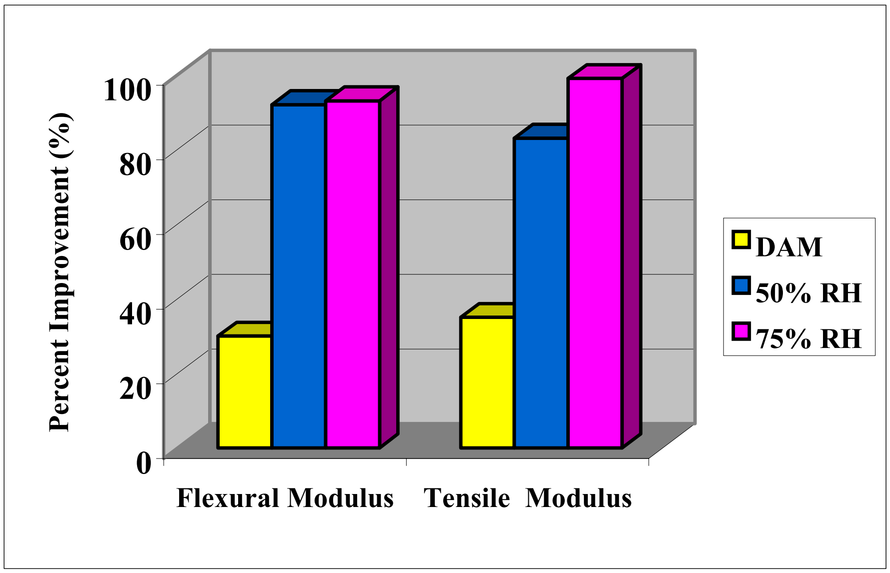
Mechanical Properties of Nylon 6 Nanocomposites*

Nanomer (wt. %)	Flexural Modulus (MPa)	Tensile Modulus (MPa)	HDT (^{o}C)
0%	3404	3117	56
2%	4374 (+35%)	4220 (+28%)	125 (+123%)
4%	4578 (+61%)	4897 (+65%)	131 (+134%)
6%	5388 (+90%)	5875 (+98%)	136 (+143%)

*For this and all subsequent tables percent improvements are indicated in parentheses.

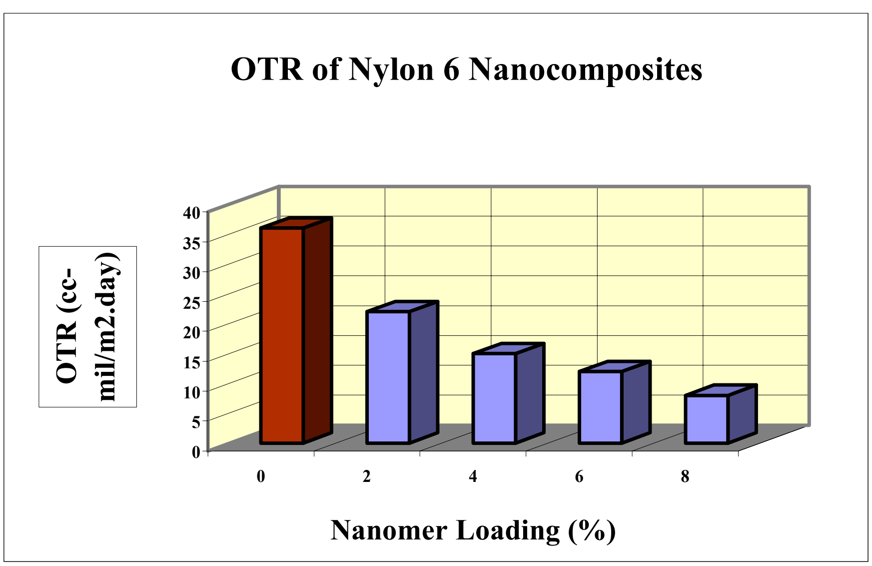
Since real world uses of nylon require performance at moderate-to-high humidity, dry-as-molded values are not indicative of actual service requirements. Fortunately, comparisons of nanocomposite performance vis-a-vis neat nylon are even better under humid conditions.

Percent Improvement For Commercial Products Versus Neat Nylon 6



Gas permeability also improves with Nanomer loading. Current commercial products deliver about 50% (2X) improvement in barrier to oxygen. At higher loadings the reduction exceeds 3X. Because Nanomers promote rapid crystallization, clarity is better than neat nylon, making nanocomposites ideal for films. Taking into account their improved strength, nanocomposites can be run at higher line speeds. Add to this the benefit of better print hold-out, and they become a superior, low cost film material.

OTR of Nylon 6 Nanocomposites (65% RH)



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Nylon nanocomposites find application in mono and multi-layer films as well as thin-wall structures. All are amenable to down-gauging, especially in instances where gas barrier is the dominating requirement. In mono-layer applications one has the obvious option of maintaining film thickness and taking advantage of additional barrier performance. In thin-wall structures and packages where stiffness is important, ie. stand-up pouches, nanocomposites offer a low cost solution, particularly in high humidity environments.

Film Applications

End Product	Fabrication Method	Property Enhancements	Benefits
Multi-layer Slipover Bag	**Blow film**	**Improved oxygen barrier**	**Down-gauging most expensive component**
Multi-layer Pet Food Bag	**Co-extrusion**	**Improved oxygen, grease and odor barrier**	**Vitamin protection Low oxidative odor after opening Greater shelflife**
Stand-up Pouch	**Cast film**	**Increased Young's modulus Improved printability**	**Stand-up stability Clarity**

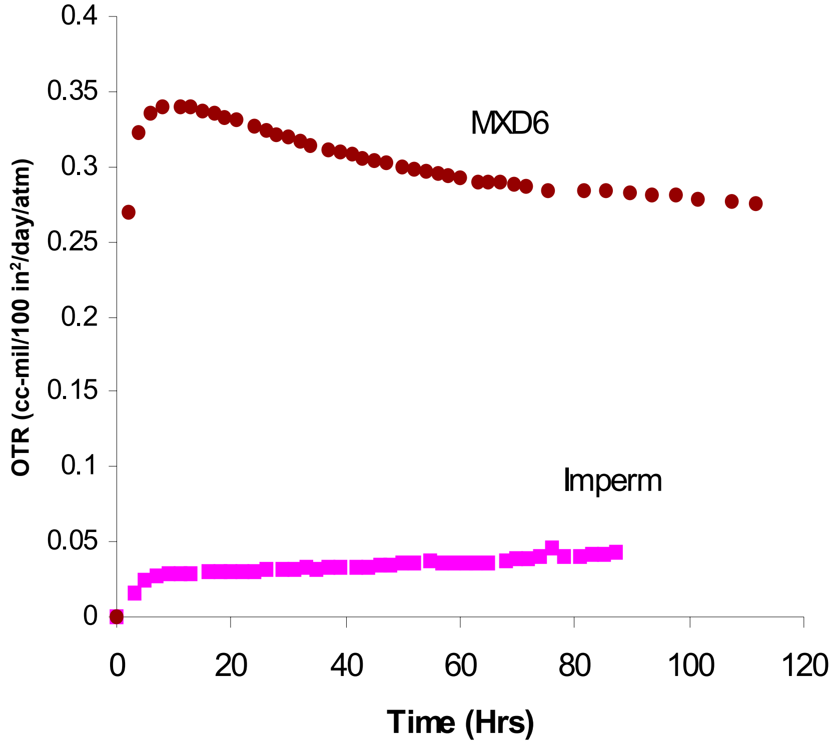
Ultra-High Barrier Nanocomposites

The inexorable movement of plastics into packages formerly dominated by glass and aluminum creates demand for very low gas barrier plastics, which are easy to process in conjunction with common resins such as polyester. One such material is Nylon MXD6*. This semi-crystalline resin exhibits very good gas barrier. Its barrier is exceptionally good at high humidity. Converting MXD6 to a nanocomposite further enhances barrier, making it superior to EVOH, the most commonly used high barrier resin. MXD6 nanocomposites were developed in conjunction with Eastman Chemical Company and are available directly from Nanocor under the tradename, Imperm™.

Imperm is appropriate for films, as well as multi-layer beverage and food containers. Oxygen barrier for films improves by 80% (5X) compared to neat MXD6. The barrier improvement in multi-layer PET containers is somewhat lower due to less-than-perfect platelet alignment during the bottle blowing process. Bottle oxygen barrier improves about 70% (3.8X) with bottle side-wall CO2 improvement of 60% (2.5X) at ambient pressure. When the bottle is pressurized at 3 volumes CO2 barrier improvement drops to slightly better than 40%. (1.7X)

* Nylon MXD6 is a product of Mitsubishi Gas Chemical Company, Inc.

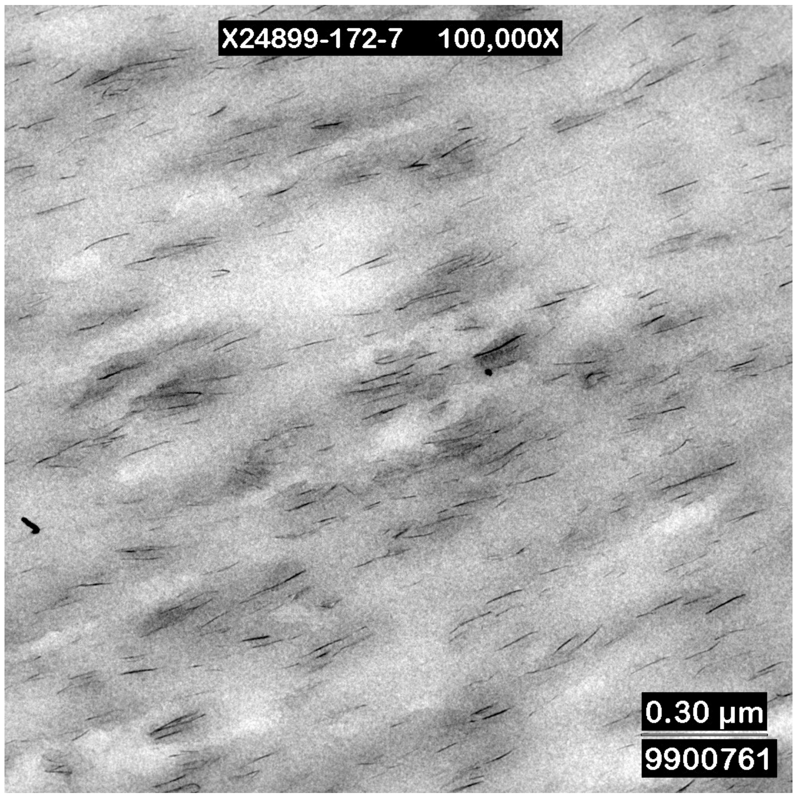
OTR of Nylon-MXD6 and Imperm



A 16 ounce. tri-layer blow molded non-pasteurized beer bottle illustrates the benefits of Imperm. This package contains a 10% barrier layer, sandwiched between PET. Because Imperm's process window overlaps that of PET, typical preform injection and blow molding process conditions are used. Since Imperm's matrix is nylon, it exhibits good adhesion to PET without the need for tie-layers.

Bottle haze is 5%, acceptable for amber-tinted bottles. Oxygen ingress is over 100 times lower than a mono-layer PET bottle of the same weight. The shelf life, based on 90% CO2 retention, is 28.5 weeks.

TEM Image: Imperm Layer of Three Layer PET/Imperm/PET Bottle



Polyolefin Nanocomposites

This area includes polypropylene and co-polymers, TPO's and TPE's. In contrast to nylon 6 nanocomposites, commercial products are not available through resin producers. Rather they are offered by independent compounders or produced at customer locations, using masterbatches supplied by masterbatch producers. Masterbatches are available from Clariant Corporation and RTP Company, among others.

Masterbatches typically consist of 40-50 wt% Nanomer and a nanocomposite usually contains 6 wt% loading for an average let-down ratio of 8:1. Polyolefin-type materials represent a wide range of hydrophobicity. Often a specific grade of Nanomer must be matched to a specific resin grade. Nanocor assists with Nanomer selection and then works with the compounder or masterbatch producer.

Both mechanical and barrier improvements drive nanocomposite use. Low melt-flow homopolymer polypropylenes (MF 2-15) yield the best mechanicals with increases ranging from

75-95% of neat resin. HDT's improve 30%. Part densities are slightly above neat resin (0.93 vs 0.90). Co-polymers, TPO's and TPE's demonstrate mechanical increases from 40-65%. HDT's for co-polymers and TPO's are somewhat lower than homopolymer.

Mechanical Properties of Injection Molded HPP Nanocomposites

Process	PP Type	Addition Level (%)	Tensile Mod. (Mpa)	Flexural Mod (Mpa)	HDT (C)
Injection	Homopolymer	-	1412	1148	87
Molding	(Low melt flow)	6%	2804 (+98%)	2043 (+78%)	116 (+33%)
Injection	Homopolymer	-	1327	1196	86
Molding	(medium melt flow)	6%	2180 (+64%)	1777 (+49%)	109 (+26%)

Depending on the polyolefin, gas permeability reductions range from 25-50% (1.3-2X). Polyolefins are low water vapor transmitters. Nanocomposites improve WVTR a more modest 10-15%.

Barrier Properties of Polyolefin Nanocomposite Films

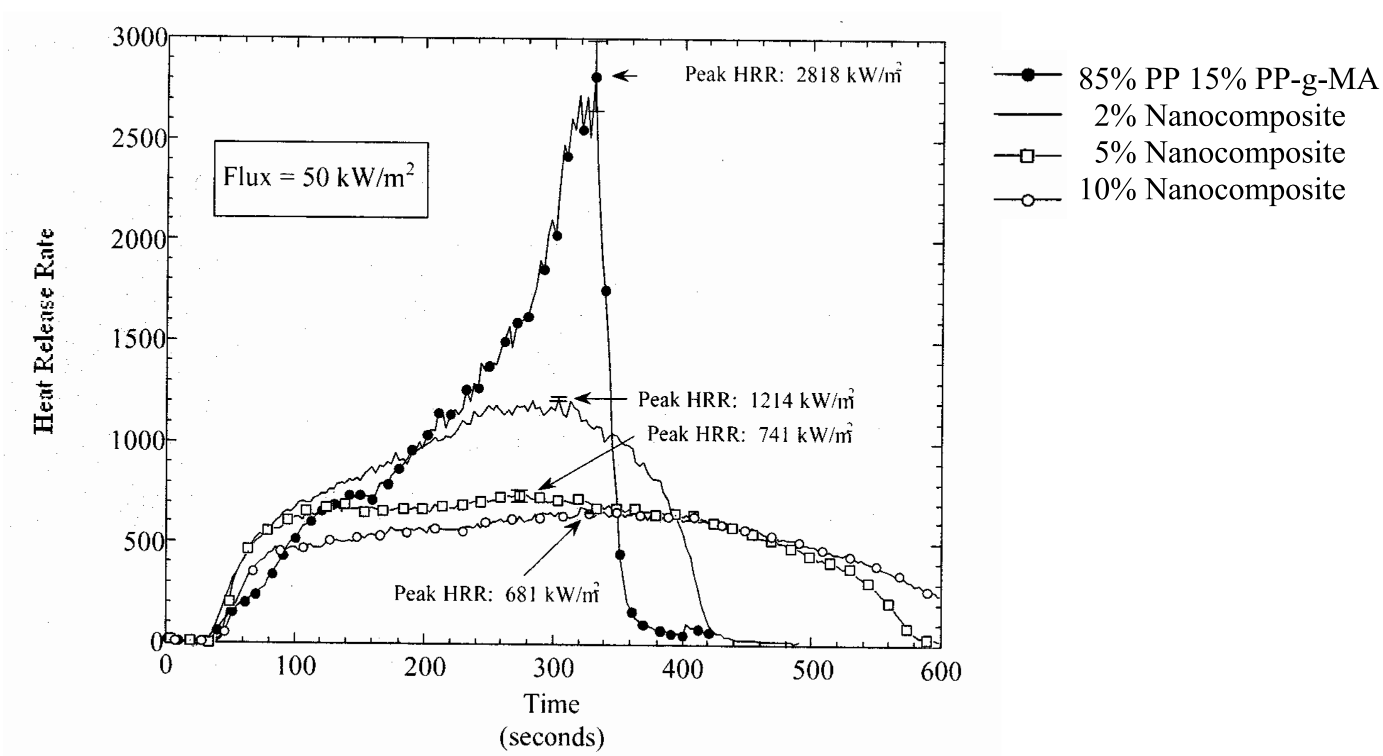
Film Process	PP Type	Addition Level (%)	OTR (cc-mil/m^2 day)	CO_2 (cc-mil/m^2 day)	H_2O (g-mil/m^2 day)
Cast	Random Copolymer	-	3.35 E+03	1.38 E+04	0.22
		6%	2.54 E+03 (+24%)	0.72 E+03 (+47%)	0.19 (+14%)
Cast	TPE	-	1.82 E+03		
		6%	1.27 E+03 (+30%)		

Blown	TPE	-	2.27 E+03		
		6%	1.01E+03 (+55%)		

Flame Retardant Plastics

A rapidly expanding area is fire retardant polyolefin nanocomposites. These materials readily form tough char layers. Char formation impedes the movement of volatilized polymer from the interior of a plastic matrix, denying fuel at the air/surface interface. For 5% loaded products peak heat release rates (HRR) are reduced by 70%. Employed in conjunction with traditional flame retardants, nanocomposites can achieve equivalent fire ratings using significantly reduced FR additive packages. With less FR additive dilution and greater reinforcement via nanocompositing itself, mechanicals are largely restored to levels seen in neat resin and at lower cost. This combination of benefits will likely make fire retardancy the largest use area longterm. Nanocomposites for FR uses are available from Gitto/Global Corporation, Lunenburg, MA.

HRR for Polypropylene Nanocomposites[1]



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Unsaturated Polyester Nanocomposites

Unsaturated polyester (UPE) nanocomposites find application in fiber reinforced products used in the marine, transportation and construction industries. UPE nanocomposite formulations are available from Polymeric Supply, Inc., Fort Pierce, FL. These formulations provide greater chemical resistance, especially to corrosive chemicals and sea water. Depending on the specific corrosive tested, ASTM D 543 Relative Uptakes can be reduced by 70%. UPE nanocomposites are also more dimensionally stable and fire resistant.

UPE/fiberglass nanocomposites are being used for boat accessories. In addition to the above benefits, accessories are less prone to color fading. Sag control is another major benefit, also seen in epoxy formulations. Sag control is the ability of the liquid resin to properly wet out and adhere to fiberglass matting prior to curing. Fumed silica has traditionally been used for sag control. Nanomers bring to thermosets the same type of rheology as fumed silica, and therefore provide sag control in addition to cured property improvements. Nanomers are easier to disperse and they are less costly, delivering the cured resin benefits at little-to-no cost increase compared to existing formulations.

Summary

Over the past eighteen months, plastic nanocomposite applications have gained their commercial footing, due in large part to the efforts of resin manufacturers, compounders and masterbatch producers who now offer user-friendly products. Although applications vary widely, they principally exploit the technology's contributions in the areas of gas barrier, reinforcement and flame retardancy. Nanocomposites differ from traditional plastic composites in that they provide these properties with minimal impact on article weight and they do so without processing penalties. Lastly, in packaging nanocomposites deliver with good clarity, a combination not possible using traditional composite approaches. A decade ago nanocomposite technology was a concept with great potential. Today, it is a reality.

References

1 **Gilman, Jeffery W., Kashiwagi, Takashi, Morgan, Alexander B., Harris, Richard H. Jr., Brassell, Lori, Vanlandingham, Mark, Jackson, Catheryn L., National Institute of Standards and Testing (NIST), "Flammability of Polymer Clay Nanocomposites Consortium: Year One Annual Report" page 25, November 1999.**

Acknowledgements

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