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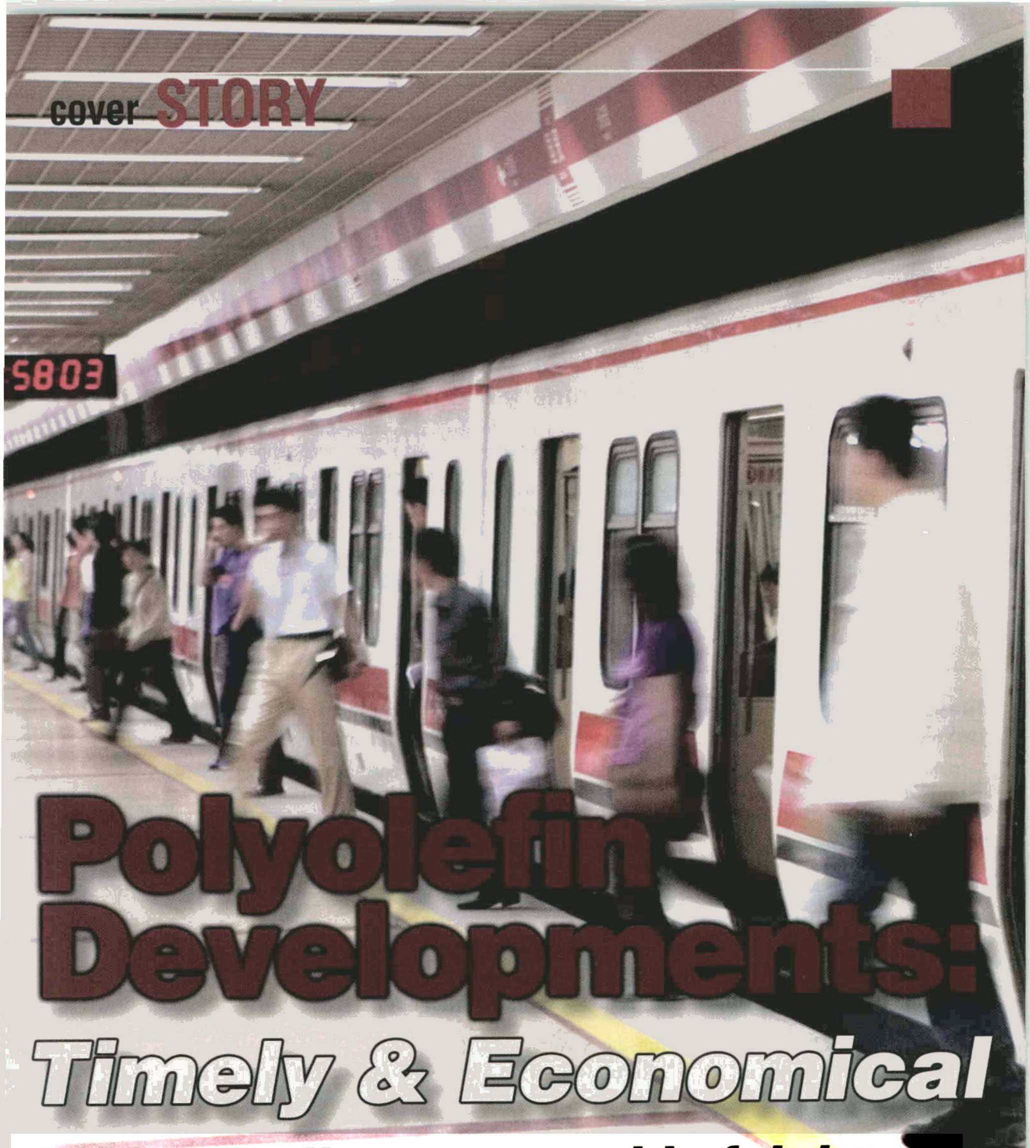
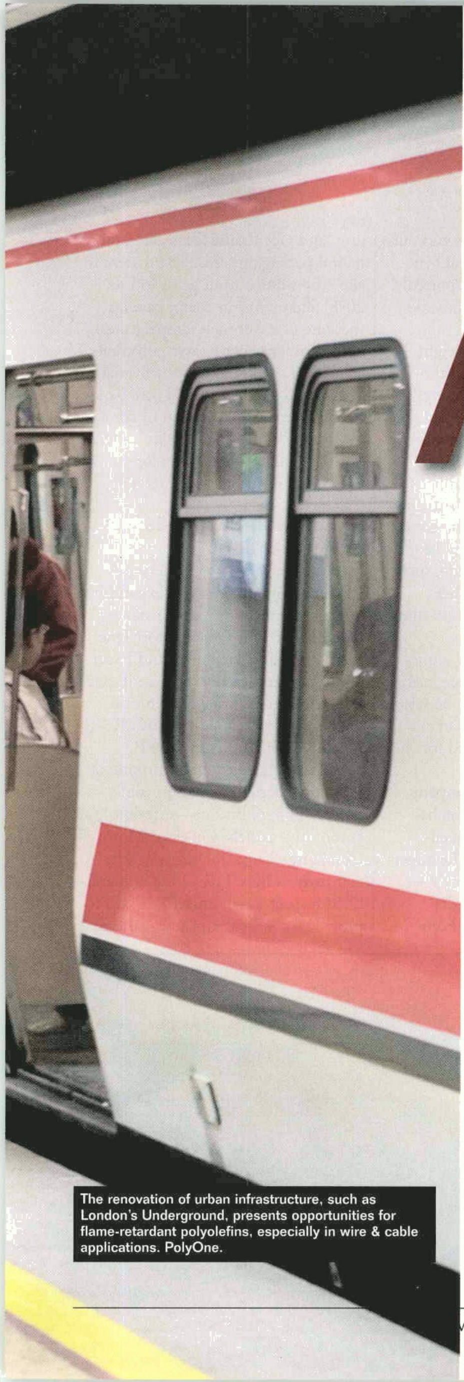


Polyolefin Developments: Timely & Economical

PE & PP adjust to a world of tighter budgets and higher expectations.



The renovation of urban infrastructure, such as London's Underground, presents opportunities for flame-retardant polyolefins, especially in wire & cable applications. PolyOne.

By Michael Tolinski

As the lowest-priced family of low-density polymers, polyolefins may be in high demand during the economic recession and recovery. The lightweight resins can be tailored to do a lot—at minimal cost.

So resin producers continue to create new grades with enhanced properties, and compounders are beefing up polyolefins for new applications—while end-users expect more sophisticated compounds and forms. Along with their well-known roles in packaging applications, newly developed polyolefin-based materials have become important in the replacement of aging urban infrastructures, and in the engineering of new lightweight vehicles.

Options Stretched With mPE Film

For years, polyolefin makers have emphasized the molecular weight and structure control that metallocene catalysts provide. Still, metallocene-based polyolefins have made only a small dent in a market dominated by resins made with Ziegler-Natta and other cost-effective, conventional catalysts. (After all, the right catalyst for a job is often a more traditional "Z-N" catalyst, which explains the technology's popularity and longevity.) But the situation is changing with time, especially for linear low-density polyethylene (LLDPE).

"Publicly available market data suggests that mLLDPE (metallocene LLDPE) resins will enjoy continued higher growth rates versus conventional LLDPE resins over the next several years," says Glenn Cozzone, manager of North American product development for LyondellBasell Industries (Wilmington, Delaware USA). In North America, for instance, general LLDPE production is expected to continue to show fairly flat growth, while mLLDPE is expected to grow at greater than 6% per year, says Cozzone. "Because of the benefits delivered by mLLDPE resins versus conventional LLDPE, the demand growth for these resins has outpaced other polyethylene materials."

With this gradual changeover in dominance in sight, LyondellBasell is expanding its Starflex line of mLLDPE resins for blown and cast films. Cozzone says the resins target certain characteristics needed in high-performance film applications such as food and medical packaging, shrink wrap, and heavy-duty shipping sacks. "Metallocene resins are well recognized for their excellent dart impact and puncture resistance, superior organoleptics, brilliant clarity, and outstanding hot tack and heat seal benefits." The Starflex materials reportedly are produced with licensed Univation processing technology.

Producers of already lightweight LLDPE film can benefit from the downgauging and material savings allowed by higher-property mLLDPE. "High-visual impact collation shrink films are an example where downgauging is being targeted," explains Cozzone. For example, a high-stiffness shrink-film LDPE (such as the company's Petrothene L3035) may be combined with a Starflex grade, such as GM1810. Produced as either monolayer or coextruded shrink films, the combination results in an improved balance of stiffness, puncture and dart-impact resistance, clarity, and shrink characteristics, he says. "Films up to 20% thinner than current films are being developed for this application."

ExxonMobil Chemical Company (Houston, Texas USA) likewise has been expanding its lines of metallocene-based film material. The target-application list of the company's Enable mPE film resins includes shrink wrap and conventional film uses, and greenhouse films and lamination packaging films. The materials allow film-line output gains (up to 20%) and extrusion energy savings (because of lower melt temperatures), among other benefits, says polyethylene global market development manager David McConville. "These benefits include the replacement of complex LLDPE blends and significant downgauging opportunities for LDPE-rich blends."

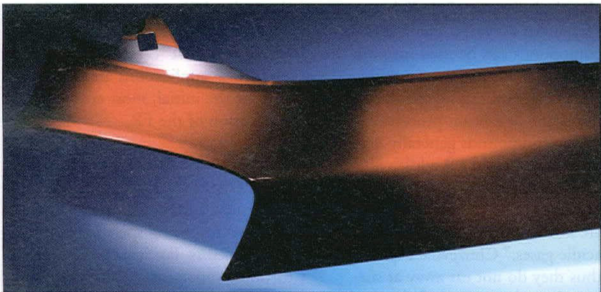
Modification Expands PP Applications

Meanwhile, various modifiers are allowing polypropylene to expand its range of applications. For instance, ExxonMobil's Vistamaxx propylene-based specialty elastomers and Exact plastomers reportedly increase impact toughness substantially when optimally blended as modifiers in PP. And LyondellBasell's Hifax PP copolymers have entered into one of the most restrictive of all possible polyolefin applications—exterior automotive panels. On Ford Motor Company's Kuga, for example, the company's Hifax TRC 280X mineral-filled impact-copolymer PP is said to provide a coefficient of linear thermal

expansion (CLTE) that is low enough to allow its use for the car's tailgate outer panel and roof spoiler.

Another approach to extending PP's reach and flexibility depends on rubber modification created inside the polymerization reactor itself. Reactor-based methods create a finely dispersed, consistently structured rubber phase distributed in a PP matrix, enhancing flexibility, surface quality, and clarity. One company becoming more visible in the area is the Japan Polypropylene Corporation (Tokyo, Japan), which produces its Welnex reactor-based thermoplastic olefin (R-TPO) using its Horizone gas-phase metallocene process.

The R-TPO material consists of a random copolymer PP matrix with a rubber phase dispersed finely enough to create high transparency in the material. Also, the R-TPO's surface is said to be less tacky because of its low content of low-molecular-weight oligomers, which, in Ziegler-Natta-based R-TPO, tend to create stickiness and higher peel strength. And when elastomer modifiers are blended with the metallocene R-TPO, novel thermoplastic elastomers result, the company reports.



The thermal expansion of parts made with LyondellBasell's Hifax TRC 280X mineral-filled PP is said to be low enough to allow the compound's use for the Ford Kuga's tailgate outer panel (above) and roof spoiler (opposite page). LyondellBasell.

Longer-Lasting Pipe

Reactor-manipulated polyethylene provides other sought-after properties. Consider the case of PE pipe, where one desired feature is high-temperature longevity. The Dow Chemical Co. (Houston, Texas USA) offers raised-temperature-resistant polyethylene (PE-RT) for hot-water and cold-water pipe that requires no crosslinking for elevated-temperature service. Recent targeted applications for PE-RT include heat-exchanger pipes and pipe networks for heating and cooling road surfaces.

The company says its Dowflex 2388 PE-RT resin has been tested thoroughly at high hot-water temperatures. The resulting data predicts pipe lifetimes extrapolated out to 50 years at 75°C application temperatures, and out to 10 years at 90°C. And recently, an actual pipe application of another Dowflex grade was examined after 20 years of service; thermal testing by Dow showed that most of the material's oxidative protection capacity remained. The PE-RT resin is an ethylene-octene copolymer produced using Dow's Insite metallocene catalyst technology, which controls polymer side-branching, resulting in improved toughness and environmental stress-cracking resistance.

Another of the company's PE pipe materials comes to the aid of plastic's corrosion-prone cousin: steel. Dow Europe GmbH has introduced a new PE topcoat and an adhesive polyolefin material for three-layer steel pipe-coating systems. The Dow 12110G HDPE and Amplify GR 320, a grafted adhesive resin, reportedly allow steel pipe to meet stringent corrosion-resistance requirements when they are used as coatings for large-diameter oil and gas pipelines. "When we entered into this new market segment, we benchmarked our new materials with the current best offerings to help ensure that we meet or even exceed their performance," says Katja Wodjereck, Dow's market manager for pipe applications in Europe, the Middle East, India, and Africa.

Flame-Retarding Polyolefins

Compounders of polyolefins are seeing the value of other infrastructure-related applications. One such company, PolyOne Corp. [Avon Lake (Cleveland), Ohio USA], is modifying polyolefins for use in wire-and-cable covering applications. In underground railway cable applications, for instance, the company's ECCOH compounds provide "low smoke and fume, zero-halogen" ("LSFOH") flame retardancy, says Murielle Chuzeville, global product manager for LSFOH in Assesse, Belgium.

Communications-related or electrical-related requirements for LSFOH flame protection are also being specified for public buildings and airports—or anywhere smoke is an issue and infrastructure is being renovated, she explains. For example, "The Olympic Games taking place in London in 2012 certainly will require up-to-date public buildings and infrastructure, where polyolefins for wire and cable will play a big role."

Chuzeville says London's Underground is a good example of where LSFOH compounds have been placed into critical use. As one of the oldest infrastructures in Europe, "the Tube" has been refurbished with ECCOH FR cable materials that won't produce the smoke and toxic gases that would quickly overwhelm people in confined spaces during a fire.

Another new use for the ECCOH compounds includes the market for solar photovoltaic cell installations, which is expanding worldwide at about 30% per year, Chuzeville reports. Here, exposed solar-panel cables must resist exterior moisture, chemicals, heat, and sunlight over a lifespan of 20 years. The LSFOH compounds can be used for both the inner cable insulation and outer sheathing, and can be crosslinked by dry silane or e-beam processes.

The compounds generally depend on mineral-based FR additives, which reduce smoke and toxic fumes during burning. "The LSFOH compounds are noncorrosive, so they do not emit acidic gases," Chuzeville explains; thus they do not eat away at surrounding electronic and electrical components. PolyOne's compounding technology for incorporating metal hydroxide and aluminum trihydrate FR fillers is said to minimize the property reductions normally caused by mineral fillers, providing a reasonable balance of tradeoffs.

Additives suppliers are also addressing the negative properties of both mineral-based and halogen-based FRs. Intumescent, phosphorus-based flame retardants (P-FRs) can be good alternatives for polyolefin users, says Guru Zingde of Amfine Chemical Corp. (Upper Saddle River, New Jersey USA), a strategic joint venture of Mitsubishi Corp. and Adeka Corp. in Japan. P-FRs avoid the unwanted byproducts and fumes of halogenated FRs and the reduced mechanical properties from high loadings of metal hydroxides. Thus the companies developed the "ADK Stabilizer FP-2000 series" intumescent FR for polyolefins to minimize heat-release rates and smoke during combustion without common unwanted effects.

The FP-2000 reportedly is not a common P-FR, but rather it has a proprietary "nitrogen-phosphorus-based" chemistry. Zingde says it does not contain any ammonium polyphosphate, which helps prevent common P-FR problems of poor thermal stability, narrow processing window, and high moisture sensitivity. He adds that "certain types of wire and cable" applications are most likely to be the initial, most cost-effective application of the FR.

Additives Shift PO Properties

Other new additives serve as alternatives for improving specific properties in polyolefins. For instance, heat-distortion temperature (HDT) can be increased with monomers that create crosslinking "bridges" between molecular chains, says Jeremy Austin, market development engineer, Functional Additives, Sartomer Company, Inc. (Exton, Pennsylvania USA).

Sartomer's SR732 "ionic monomer" reportedly has been shown to increase HDT by roughly 10°C to 20°C in LDPE and PP, at 2% to 5% loadings. The ionic monomer can be described as an organometallic salt with acrylate functional groups that activate during the heat and shear of screw processing, creating the crosslinking bonds.

The goal of the ionic monomer's development should have a familiar ring to everyone who strives to enhance polyolefins: "the ability to take something that's fairly inexpensive and give it the performance characteristics of something more expensive," says Austin. In this case, polyolefin applications are often restricted by their limited temperature stability, excluding them from applications dominated by nylons and other engineering polymers. "If we could improve the thermal characteristics of the polyolefin, we can pick off some of the 'low-hanging fruit,' " he says—that is, higher-heat applications such as under-hood automotive parts.

SR732 comes in powder form and can be incorporated using standard twin-screw extrusion (though its current granule size makes it "a challenge" to use in film applications, says Austin, motivating the company's interest in developing smaller particle sizes). During screw processing, the modifier does not melt but rather reacts with the polymer's free radicals created by heat and shear.

However, this reaction is different from that in common polyolefin crosslinking. "We're generating an ionic crosslink, as opposed to a covalent [bond]," Austin explains. This allows the compounded pellets to be remelted and processed like standard resin grades in screw processing and molding. "Think of it like a bridge between adjacent molecular chains at the point where the ionic monomer reacts within the backbone. So when you add temperature to it, that cluster becomes migratory and mobilizes, so your polymer chains conform with and slide past each other." When the molded article is cooled, the bridge links re-form.

Other low-molecular-weight additives, such as polypropylene waxes, are useful for influencing specific polyolefin characteristics. These waxes have traditionally been based on Ziegler-Natta polymerization chemistry, and are often functionalized by peroxide-induced radical grafting of maleic anhydride, explains Paul Hanna, senior chemist for Baker Hughes (Sugar Land, Texas USA). However, "The introduction of metallocene technology has allowed the development of significant improvements in the control of the properties of low-molecular-weight polypropylene waxes."

Hanna says that when functionalized in various ways, derivatives of metallocene-based waxes can serve as effective adhesion promoters, dispersants, and compatibilizers. Specifically, metallocene technology helps control the wax's isotacticity (which affects melting point); provides the ability to easily introduce comonomers randomly; and provides the flexibility "to prepare a wide variety of functional derivatives based on the presence of a single double-bond on the end of each molecule," says Hanna. "These metallocene polymers also have a low polydispersity, which decreases melt viscosity," the chemist adds.

"Lightweighting" Polyolefins

Though their densities are already relatively low, filled polypropylene and polyethylene compounds are being modified to accomplish more with even less total mass. One weight-saving approach is to replace a relatively high loading of reinforcing filler with

Two new uses of PP in automotive indicate the material's growing importance. Above: The Ford Flex's quarter trim bin is made from PP filled with wheat straw, from A. Schulman. Right: The Lincoln MKT CUV console's side panels are made from a color-matched, 20% glass fiber-reinforced PP from Ticona Engineering Polymers. Both applications were finalists in the 2009 SPE Automotive Innovation Awards competition. SPE.

a lower loading of filler that provides the same properties to the resin. One organization developing its own reinforcing agent for lightweighting polyolefin compounds is nucleation-agent specialist Milliken Chemical, a division of Milliken & Company (Spartanburg, South Carolina USA).

The company's David Lake says that lighter-weight alternatives to traditional fillers and glass reinforcement are especially important for future automotive uses of polyolefins. As proof, he cites increasing CAFE fuel-economy standards, directives to reduce carbon dioxide emissions, and "the $1 to $5 of value per kilogram removed from a car." With about 40 kg of filled PP compounds in each vehicle, a 10% weight reduction in the compound would add up to significant monetary savings, he argues.

With the goal of weight/density reduction, Milliken's Hyperform HPR reinforcement is said to provide equivalent or better properties than talc, even when loaded in PP at much lower loadings. In TPO, Lake says, the stiffness provided by 30% talc loading is possible with only 10% loading of HPR, which reduces the TPO's density by 15% as well (0.958 vs. 1.127 g/cc). The HPR also matches talc in terms of other properties such as shrinkage, flexural modulus, HDT, and tensile strength, with only about one-quarter to one-third as high an HPR loading.

In terms of costs, the HPR filler does have a heftier price per pound, but Lake argues that this is offset by the value of its weight savings and lower loading. For example, when compared with the 30%-talc TPO of equivalent stiffness, the 10%-HPR TPO's additional costs can be justified as long as its corresponding weight savings are valued at $2/kg or higher, according to the company's calculations.

The HPR material is not talc, glass, or carbon black, but is described as an "inorganic mineral based reinforcing agent" with particles having a fiber-like morphology. "The fiber dimensions are about 0.5 micron in diameter and 25 microns in length," says Lake. "The 500-nm diameter may or may not qualify it as a 'nano' reinforcing agent," he adds, depending on the definition used.

PO Packaging Cushions Sustainably

Packaging converters are also becoming cleverer about achieving new, desirable properties in polyethylene. For instance, the "hybrid cushioning" HC Renew material of Pregis Corp. (Deerfield, Illinois USA) is an LDPE film formed with multiple small air chambers. It's manufactured by feeding flat, perforated rollstock into a machine that creates the rows of air-filled pockets, which, the company says, make the product stronger than traditional single-chamber air-filled cushioning pillows. (See page 38.)

Another touted feature of the HC material is its biodegradability. The company says it contains an organic additive "that accelerates microbial degradation, without compromising recyclability." Without containing heavy metals or salts found in other "oxo-biodegradable" films, the material is said to be compliant with ASTM D5511, which tests the rate of degradation in anaerobic, landfill-type conditions.

Polyolefin foam is another common form of cushioned packaging. Closed-cell foam is effective for transporting and protecting fragile items, but foam converters are seeking better foam-surface qualities and easier fabrication. To this end, foam manufacturer Sekisui Alveo AG (Lucerne, Switzerland) developed its Alveobloc product, a closed-cell crosslinked PO roll-foam.

The material is hot-air laminated, creating a structure that reportedly allows milling, punching, or water-jet cutting, while also having a smooth foam skin on each side that is said to resist scratches and soiling. This combination of properties allows the material to be used as case inserts for transporting sensitive items, for which the foam is machined with various cutouts. Moreover, the skin does not have to be removed before fabrication, as with molded block-foam materials, the company adds.

Companies Mentioned in This Article:

Alveo AG
Ametek Westchester Plastics
Amfine Chemical Corp.
A. Schulman
Baker Hughes
BASF Corp.
Chevron Phillips Chemical Co.
Dow Chemical Co.
ExxonMobil Chemical Co.
Ford Motor Co.
Ingenia Polymers Group
Japan Polypropylene Corp.
LyondellBasell Industries
Milliken & Co.
PMC Group
PolyOne Corp.
Pregis Corp.
Sartomer Co.
Ticona Engineering Polymers

Michael Tolinski is the author of *Additives for Polyolefins — Getting the Most out of Polypropylene, Polyethylene and TPO*, published in 2009 by Elsevier.
www.additivesforpolyolefins.com

SPE Presents All Things Polyolefin in February

The 2010 SPE International Conference on Polyolefins, co-located with FlexPackCon® 2010, will be held February 21-24 at the Hilton Houston North Hotel (Houston, Texas USA). The combined event is sponsored by South Texas Section of SPE, in partnership with three SPE Divisions: Polymer Modifiers & Additives, Thermoplastic Materials & Foams, and Flexible Packaging.

Conference co-chair Jill Martin of The Dow Chemical Company emphasizes the diversity of the event. "We have a diverse set of participants, from additive suppliers to converters, the latter as a result of both the suppliers' interests, as well as the alignment with the Flexible Packaging Division of SPE." Houston is an ideal location, she adds, given the strong local chemical and energy industries. "Small and new players will have an opportunity to interact with some of the largest members of those markets at this conference. While this conference is a place where industry meets to discuss innovation and technology, we also offer a chance to network both during our golf outing on Sunday afternoon and reception Monday evening."

Conference presentation topics (tentatively scheduled as of press time) will range from catalysts and additives to nanofillers and modifiers. For example:

- Bimodal and tandem catalyst systems are scheduled to be covered by Chevron Phillips Chemical Co. (The Woodlands, Texas USA).
- The stabilization of durable PP fibers is slated for coverage by presenters from Ciba, now part of BASF Corp. (Tarrytown, New York USA).
- Ingenia Polymers Group (Houston) reportedly will cover the performance of polyolefins that incorporate different forms of highly concentrated additive blends, including new masterbatches, melt-formed pastilles, compacted pellets, and melt-extruded pellets.

Other session topics will cover polyolefin testing, processing, and converting technologies, while tentatively scheduled application-related topics will cover barrier materials for packaging, life-cycle analysis, and polyolefins for batteries.

Despite the economy, exhibiting companies continue to support the event loyally. As early as this past October, exhibitors had already signed up for all but eight of the 70 available spaces, says exhibitor contact Bill Diecks of Ametek Westchester Plastics (Houston, Texas USA). To support exhibitors' needs, Diecks says, free WiFi will be supplied for all the booths this year. He also emphasizes how much the event's organizers appreciate the key sponsors, especially "Platinum" sponsor PMC Group, Inc. (Mount Laurel, New Jersey USA), and "Gold" sponsors Chevron Phillips and Ingenia Polymers.

Along with the seasoned professionals attending the conference, student involvement and support are important features of the event, says consultant and conference co-chair Don Witenhafer. "About 90% of the excess funds acquired by the South Texas Section of SPE goes to support students at Texas universities through scholarships, SPE student chapter grants, support for university plastics research, and student attendance at the Polyolefins Conference." Although the poor economy reduced last year's cash flow, he says that in "a normal year" over $80,000 is contributed to students. Thus, "Attendance at the Polyolefins Conference is a substantial financial contribution to students, in addition to helping you gain the latest knowledge about the industry!"

> "We have a diverse set of participants, from additive suppliers to converters, the latter as a result of both the suppliers' interests, as well as the alignment with the Flexible Packaging Division of SPE."

For more information or to register, visit www.spe-stx.org/PolyolefinsConference.htm for updates about the event, or contact registration chair Suzanne Biggs at +1 713-829-9226 or email suzbiggs@comcast.net.