Nanocomposites

General Motors' 2002 Safaro amd Astrp vans represent the commercial debut of polyolefin nanocomposites, appearing in the TPO step assist.

Nanocomposites are gradually gaining acceptance in the mainstream of global plastics processing. These polymer com-pounds, containing relatively low load-ings (under 6% by weight) of nanometer -sized mineral part-icles, are beginning to show up in polypropylene and TPO-based auto-motive exterior cladding (see sidebar), barrier beer bottles, nylon packaging films, polyethylene pipe and wire/cable coatings, and more.

Optimism sur-rounding these novel materials has increased since they burst into industry consciousness two or three years ago. Exploratory effort has intensified as a growing body of data substantiates the potential of established nylon/clay nanocomposites, emerging polyolefin versions, and a range of other resin matrixes and nano-fillers (see Table 1).

Real-world applications are coming more slowly, in part because of the need to validate cost-effectiveness in the face of high price tags for nano-particle ingredients. Some early application-development programs have lapsed for cost reasons. Such casualties include an automotive timing-belt cover based on nylon 6 nanocomposite from Japan's Unitika and an automotive mirror housing of conductive PPO/nylon alloy from GE Plastics.

Yet the promise of nanocomposites is undiminished. They can improve polymers' stiffness, HDT, dimensional stability, gas barrier, electrical conductivity, and flame retardancy. Nano-particles are so small and their aspect ratio (L/D) so high that properties improve with lower loadings and fewer penalties (such as higher density, brittleness, or loss of clarity) than with conventional reinforcers like talc or glass.

Nano-clays are believed to increase barrier properties by creating a maze or "tortuous path" that slows the progress of gas molecules through the matrix resin. At the same time, these nano-platelets are only 1 nm thick, less than the wavelength of light, so they do not impede light's passage.

As shown in Table 1, nanocomposites now draw on a wider menu of resin matrices, including PP, TPO, EVA, acetal, polycarbonate, biodegradable polylactic acid (PLA), and inherently conductive polyaniline. The nano-particles most widely used so far in these compounds are clays supplied by Nanocor and Southern Clay Products. But a new generation of emerging nano-materials—including nanostructured silicas, carbon nano-tubes, and ceramic nano-fibers—suggest that impressive gains in nanocomposite performance lie just a few years ahead.

Nanocomposites are surfacing in exterior auto parts, beer bottles, and ESD applications. An expanding supply base, a growing range of matrix resins, and new-generation reinforcements all point to broad market impact in the next few years.

By Robert Leaversuch, Executive Editor

Broaden Roles in Automotive, Barrier Packaging

New focus on nano-PP

"Progress has moved beyond nylon 6/clay composites to include products based on PP and PE," declares Nanocor president Peter Maul. Nanocor's data show up to 98% stiffness improvement in PP and up to 52°F higher HDT (Table 2). The company says the nanocomposite has virtually the same impact strength as unfilled PP homopolymer.

General Motors recently announced the first-ever automotive production part in an olefinic nanocomposite. It's an exterior step assist for 2002 vans, made of a nano-clay/TPO compound from Basell. William Windscheif, Basell's global business v.p. for advanced polyolefins, calls this application "a small step, but a giant one for nanocomposites," adding that it heralds a broader shift to nano-PP in automotive.

Initially, the auto industry expressed most interest in nylon 6 nanocomposites for use under the hood, where higher HDT and light-weighting were the goals. Ingolf Buethe, senior v.p. for polymer research at BASF in Germany, says nylon nanocomposites show considerable promise in terms of enhanced stiffness, heat resistance, and gloss. But a serious downside for a 5%-nano-clay nylon compound tested by BASF was a loss of toughness more pronounced than with standard fillers.

More recently, automotive OEMs and molders have turned their attention to PP and TPO nanocomposites. These polyolefin materials potentially offer engineering-thermoplastic properties at 20% lower density and 50% lower cost per pound.

Consultant Kenneth Sinclair, head of STA Research in Snohomish, Wash., says the auto makers find that combination difficult to ignore. He estimates that about 30% of nano-PP usage by 2004 will be in autos, mostly cannibalizing existing PP applications. But replacement of metals and engineering thermoplastics will follow.

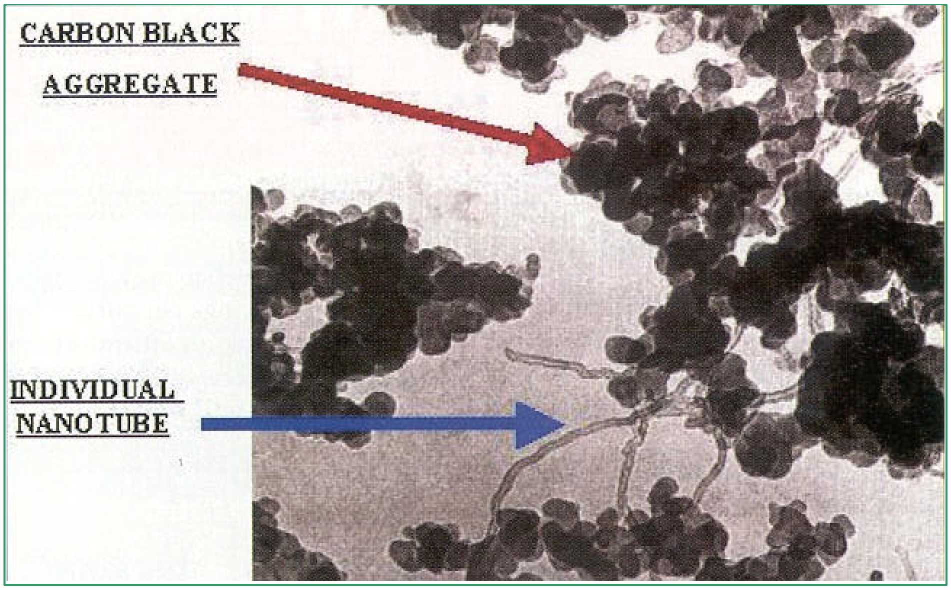
Sinclair says nano-PPs are stiffer and process better than standard PPs, so thin-walling of parts by around 40% is feasible. In turn, thin-walling permits around 25% reduction in cycle times, for 60-80% total savings per part.

Nonetheless, an official at one of GM's domestic competitors insists that

Table 1 ¾ Partial Listing of Nanocomposite Suppliers

Supplier & Tradename	Matrix Resin	Nano-Filler	Target Market
Bayer AG (Durethan LPDU)	Nylon 6	Organo-clay	Barrier films
Clariant	PP	Organo-clay	Packaging
Creanova (Vestamid)	Nylon 12	Nano-tubes	Electrically conductive
GE Plastics (Noryl GTX)	PPO/Nylon	Nano-tubes	Automotive painted parts
Honeywell (Aegis)	Nylon 6	Organo-clay	Multi-purpose
	Barrier Nylon	Organo-clay	Bottles and film
Hyperion	PETG, PBT PPS, PC, PP	Nano-tubes	Electrically conductive
Kabelwerk Eupen of Belgium	EVA	Organo-clay	Wire & cable
Nanocor (Imperm)	Nylon 6	Organo-clay	Multi-purpose
	PP	Organo-clay	Molding
	Nylon MDX6	Organo-clay	PET beer bottles
Polymeric Supply	Unsaturated polyester	Organo-clay	Marine, transportation
RTP	Nylon 6, PP	Organo-clay	Multi-purpose, electrically conductive
Showa Denko (Systemer)	Nylon 6	Clay, mica	Flame retardant
	Acetal	Clay, mica	Multi-purpose
Ube (Ecobesta)	Nylon 6, 12	Organo-clay	Multi-purpose
	Nyon 6, 66	Organo-clay	Auto fuel systems
Unitika	Nylon 6	Organo-clay	Multi-purpose
Yantai Haili Ind. & Commerce of China	UHMWPE	Organo-clay	

Source: Bins & Associates, Sheboygan, Wis.



Carbon nano-tubes dispersed in plastic create electrically conductive networks that provide static-dissipative performance (Photo: Hyperion)

car companies will balk at paying a premium for new materials. Nanocor, concluding that automotive OEMs want lighter parts at no extra cost, has focused its attention on non-automotive uses, including pallets, electronics, and appliance housings.

Volvo Corp. of Sweden has studied 5%-nano-clay composites based on Basell TPO modified with maleic anhydride as a coupling agent. Volvo observed 32% to 50% higher stiffness than 20% talc-filled PP. Impact strength was lower than unmodified TPO but higher than 20% talc-filled TPO. Volvo found that nano-TPO still has 68% lower stiffness than aluminum sheet.

A long-term goal for Dow Plastics is in-reactor compounding of nano-PP by using nano-clays as the catalyst support for in-situ polymerization of PP homopolymer. Dow's effort is focused on highly loaded (up to 10% clay) nano-PPs for semi-structural automotive uses. Dow sources say preliminary findings show "quite promising" performance of these composites.

Nanocor has developed a 40-50% nano-clay concentrate in PP. One potential use is in heavy-duty electrical enclosures that must meet various fire ratings plus demanding specs for low-temperature toughness and weatherability. Switching to nano-PPs could bring 18% weight savings and permit use of less halogenated FR additives to reach a given UL rating.

In other polyolefins, Kabelwerk Eupen of Belgium says melt blending of nano-clay into EVA shows promise for wire and cable compounds. Calorimeter tests reveal a dramatic decline in heat release at relatively low 3-5%) loadings. Nano-EVAs also exhibit superior mechanical properties, chemical resistance, and thermal stability.

Meanwhile, not all automotive work in nanocomposites involves polyolefins. A role for nanocomposites in polycarbonate automotive glazings is being explored by Exatec of Wixom, Mich., the joint venture of Bayer and GE Plastics that is dedicated to PC auto-glazing development. Exatec marketing director Fritz Stein says nano-technology is being considered for the exterior coating needed to achieve weatherability and abrasion resistance without reducing clarity. A Bayer coating containing nano-particles is one of several promising approaches being pursued, Stein reports.

Advances in packaging

The major application focus for nylon 6 nanocomposites today is in high-barrier packaging. Much of the attention is on PET bottles, where nanocomposites demonstrate improved oxygen and carbon dioxide barrier. Honeywell offers a 2%-nano-clay nylon 6 for bottles and has a 4% nano-clay version in development. An early commercial use is a pasteurizable beer bottle that will be introduced in China later this year (see p. 18).

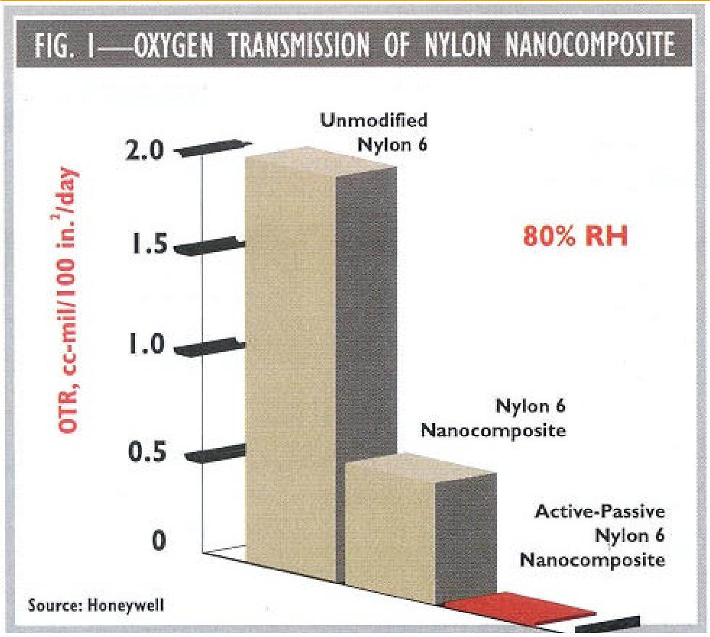
Nano-clays also enhance the oxygen barrier and stiffness of nylon 6 films. That could permit downgauging of packaging of oxygen-sensitive products—pet foods, boil-in-bags, vacuum packs, and stand-up pouches. No modification of cast film equipment is needed.

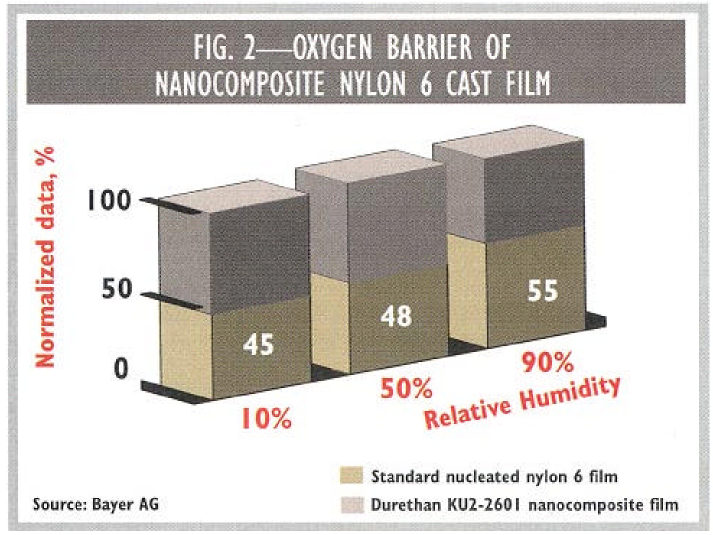
"Nano-clays significantly boost the barrier performance of nylon 6 while retaining most of its existing favorable characteristics," states Lance Altizer, Honeywell's market-development manager. He notes that nanocomposites retain nylon's toughness, clarity, hot-fill heat resistance, and oil/grease resistance. Honeywell claims that nylon 6 with 2% nano-clay has three times the oxygen barrier of straight nylon 6, and 4% nano-clay confers a six-fold

Table 2 ¾ Effect of 6% Nano-Clay On PP Homopolymer Properties

PP Type, MFR	Flexural Modulus, psi		Heat Deflection Temp., F	
	Unmodified	Nano-PP	Unfmodified	Nano-PP
Conventional 4 g/10 min	166,000	296,000	189	241
Conventional 14 g/10 min	173,000	258,000	187,000	228
Nucleated 35 g/10 min	231,000	335,000	235	250

Source: Nanocor





improvement. That makes Honeywell's Aegis NC nano-nylon a candidate for medium-barrier bottles and films—those offering around 0.5 to 1 cc/mil/day O_2 transmission rate (OTR). Data also show a doubling of stiffness, higher HDT, and improved clarity for nano-nylon 6 packaging.

Honeywell has turned its attention to creating nano-nylon materials that can beat the cost of high-barrier plastics or even glass. Its current contender is an active-passive barrier system called Aegis OX, which synergizes nano-clays as the passive barrier and a proprietary, nylon-specific oxygen scavenger as the active agent.

Honeywell claims this one-two punch brings a 100-fold reduction in OTR versus nylon 6, taking oxygen ingress to near-zero levels (Fig. 1). It also addresses a drawback of existing O_2 scavengers: In the Honeywell system, the passive barrier protects the scavenger from premature depletion. Efficiency of the system is also9 improved by uniform dispersion of the nano-platelets and by ensuring that the scavenger is positioned "to easily find the oxygen," as a Honeywell source puts it.

Aegis materials are being tested by major PET bottle makers. Honeywell says nano-nylon 6 tends to stretch and orient in ways compatible with stretch-blow bolding processes. Current barrier requirements for beer bottles (in which Aegis OX would be the core of a three-layer structure) set a maximum limit on oxygen ingress over 120 days, as well as a limit of 10% CO_2 escape in that time. The beer industry appears headed toward a 180-day barrier standard for both gases.

"We feel Aegis OX will compete against any existing barrier system for beer," says Honeywell's Altizer. He claims that Aegis OX meets both 120-day requirements and that the 180-day standard is achievable with processing refinements.

Nanocor has come up with a different high-barrier option. Its Imperm compound supplements the inherent gas barrier (0.35 cc/mil/day) of amorphous MDX6 nylon from Mitsubishi Gas Chemical with the addition of a nano-clay. Used as the core of a three-layer PET bottle, Imperm is said to have 100-fold lower OTR than that of straight PET. It is being used in a 16-oz, non-pasteurized beer bottle in which the Imperm core (10% of bottle thickness) reportedly ensures a 28.5-week shelf life. Imperm is said to adhere to PET without tie layers. Sufficient clarity is retained to meet requirements for the amber bottle.

Bayer is aiming nylon 6 nanocomposites at cast film for multi-layer packaging, protective films for medical and corrosion-prone items, and more. Bayer's pre-commercial Durethan KU2-2601 compound uses Nanocor's clay to reduce OTR by around 50% versus nucleatednylon 6 (Fig. 2). Stiffness of the nanocomposite is doubled, and its gloss and clarity rival those of a costly high-clarity copolyamide film, Bayer reports. Anti-blocking properties are also improved.

Meanwhile, nanocomposites also limit emissions of gasoline, methanol,

A Wealth of Data on Nanocomposites

Two U.S. conferences this past June presented a total of 63 papers on the latest work on nanocomposites. For proceedings of "Nanocomposites 2001: The Path to Commercialization," contact the sponsor, Principia Partners, Exton, Pa (888-680-2199). For proceedings of Nanocomposites 2001: Delivering New Value to Plastics," contact Executive Conference Management, Plymouth, Mich. (734-737-0507).

Another source of information is Bins & Associates, Sheboygan, Wis., a market-research firm specializing in plastics, which has prepared a report on the prospects for nanocomposites (920-208-0250).

Big Step for Nanocomposites In Automotive Exteriors

For the first time, a PP-based nanocomposite has been adopted for use in an automotive part production part. A step-assist for 2002 General Motors Safari and Astro vans is molded by Blackhawk Automotive Plastics, Troy, Mich., from a TPO matrix reinfirced with 2.5% nano-clay supplied by Southern Clay Products. The part is a low-volume, dealer-installed option. The nano-TPO replaces a 15% talc-filled PP but is molded in the same tool.

"This is a beginning. Parties to this effort are investigating other exterior and interior automotive parts," declares William Windschief, global business v.p. for advanced olyolefins at Basell, supplier of the TPO and processing expertise used for the application.

Bob Ottavianni, a GM technical specialist, says the nano-TPO delivers stiffness equivalent to the talc-filled PP it replaced, translating into 7-8% weight savings. Further, nano-TPO improves low-temperature impact strength and part surface quality. GM officials termed the project "cost-neutral," explaining that the higher price of Basell's nano-TPO is offset by lightweighting and other cost benefits.

"The nano-TPO processes at a somewhat lower temperature than talc-filled PP, decreasing cycle time, while also decreasing knit-line creation and other surface imperfections," says Mark Bennett, Blackhawks' advanced-technology manager. He also reports molding other prototype exterior claddings, including rocker and sail panels and body side moldings. Blackhawk is investigating newer versions of Basell materials, including some containing up to 5% nano-clay and offering stiffness comparable to 30-40% talc-filled PP. Basell's Windscheif notes that the much lower filler levels in nano-TPOs result in smoother surfaces while enhancing scratch resistance.

When GM's R&D unit first announced the nano-TPO project in 1999, emphasis then was on vertical body panels and interior poarts. Instead, the first commercial application is a relatively simple, low-volume part. But Alan Taub, GM's executive director of science, declares that there is no retreat from the applications initially targeted. He says work is well under way on a rocker-panel prototype that is 20% lighter than one of talc-filled PP. Taub says interior trim is also being actively explored.

Taub says a significant advance in chemistry by GM is critical to success of the van step. It allows more complete exfoliation (layer separation) and better dispersion of nano-clay particles into TPO. GM has granted Basell exclusive rights to use its advances in nano-PP technology. In turn, GM has been guaranteed exclusive rights to use Basell's nano-TPO's in the automotive field.

First automotive production part of a polyolefin nanocomposite is a TPO step-assist for 2002 General Motors Safari

and organic solvents. Ube America developing nanocomposite barriers for automotive fuel systems. It uses up to 5% nano-clay in nylon 6 and 6/66 blends. Nylon 6 with 2% nano-clay is said to be five times more resistant to gasoline permeation than unmodified nylon 6. Ube has developed a coextruded barrier fuel line, trade-named Ecobesta, using nylon 6/66 nanocomposite as the core layer.

New spark in conductivity

chemicals, nano-fibers, and nano-tubes argue that the potential of their technologies exceeds that of current nano-clay materials. But the prices are prohibitively high, and practical impacts probably lie five years ahead.

Static dissipative applications are emerging as one potentially large market. Applied Sciences has developed a vapor-grown carbon nano-tube made by pyrolysis of coal. Pyrograf-III comes in 100- and 200-nm diam. and has potential as an electrically conductive additive and modifier of plastics' coefficient of thermal expansion.

Max Lake, president of Applied Sciences, says the nano-tubes enhance electrical conductivity over a broad resistivity range and boost mechanical properties. Just 0.5% loadings provides volume resistivity in the 10^4 ohm-cm range.

Another class of nano-tube is a graphitic carbon type that is designed primarily to enhance electrical conductivity. These nano-tubes or "fibrils" are made from a hydrocarbon gas by Hyperion Catalysis International. They offer surface resistivity of 10^3 to 10^5 ohm/sq at 4% to 7% loadings.

"Fibrils are more efficient at building electrical conductivity into plastics than carbon black or PAN carbon fibers," states John Hagerstrom, Hyperion's technical service manger. He says the fibrils' small diameter (10 nm average) and high aspect ratio (1000:1) mean a given level of conductivity is achieved at lower loadings than with conventional carbon particles or fibers. That reportedly means less sacrifice of matrix properties, lower warpage, and better surface smoothness. Fibrils have been

Conductive nanocomposites can assist electrostatic painting of automotive parts. (Photo: Visteon.)

used to enhance electro-static painting of automotive mirrors, and as a static-dissipative additive in semiconductor components and disk drives, where the non-sloughing feature of nano-tubes helps retain purity.

Hybrid Plastics offers "POSS" nano-chemicals, named for their polyhedral oligomeric silsesquioxane molecular building blocks. These molecular silicas are hybrid organic-inorganic materials said to bridge conventional differences between minerals and monomers.

POSS molecules are cage-like structures typically measuring 1.5 nm along each axis. "The single-molecule particles are truly dispersible and have no affinity for one another," says Joseph Lichtenhan, Hybrid's president. Even loadings of 50% or more by weight reportedly disperse without agglomeration. POSS molecules dissolve in a plastic melt, then recrystallize on cooling into a network that enhances mechanical and thermal properties, as well as flame-retardancy.

"These chemical tools allow the creation of superior reinforced, crosslinked, and chemically coupled alloys," Lichtenhan claims. A 10% POSS loading elevates PP's flexural modulus by 12%, HDT by 21%, and impact strength by 36%. A 50% POSS loading in crystal PS reportedly has no effect on optical clarity. Hybrid cites optical disks, micro-electronics, and medical products as target niches. At present, POSS costs around $200/lb. A larger plant for making POSS nano-chemicals, duo on-line in early 2002, could push down the cost of some POSS products to about $15/lb. Hybrid Plastics' sales and marketing arm is Divex, Inc.

Argonide has a technology for producing alumina ceramic nano-whiskers by electro-explosion of metal wire. These NanoCeram whiskers offer potential for reinforcement because of their small size (2 nm diam.) and high aspect ratio (50:1 average). Applications for NanoCeram are being pursued as reinforcements and thermally conductive additives. Current price of pilot-plant materials is $280/lb, but that is likely to fall as usage develops. PT

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NO.	COMPANY
121	Applied Sciences, Cedarville, Ohio
122	Argonide Corp., Sanford, Fla.
123	BASF Corp. Plastic Materials, Mt. Olive, N.J.
124	Bayer Corp., Polymers Div., Pittsburgh, P.A.
125	Basell North America, Wilmington, Del.
126	Creanova Inc., Somerset, N.J.
127	Divex, Inc., Tiburon, Calif.
128	Dow Plastics, Midland, Mich.
129	GE Plastics, Pittsfield, Mass.
130	Honeywell Engineered Applications & solutions, Morristown, N.J.
131	Hyperion Catalysis International, Cambridge, Mass.
132	Nanocor, Arlington Heights, Ill.
133	Polymeric Supply, Ft. Pierce, Fla.
134	Showa Denko K.K., Tokyo, Japan
135	Southern Clay Products, Gonzalez, Texas
136	Ube America, Inc., N.Y.C.
137	Unitika Ltd., Osaka, Japan