Plastics Testing and Analysis

By Nancy Lamontagne

Knowing all the characteristics of a plastic you're working with and how it will react under various conditions is important for developing new materials or new products. Thorough testing and analysis can help determine how additives, weathering, or downgauging will affect the material or the final plastic part. If a failure occurs, a scientific approach to analyzing the failure can provide a way to prevent the problem in the future.

New analysis techniques are being developed to take a look at structure on the nanoscale and to perform testing on new stronger materials. Also, analysis instruments once found only in the laboratory are moving to the manufacturing plant.

Polyolefin Analysis

Polymer Char specializes in instrumentation for analysis of polyolefins, which include polypropylenes and polyethylenes. Polyolefins are among today's most used polymers. Despite their simple chemistry, with only carbon and hydrogen atoms, they still possess a complex microstructure. Polyolefins have a strong chemical resistance. Thus they require high temperatures to dissolve, which puts special challenges on analytical separation techniques, explains Benjamin Monrabal, the R&D director at Polymer Char in Valencia, Spain.

"Even though polyolefins are so simple and have been used for years, there is still tremendous room for development," Monrabal says. For example, manufacturers are looking to downgauge polyolefin parts to save money while maintaining performance of the final product. In the automotive market, companies are developing new polypropylene copolymers to increase their impact resistance for applications such as car bumpers. "Each time a process is changed or a new product is developed, it is important to check the microstructure of the resulting polymer," he says.

The individual polymer chains of polyolefins typically have different degrees of polymerization. Thus analysis of the molar mass distribution of polyolefins is important. Polymer Char's polyolefins-dedicated Gel Permeation Chromatograph (GPC-IR) offers fully automated sample preparation and filtration with optimum infrared detection for determining concentration and composition. The chemical distribution of copolymers can be analyzed using the company's CRYSTAF or TREF instruments. For even more detailed polyolefin analysis, the interplay of molecular and chemical composition can be examined with the Cross-Fractionation Chromatograph (CFC) instrument, which combines Temperature Rising Elution Fractionation (TREF) and GPC to provide highly detailed 3-D bivariate distribution analysis.

Monrabal says that the company's analytical instruments have been traditionally used in R&D labs, but that Polymer Char has recently started making instruments for quality-control applications in manufacturing plants. This year it will introduce new instruments designed for manufacturing plants, particularly for the analysis of xylene solubles in polypropylene-manufacturing plants and for measurements of intrinsic viscosity. These instruments perform the same types of analysis as the company's other instruments but in a robust, faster, and simpler-to-use package. "I think our contribution in this area will be significant," Monrabal says.

Polymer Char specializes in instrumentation analysis of polyolefins.

Automotive Plastics

Materials used in the automotive market must meet several requirements, depending on the application. Automotive materials have to comply with specific safety and performance standards as well as match the consumer's perception in terms of design and quality. Intertek Group plc tests, certifies, and characterizes materials and products in a variety of industries, including automotive plastics. "Intertek can independently investigate, test, and analyze materials during the early stages of development, so that materials are qualified before they move to the next part of the automotive polymer value chain," says Morris Geissler, director, Automotive Industry, at Intertek. This means that manufacturers know at a very early stage that the material will meet the requirements for an intended application.

Recently, Intertek assisted Polyscope Polymers B.V. by providing extensive laboratory support for development of automotive materials for use in car interior parts, such as the dashboard carrier. Polyscope decided to develop an improved range of styrene maleic anhydride (SMA) products called Xiran® after Nova Chemicals discontinued production of its Dylark® SMA engineering resins, important materials for dashboard carriers and other car components. "Polyscope had the material expertise, and we assisted them with their activities to fine-tune the material so it could meet the requirements of the automotive market" Geissler says. Intertek performed physical and chemical analyses such as shrinkage and impact resistance testing, which helped Polyscope achieve the properties it required from the material. For example, a carrier must withstand external impact and achieve optimal assembly characteristics.

"In the automotive business, sustainability, comfort, and design are driving innovation," Geissler says. "Cars need to be lightweight to reduce carbon emissions." It is important to investigate the weight and performance characteristics of new materials to make sure they perform the same as, or even better than, currently used materials. As the application of new automotive materials—such as composites—grows, Intertek is extending its laboratory, processing, and knowledge capabilities to study these materials. "These innovative materials are

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stronger and more resistant to impact, so specialized equipment and expertise are needed for characterization," Geissler says.

A processed real-size automotive component for material characterization. Intertek.

Failure Analysis

When a problem with a plastic part arises—whether experienced by the consumer or noticed after a part is molded—it is important to analyze why the failure occurred. Failure analysis can also be used to anticipate problems or to find out why prototype parts may have failed.

The Madison Group in Madison, Wisconsin, USA, provides failure analysis for plastics. Engineering manager Jeffrey A. Jansen says that companies sometimes think they don't have the time or resources for failure analysis, but a scientific approach to addressing a problem is more cost- and time-effective than guessing at the problem and trying solutions that might not work. During an analysis, engineers from the Madison Group aim to find out both how and why a failure occurred. In general, five factors are involved in failure: material, processing, design, installation, and service conditions.

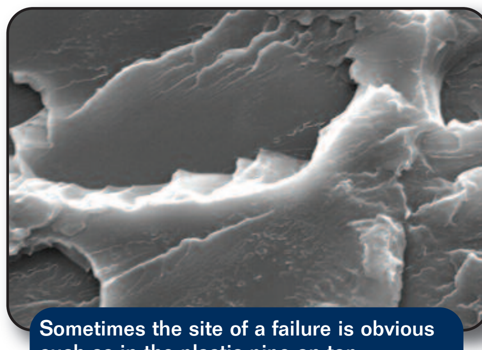
The company begins an analysis by gathering background information on the failed component, such as how the part was made and its service history. They then perform a visual examination, checking to see if the failure is happening in the same place on all the parts or whether discoloration is present, for example. Microscopic analysis is used to examine the fracture surface, which shows how and where a crack began and where it spread.

Analytical characterization of the polymer's molecular weight, composition, and mechanical properties is required to understand why the failures occurred. "Ideally we can compare the characteristics of a failed part to a control that didn't fail to show if some type of degradation, contamination, or material anomaly was involved," Jansen says.

All this information is used to piece together the primary cause of the failure as well as other contributing factors. "It is usually not just one factor; usually two or three things overlap," Jansen says, "particularly if only 0.1 percent of the parts made are failing." For example, consider a part with sharp corners and notches that focus forces. During molding, molecular degradation occurs that compromises the material. Then during use, it undergoes strong impact. The failure wouldn't have happened if any of those things weren't present—the sharp corners and notches that concentrate the force, the compromised material, or the strong impact during use.

Viscoelastic Measurements

Timothy A. Cassell, national sales manager for rheology and solid surface analysis at Anton Paar USA,



Sometimes the site of a failure is obvious such as in the plastic pipe on top. However, a closer look with microscopy (above) can reveal where a crack began. The Madison Group.

says there is a wider range of additives on the market today for use in plastics. "With each additive it is important to characterize the material. The goal is to understand how the product will behave under manufacturing conditions and under

The MCR from Anton Paar USA characterizes a polymer's viscoelastic properties.

use." The Modular Compact Rheometer (MCR) from Anton Paar can be used to measure the properties of unmodified as well as modified samples to identify the changes.

The MCR characterizes a polymer's viscoelastic properties, information that can be used to understand how the material behaves under application and in storage conditions as well as the inherent structure of the material. The rheometer also allows the addition of environmental accessories for a variety of application-specific measurements. "Versatility is important; people want one instrument that can do multiple types of testing and handle multiple types of samples," says Cassell.

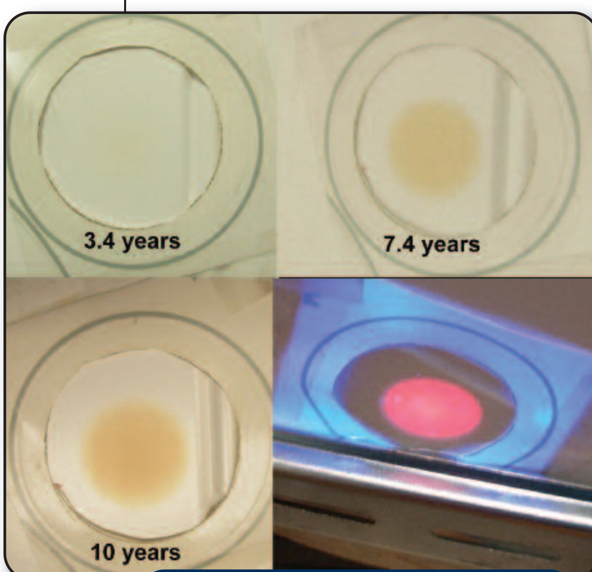
With the MCR, a user can measure the extensional and torsional properties of solid samples for dynamic mechanical thermal analysis. The addition of light-scattering and optical viewing modules can allow study of microstructures and the molecular or structural changes that result from additives. Cassell says that there continues to be growth in application of plastics as lower-cost and lighter-weight alternatives to metals. When plastic is used for moving parts in assemblies, measuring the friction factor for the part is important. The company's tribology module allows the user to analyze how a plastic part would wear over time.

Weathering Analysis

Developing a new formulation or changing an existing resin, additive, or color for a plastic part used outdoors requires assessing how well the plastic will weather over time. In the case of a change of manufacturing location or a change in raw-material source, a company may wish to revalidate the UV endurance of the product. In other cases, companies may use weathering testing to troubleshoot product failures. As one example, when a seal on a part failed, the customer speculated that sunlight had changed the plastic's material properties. Weathering testing showed that although the color did not change, the surface changed from glossy to matte, and that there was a strong possibility that the change in surface texture also affected the seal.

Solar Light Company is a U.S. manufacturer of precision UV light sources, solar simulators, radiometers, sensors, and detectors for several industries. It also offers testing services and has seen increasing requests for these services over the past few years. Filters in the company's solar simulator tune the light source to simulate only the UV portion of the spectrum, which has the advantage of minimizing the temperature increase of the sample to only a few degrees above ambient temperature. Because Solar Light's instrument sends light through a lens, it can amplify irradiance by reducing the area of the sample that is exposed. "Using a 57-mm-diameter circle of light, we can produce six years of exposure in one year of accelerated testing time," explains Drew Hmiel, a physicist at the company. "However, by reducing the circle to a 20-mm diameter we can further accelerate six years of exposure to only one month of testing."

Solar Light is currently correlating accelerated laboratory results to outdoor exposure for a wide range of polymers. The company measures color and appearance changes of weathered samples using colorimetry as well as reflectance and transmission spectrophotometry. UV transmittance can be measured as well. The company does not offer tensile testing, although customers can do this testing elsewhere if they desire. Hmiel notes that simulation



A plastic building product underwent an exposure test for 10 years. The lower-right photo illustrates the exposure arrangement. Solar Light.

of indoor exposure of plastics is increasingly requested. For example, exposing a sample behind glass simulates sunlight coming through a window. Using specific fluorescent lamps to generate UVA light simulates exposure to indoor fluorescent lighting, such as in a retail display case. Solar Light is currently working on accelerating this type of exposure and correlating it to actual "shelf-time."

Thin Film Analysis

Polymer thin films, typically less than ~500 nm thick, are used as protective coatings on windshields, helmets, and other products. The optical and mechanical properties of these films play an important role in the overall lifetime of the product, and these properties can change at lower temperatures than they would in the bulk material. Cyclical temperature changes that oscillate from below to above the glass transition temperature of the polymer can cause transparent films to become "fuzzy" and flexible films to become brittle, for example. Currently, most reliable analysis methods don't have the resolution necessary to accurately measure the true behavior of polymer thin films at the nanoscale.

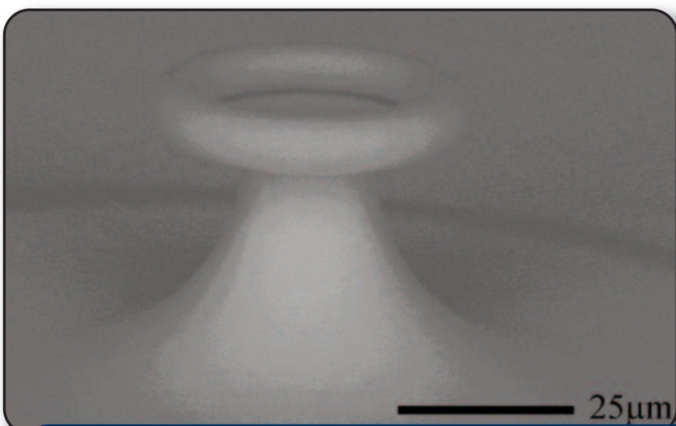
Researchers from the University of Southern California (USA) have developed a method to characterize polymer thin films using hybrid optical microcavity resonators.[1] These sensors operate using evanescent field whispering gallery mode resonant cavities. Under laser illumination, the circulating optical field interacts with the microcavity, and any changes in the material cause a detectable shift in the resonant wavelength of the device. By coating a microcavity with a polymer film, the researchers created a sensor that could detect the optical properties and mechanical behaviors of a polymer film. The method is nondestructive, which is important for measuring the effect of cyclic temperature changes on a polymer thin film.

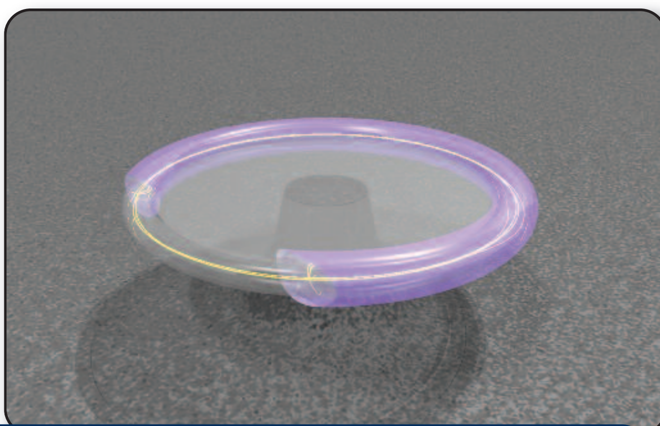
The researchers tested the technique with polystyrene. "We specifically chose this polymer because it is very commonly used in foams, food containers, and other common goods, and it has a moderate glass transition temperature," says Dr. Andrea M. Armani, who led the research team. "We performed the measurement several times, verifying that it is nondestructive, and showed that the sensitivity to changes in the optical properties of the device was improved by nearly three orders of magnitude over alternate methods."

The technique is ideally suited for thin films and cannot be used on thick samples because the illuminating light interacts with only the first ~100 to 150 nm of the film depth. The method is currently useful only in a laboratory setting, but the researchers are working on alterations that might make it more useful in industrial settings.

Developing New Materials

Researchers at the U.S. Oak Ridge National Laboratory (ORNL) and the Technische Universität





A scanning electron microscope image (left) shows the sensor device, which is approximately 25 microns in diameter. An artist's rendering (right) shows the laser confined within the sensor device interacting with a polymer thin film. This interaction enables detection of changes in the film's properties. University of Southern California.

München (Germany) are using the Magnetism Reflectometer at ORNL's Spallation Neutron Source to analyze new functional nanocomposite thin films they are developing.[2] As more materials incorporate nanoparticles, new techniques are needed to analyze their structures on the nanoscale.

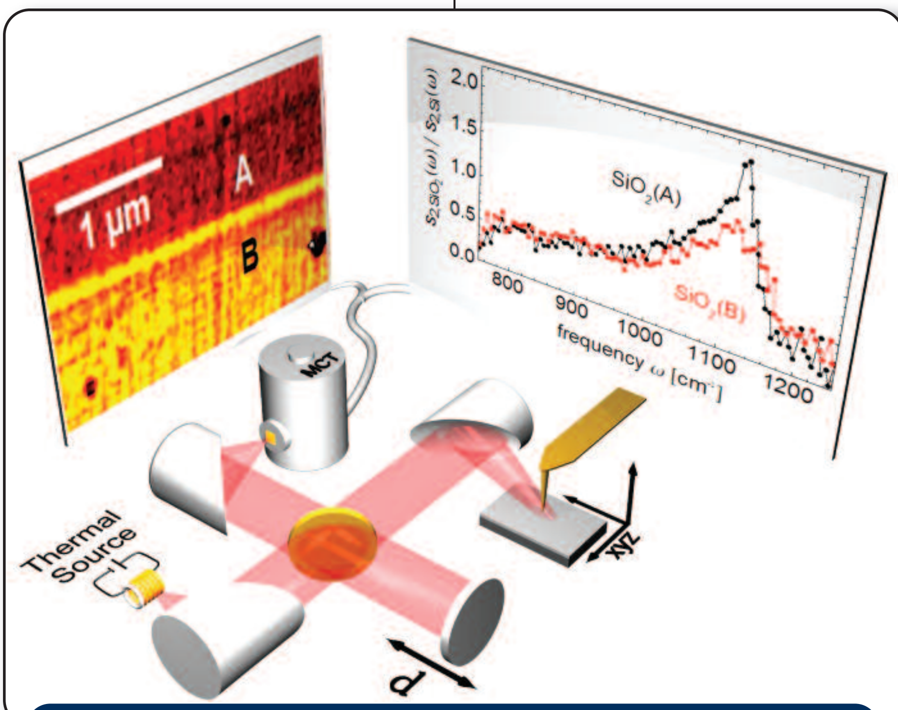
The thin films combine Fe_3O_4 nanoparticles with matrices of the diblock copolymer poly(styrene-*block*-n-butyl methacrylate), P(Sd*b*-nBMA). The components self-assemble into a well-ordered structure that remains stable with up to 10% nanoparticle content. The challenge in making these nanocomposite thin films is that well-controlled placement of nanoparticles in the diblock copolymers can be difficult. Big nanoparticle clusters can form, and sometimes the morphology of the diblock copolymer matrix gradually disappears. The researchers used asymmetric diblock copolymers, which have two unequal block lengths. They fabricated and studied composite thin films of asymmetric P(Sd*b*- BMA) diblock copolymer and large magnetite Fe_3O_4 nanoparticles (10 nm average diameter). Their samples contained 5% and 10% volume fractions of nanoparticles.

High-contrast neutron scattering performed with the Magnetism Reflectometer showed that before annealing, the internal structure of the films was not uniform. Both with and without nanoparticles, there was a partial phase separation in the asymmetric films. After annealing, the neutron reflectometry showed that a combined, well-organized two-layer structure had become imprinted in the thin films. Furthermore, the structure remained stable after the incorporation of the nanoparticles. "The studies demonstrate that the self-assembly of such materials is strongly influenced by the energies generated between the interfacing materials and the surface energies of the blocks and substrate," says Valeria Lauter, a member of the research team.

Analyzing Nanomaterials

Researchers from Neaspec GmbH in Martinsried, Germany, recently developed an infrared near-field microscopy platform that can analyze nanomaterials with a spatial resolution of about 10 nm. However, analysis using this platform is usually performed with a tunable infrared laser as the light source, and the spectral coverage of laser-based light sources is still limited. Now, researchers from the Basque Nanoscience Research Center, CIC nanoGUNE (San Sebastian, Spain), and Neaspec GmbH have developed a novel near-field spectroscopy platform with a thermal source.[3] "The instrument that we call nano-FTIR allows the recording of broadband infrared spectra with nanoscale spatial resolution," says Rainer Hillenbrand, leader of the Nanooptics group at nanoGUNE. The new setup could be used to analyze polymer nanocomposites with 100 to 1000 times better resolution than conventional Fourier-transform infrared (FTIR) spectroscopy.

Because the technique is based on atomic force microscopy (AFM), it simultaneously provides topographic information about the sample's surface, says Hillenbrand. As the sharp metallic AFM scans a sample surface, it is illuminated with the infrared light from a thermal source. Acting like an antenna, the tip converts the incident light into a nanoscale infrared spot at the tip apex. By analyzing the scattered infrared light with a specially designed FTIR spectrometer, the researchers can record infrared spectra from ultra-small sample volumes.



For infrared nanospectroscopy with a thermal source, an atomic force microscope tip probes a sample. The tip is illuminated with the broadband infrared radiation from a thermal source and the backscattered light is analyzed with a Fourier-transform spectrometer, yielding local infrared spectra with a spatial resolution better than 100 nm. The displayed graph shows local infrared spectra of differently processed oxides in an industrial semiconductor device. Copyright F. Huth, CIC nanoGUNE.

"Our technique allows for recording spectra in the near-to-far-infrared spectral range. These spectra can be used to chemically identify the composite components by their specific infrared 'fingerprint' spectrum," Hillenbrand explains.

They expect that polymer samples will have weaker signals than the samples of silicon and oxides they have studied so far. The current version of the instrument could be used for chemical mapping of thin polymer films with a resolution better than 100 nm and an imaging time of a few hours. "By improving the signal-to-noise in the spectra with the use of more powerful thermal sources (e.g. operating at increased temperature) and optimized near-field probes, we aim on rapid spectroscopic imaging with a resolution in the 10-nm range," says Hillenbrand. With such improvements, the researchers think that the instrument will provide a way to identify and analyze polymers with nanoscale spatial resolution, broad spectral coverage, and a light source that is relatively simple and inexpensive.

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