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Characterization of Plastics in Failure Analysis

Jeffrey A. Jansen, The Madison Group

THE ULTIMATE OBJECTIVE of a failure analysis is to ascertain the mode and the cause of the failure, regardless of the material from which the part was fabricated. The investigation is performed in generally the same manner, whether the failed component was produced from metal or plastic or a combination of these materials. Thus, the same typical steps are required to conduct a comprehensive failure investigation, and these are outlined in Fig. 1. Conceptually, the failure analysis process is analogous to putting together a jigsaw puzzle. A failure analysis requires assembling bits of information into a coherent and accurate portrayal of how and why the part failed. Reaching the objectives of the plastic failure analysis—namely, the determination of the mode and cause of the failure or, expressed alternatively, evaluating how the part failed and why it failed—requires a scientific approach and broad background knowledge of polymeric materials.

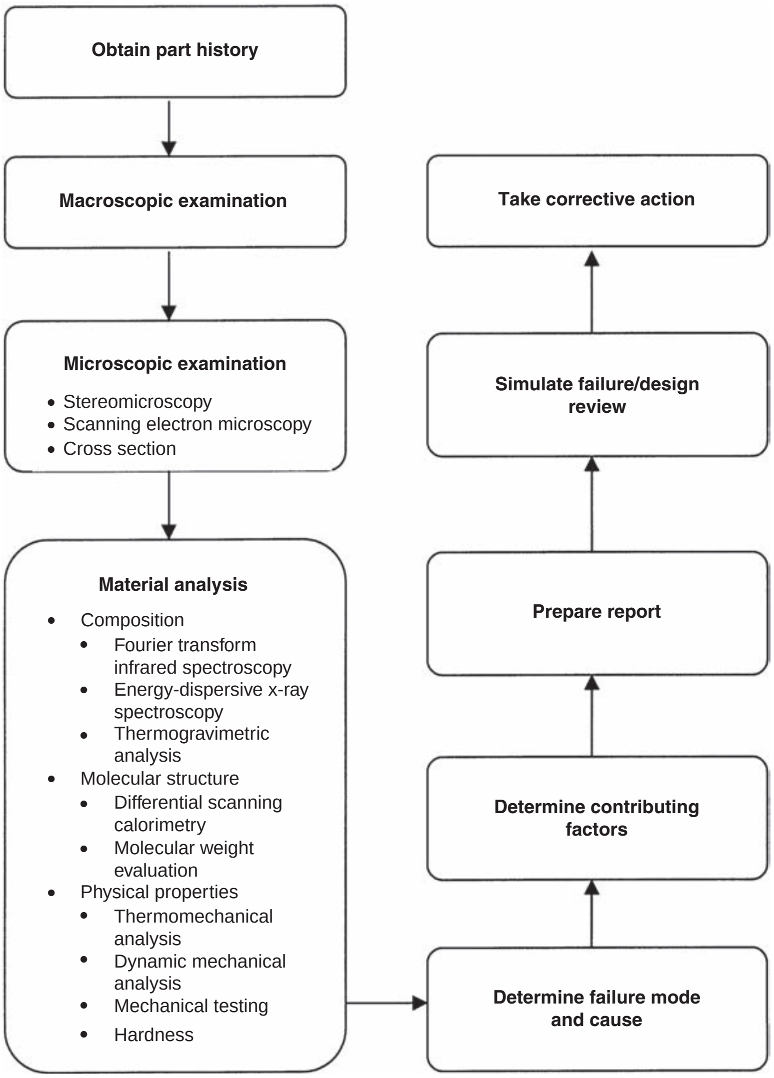


Fig. 1 Steps for performing failure analysis. The steps are the same regardless of the material.

Failure within plastic components can occur in several different ways, including esthetic alteration, deformation/distortion, degradation, wear, and fracture. In the case of failure involving fracture, there are a number of common plastic failure mechanisms, such as ductile overload, impact, creep rupture, environmental stress cracking, and fatigue. The determination of the fracture failure mode involves identifying the crack-initiation mechanism and the propagation mode. This is usually ascertained using visual-based techniques such as stereomicroscopy, scanning electron microscopy, and the preparation of mounted cross sections. Assessing the mode of the failure is often not as difficult as establishing why the part failed. Evaluating why the part failed, regardless of the type of failure, usually requires analytical testing beyond the visual-based techniques. In many cases, a single cause cannot be identified because multiple integrated factors may have contributed to the failure. All the factors that affect the performance of a plastic component can be classified into one of four categories: material, design, processing/manufacturing, and service conditions/environment (Ref 1). These factors do not act independently on the component but instead act in concert to determine the performance properties of a plastic component. This is represented graphically in Fig. 2 (Ref 1).

The principal differences between how failure analyses are performed on metal and plastic materials center primarily on the techniques used to evaluate the composition and structure of the material. Unlike metals, polymers have a molecular structure that includes characteristics such as polymer functional groups, molecular weight, molecular weight distribution, crystallinity, tacticity, molecular orientation, and fusion. These characteristics have a significant impact on the properties of the molded article. Additionally, plastic resins are formulated with additives such as reinforcing fillers, plasticizers, colorants, antidegradants, and process aids. It is this combination of molecular structure and complex formulation that requires specialized testing (Ref 2). While the chemical composition of a failed metal component can often be evaluated using a single spectroscopic technique, a similar determination requires multiple analytical approaches for a part produced from a plastic resin.

This article reviews those analytical techniques that are most commonly used in plastic component failure analysis. This description of the techniques is not designed to be a comprehensive review and tutorial, but instead it is intended to familiarize the reader with the general principles and benefits of the methodologies. The descriptions of the analytical techniques are supplemented by a series of case studies to illustrate the significance of each method. The case studies also include pertinent visual examination results and the corresponding images that aided in the characterization of the failures.

Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a nondestructive microanalytical spectroscopic technique that involves the study of molecular vibrations (Ref 2). The analysis results provide principally qualitative, but also limited quantitative, information regarding the composition and state of the material evaluated. Fourier transform infrared spectroscopy uses infrared energy to produce vibrations within the molecular bonds that constitute the material being evaluated. Vibrational states of varying energy levels exist in molecules. Transition from one vibrational state to another is related to absorption or emission of electromagnetic radiation (Ref 3). These vibrations occur at characteristic frequencies, which correspond to functional groups within the molecular structure of the sample. Fourier transform infrared spectroscopy produces a unique spectrum, which is comparable to the fingerprint of the material. It is the principal analytical technique used to qualitatively identify polymeric materials. It is commonly the first analytical technique used in a plastics failure analysis.

Method

Several different sampling techniques, all involving either transmission or reflection of the infrared energy, can be used to analyze the sample material. This allows the evaluation of materials in all forms, including hard solids, powders, liquids, and gases. Depending on the spectrometer and the corresponding accessories, most samples can be analyzed without significant preparation or alteration. In the analysis of polymeric materials, the most common sampling techniques are transmittance, reflectance, and attenuated total reflectance. Additionally, a microscope can be interfaced with the spectrometer to focus the infrared beam and allow the analysis of samples down to 10 μm. Regardless of the sampling technique, the beam of infrared energy is passed through or reflected off the sample and directed to a detector. The obtained spectrum shows frequencies that the material has absorbed and frequencies that have been transmitted, as illustrated in Fig. 3.

Results

The results generated through FTIR analysis are referred to as an infrared spectrum. The spectrum graphically illustrates the relative intensity of the energy absorbed on the *y*-axis versus the frequency of the energy on the *x*-axis. The frequency of the energy can be represented directly in microns (μm) or, more popularly, as reciprocal centimeters (cm^{-1}) referred to as wave numbers. The spectrum can be interpreted manually or, more commonly, compared to voluminous library references with the aid of a computer. The discrete spectral features present in an FTIR spectrum are known as absorption bands, and they correlate to functional groups within the molecular structure of the sample.

Uses of FTIR in Failure Analysis

Material Identification

Possibly the most important use of FTIR in failure analysis is the identification of the base polymer that comprises the sample. Determining the composition of the failed component is an essential part of the investigation. Because different polymers have a wide variation in their physical, mechanical, chemical resistance, and aging properties, the use of the wrong resin can yield detrimental results in many applications. Fourier transform infrared spectroscopy is well suited for the identification of polymers that have different molecular structures, and this is illustrated in Fig. 4. Confirming that the failed article was produced from the specified material is a primary consideration of the failure analyst in assessing the cause of the failure. Thus, FTIR is often the first analytical test performed during a plastic failure analysis. The use of FTIR in characterizing the composition of the plastic-resin base polymer is illustrated in Examples 1, 4, 7, and 9 in the article "Characterization of Plastics in Failure Analysis" in *Characterization*

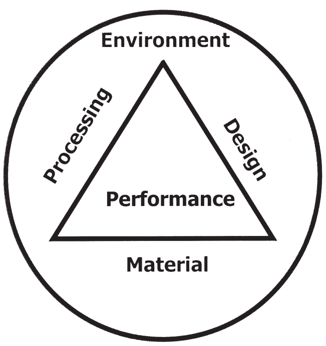


Fig. 2 Graphical representation of the four factors influencing plastic part performance

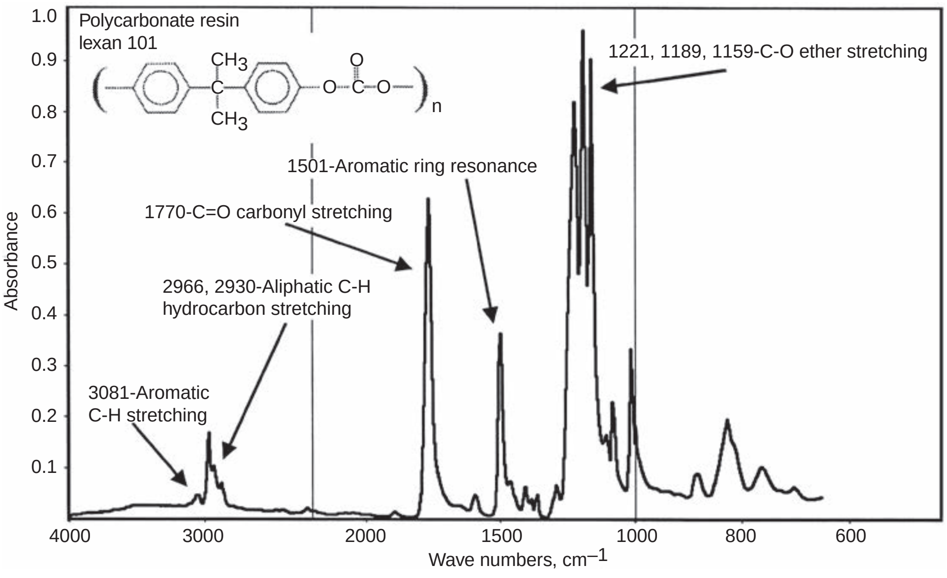


Fig. 3 Typical Fourier transform infrared spectroscopy spectrum illustrating the correlation between structure and absorption bands

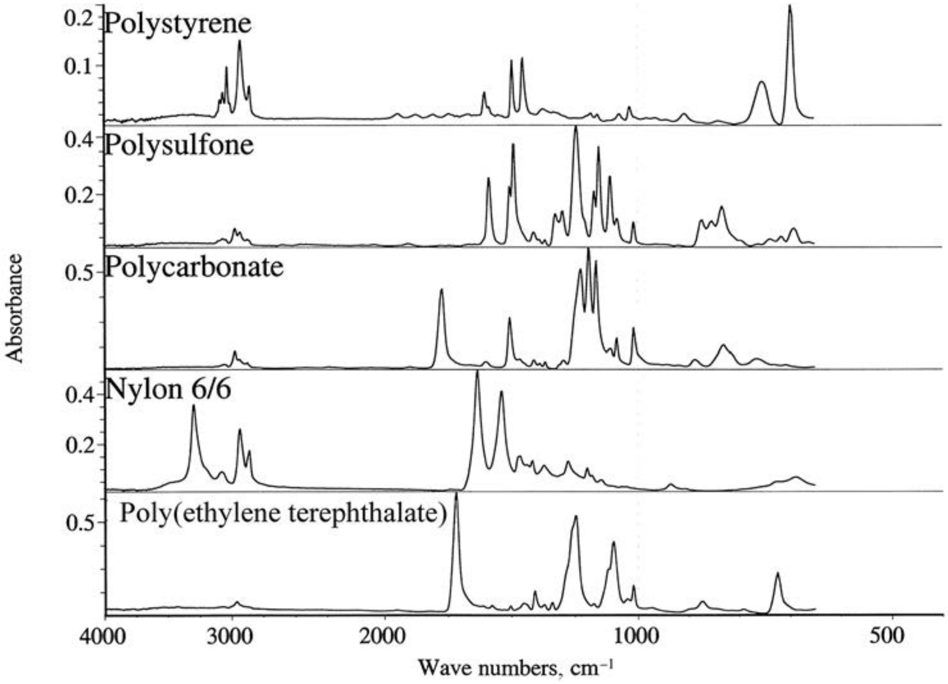


Fig. 4 Fourier transform infrared spectroscopy spectral comparison showing distinct differences between the results obtained on various plastic materials

and Failure Analysis of Plastics, ASM International, 2003 (Ref 4). One area in which FTIR is inadequate is differentiating polymers that have similar molecular structures, such as the members of the nylon family, between poly (ethylene terephthalate) and poly(butylene terephthalate), and between polyacetal homopolymers and copolymers. In these cases, other techniques, such as differential scanning calorimetry, must be used to augment the FTIR results.

Aside from the determination of the base polymer, FTIR can be helpful in characterizing other formulation constituents. Fourier transform infrared spectroscopic analysis can provide information regarding the presence of additives and filler materials. Due to the nonlinearity of infrared absorptivity of different molecular bonds, it is not possible to accurately state minimum concentration detection limits. However, it is generally considered that materials that are present within a compounded plastic resin at concentrations below 1% may be below the detection limits of the spectrometer. Given this restriction, it is likely that most major formulation additives such as plasticizers can be characterized, while low-level additives, including antioxidants, may go undetected. Given that FTIR is principally used for the analysis of organic materials, its use in the evaluation of inorganic filler materials is somewhat limited. However, some commonly used fillers—such as calcium carbonate, barium sulfate, and talc—produce unique, identifiable absorption spectra. Example 6 in Ref 4 and Example 5 in this article show the analysis of plastic-resin formulation constituents.

Another application related to material identification is the comparative qualitative assessment of copolymers and blends. While FTIR is not practical for quantifying the polymer constituent in a blend or copolymer, it is highly effective for comparing two materials to determine if they are similar or distinctly different, for example, comparing failed and reference parts to determine if they were molded from polycarbonate/poly(butylene terephthalate) (PC + PBT) resins having similar relative levels of PC and PBT. This application of FTIR is illustrated in Example 1 in this article.

Contamination

Similar to its ability to identify plastic formulation constituents, FTIR is extremely useful in the determination of contaminant materials within the failed part material. The presence of contamination certainly can have a deleterious impact on the properties of the molded component. Through the electronic manipulation of the obtained FTIR results, including spectral subtraction, extraneous absorption bands that are not attributed to the base resin can be used to characterize contaminant materials. Fourier transform infrared spectroscopy is useful in the identification of contaminant material, whether it is mixed homogeneously into the resin or present as a discrete inclusion. The role of FTIR in the identification of contaminants is illustrated in Examples 3 and 8 in Ref 4.

Degradation

Fourier transform infrared spectroscopy is a valuable tool in assessing a failed component material for degradation such as oxidation and hydrolysis. Molecular degradation, often involving molecular weight reduction, has a significant detrimental impact on the mechanical and physical properties of a plastic material. This degradation can result from several stages in the material life, including resin compounding, molding, and service. As a polymeric material is degraded on a molecular level, the bonds comprising the material are altered. Fourier transform infrared spectroscopy detects these changes in the molecular structure. While FTIR cannot readily quantify the level of degradation, it is useful in assessing whether the material has been degraded and in determining the mechanism of degradation. Specifically, several spectral bands and the corresponding molecular structure can be ascertained. These include carbonyl band, particularly carboxylic acid, formation representing oxidation; vinylidene group formation as an indication of thermal oxidation; the abstraction of bands associated with unsaturation resulting from thermal degradation; vinylene functionality for photooxidation; and hydroxyl group formation indicating hydrolysis (Ref 5). Case studies showing the effectiveness of FTIR in assessing molecular degradation are presented in Examples 1, 13, and 15 in Ref 4.

Chemical Contact

Similar to the application of FTIR in addressing polymeric degradation, the technique is also useful in evaluating the failed sample material for chemical contact. Plastic materials can be affected in several ways through contact with chemical agents. Depending on the polymer/chemical combination, solvation, plasticization, additive abstraction, chemical attack, or environmental stress cracking can occur. In the case of property alteration through solvation or plasticization, FTIR can be helpful in identifying the absorbed chemicals. Because these chemicals are present within the failed plastic material, the likelihood of distinguishing the agents is high. Based on the observed spectral changes, mechanisms and chemical agents producing chemical attack—including nitration, sulfonation, hydrolysis, and aminolysis—can be detected (Ref 5). Environmental stress cracking, the synergistic effect of tensile stress while in contact with a chemical agent, is one of the leading causes of plastic failure. The chemical agent that is responsible for the cracking may be identified using FTIR. However, given that such materials are often volatile organic solvents, the chemical may not be present within the sample at the time of the analysis. Examples 2, 9, and 14 in Ref 4 illustrate the identification of chemicals that had been in contact with a failed plastic component.

Energy-Dispersive X-Ray Spectroscopy

Energy-dispersive x-ray spectroscopy (EDS) is a nondestructive chemical microanalytical spectroscopic technique used for the elemental analysis or chemical characterization of a material. The analysis results are qualitative and semiquantitative, allowing both the identification of elements present as well as the determination of their relative concentration. The technique uses x-rays emitted by the matter in response to being hit with charged particles, which is characteristic of the atomic structure of an element. Given the elemental nature of the results, EDS has utility for the analysis of inorganic materials, and it is also useful in the evaluation of organic constituents.

Method

Energy-dispersive x-ray spectroscopy analyses are typically performed in conjunction with scanning electron microscopy (SEM). The SEM allows the selection of particular areas for analysis across a wide range of magnification. Essentially, if an area of interest can be seen in the SEM, it can be analyzed via EDS. Because the sample is placed in the SEM for analysis, the samples must be nonvolatile. As such, samples are limited to hard solids, powders, and particulate matter. The specimen to be analyzed can be stand-alone or a localized area on a larger nonhomogeneous sample. Minimal sample preparation is required for EDS analysis.

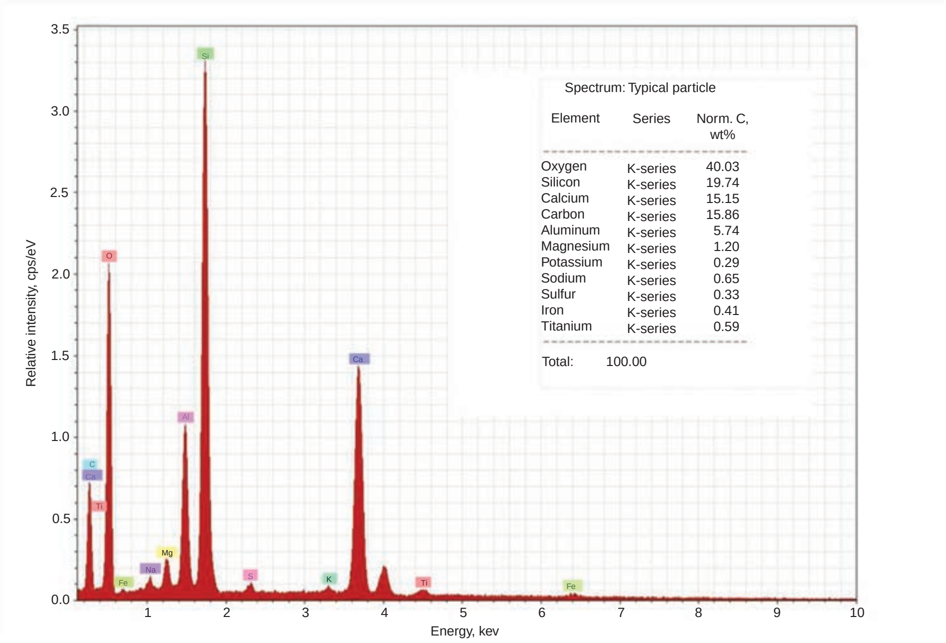
Results

The results generated through EDS analysis are referred to as an EDS spectrum. The spectrum graphically illustrates the relative intensity on the *y*-axis versus the energy in kiloelectron volts (keV) on the *x*-axis, as illustrated in Fig. 5. The obtained results are evaluated semiquantitatively by comparison through the instrument computer to internal standards.

Uses of EDS in Failure Analysis

Identification of Contaminants or Inclusions on or within a Failed Part

A very important application of EDS in the failure analysis of plastics is the characterization of the elemental profile of contaminants within a failed component. Just as FTIR is useful for the identification of organic-based contamination, EDS provides a method for the unification of inorganic contamination. Often, a comparison of the elemental profile of the base material with an inhomogeneity will elucidate the composition of the included material. This can also provide information on whether the inclusion is a foreign particle or an undisbursed formulation constituent. Example 2 in this article shows the use of EDS.



Spectrum: Typical particle

Element	Series	Norm. C, wt%
Oxygen	K-series	40.03
Silicon	K-series	19.74
Calcium	K-series	15.15
Carbon	K-series	15.86
Aluminum	K-series	5.74
Magnesium	K-series	1.20
Potassium	K-series	0.29
Sodium	K-series	0.65
Sulfur	K-series	0.33
Iron	K-series	0.41
Titanium	K-series	0.59
Total:	100.00	

Fig. 5 Typical energy-dispersive x-ray spectroscopy spectrum showing absorption features indicative of unique elements and the quantitation of those elements. cps, counts per second

Characterization of Inorganic Fillers

One of the most common applications of EDS analysis of plastics is the characterization of inorganic fillers. Plastics are routinely formulated with filler materials such as calcium carbonate, talc, aluminum silicate, and barium sulfate. All these fillers have a unique elemental profile. Fillers may be added for performance reasons or to simply lower the cost of the resin. Energy-dispersive x-ray spectroscopy can identify these fillers, which may not be identifiable through FTIR analysis. The fillers can be analyzed directly within the molded sample or isolated, such as the residue remaining after thermogravimetric analysis.

Elemental Profile of Formulation Additives

Another application of EDS in plastics failure analysis is the identification of formulation additives. For example, many flame-retardant packages are based on brominated organic compounds and antimony oxide. As such, the detection of bromine and antimony can indicate that the material is formulated with a flame retardant. Comparison of the relative levels of bromine can also be used to understand whether one sample contains more of the flame retardant than another. Another example is the identification of pigment materials. The detection of titanium is often associated with titanium dioxide. Many blue pigments are based on copper compounds. As with the identification of fillers, EDS analysis can provide insight into the plastic formulation. The analysis of additives within a plastic formulation is illustrated in Example 5 in this article.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a thermoanalytical technique in which heat flow is measured as a function of temperature and/or time. The obtained measurements provide quantitative and qualitative information regarding physical and chemical changes involving exothermic and endothermic processes, or changes in the heat capacity, in the sample material (Ref 2). Differential scanning calorimetry monitors the difference in heat flow between a sample and a reference as the material is heated or cooled (Ref 6). The technique is used to evaluate thermal transitions within a material. Such transitions include glass transitions, melting, evaporation, crystallization, solidification, cross linking, chemical reactions, and decomposition. A typical DSC result is presented in Fig. 6. Differential scanning calorimetry uses the temperature difference between a sample material and a reference as the raw data. In the application, the instrumentation converts the temperature difference into a measurement of the energy per unit mass associated with the transition that caused the temperature change. Any transition in a material that involves a change in the heat content of the material can be evaluated by DSC (Ref 6), the limitation being that commercially available equipment may not be able to detect transitions within materials that are present at concentrations below 5% (Ref 5).

Method

Sample preparation for DSC analysis includes placing the specimen within a metal pan. The pan can be open, crimped, or sealed hermetically, depending on the experiment. A reference is used, either an empty pan of the same type or an inert material having the same weight as the sample. The most commonly used metal pan material is aluminum; however, pans made of copper and gold are used for special applications. The sample and reference pans rest on thermoelectric disc platforms, and thermocouples are used to measure the differential heat flow (Ref 6). Specimen size typically ranges between 1 and 10 mg, although this can vary, depending on the nature of the sample and the experiment. The normal operating temperature range for DSC testing is −180 to 700 °C (−290 to 1290 °F), with a standard heating rate of 10 °C/min (18 °F/min). A dynamic purge gas is used to flush the sample chamber. Nitrogen is the most commonly used purge gas, but helium, argon, air, and oxygen can also be used for specific purposes. Often, two consecutive heating runs are performed to evaluate a sample. A controlled cooling run is performed after the initial analysis to erase the heat history of the sample. The first heating run assesses the sample in the as-molded condition, while the second run evaluates the inherent properties of the material.

Results

The plotted results obtained during a DSC analysis are referred to as a thermogram. The thermogram shows the heat flow in energy units or energy per mass units on the *y*-axis as a function of either temperature or time on the *x*-axis. The transitions that the sample material undergoes appear as exothermic and endothermic changes in the heat flow. Endothermic transitions require heat to proceed, while exothermic transitions give off heat.

Uses of DSC in Failure Analysis

Melting Point and Crystallinity

The primary use of DSC in polymer analysis is the detection and quantification of the crystalline melting process. Because the crystalline state of a polymeric material is greatly affected by properties including stereoregularity of the chain and the molecular weight distribution as well as by processing and subsequent environmental exposure, this property is of considerable importance (Ref 6). The melting point (T_m) of a semicrystalline polymer is measured as the peak of the melting endotherm. A composite thermogram showing the melting transitions of several common plastic materials is presented in Fig. 7. The T_m is used as a means of identification, particularly when other techniques such as FTIR cannot distinguish between materials that have similar structures.

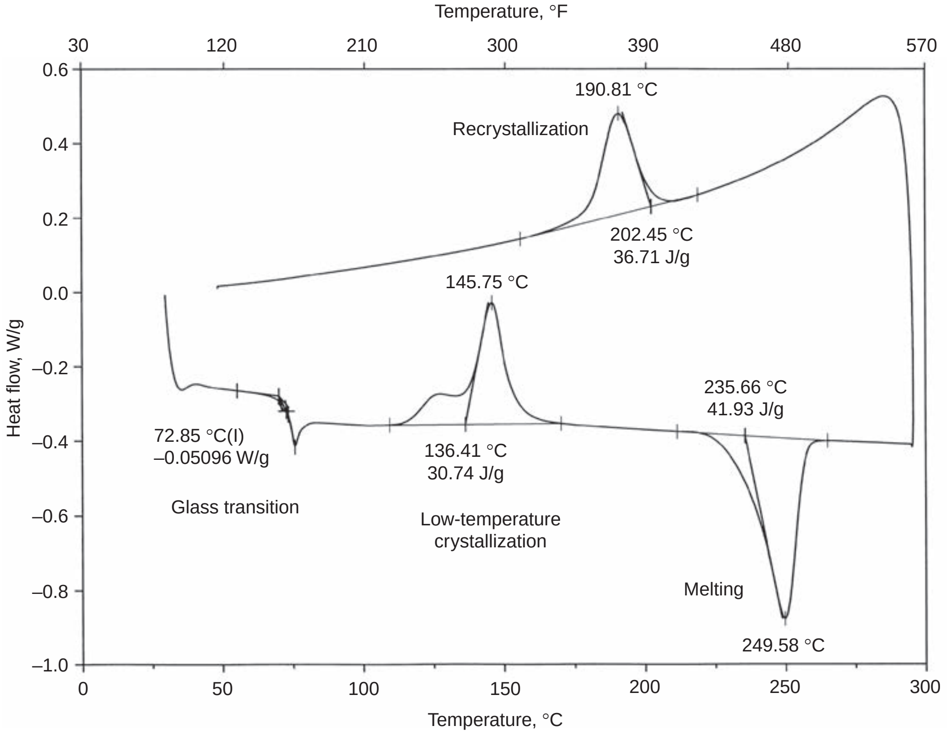


Fig. 6 Differential scanning calorimetry thermogram showing various transitions associated with polymeric materials. The "(I)" indicates that the numerical temperature was determined as the inflection point on the curve.

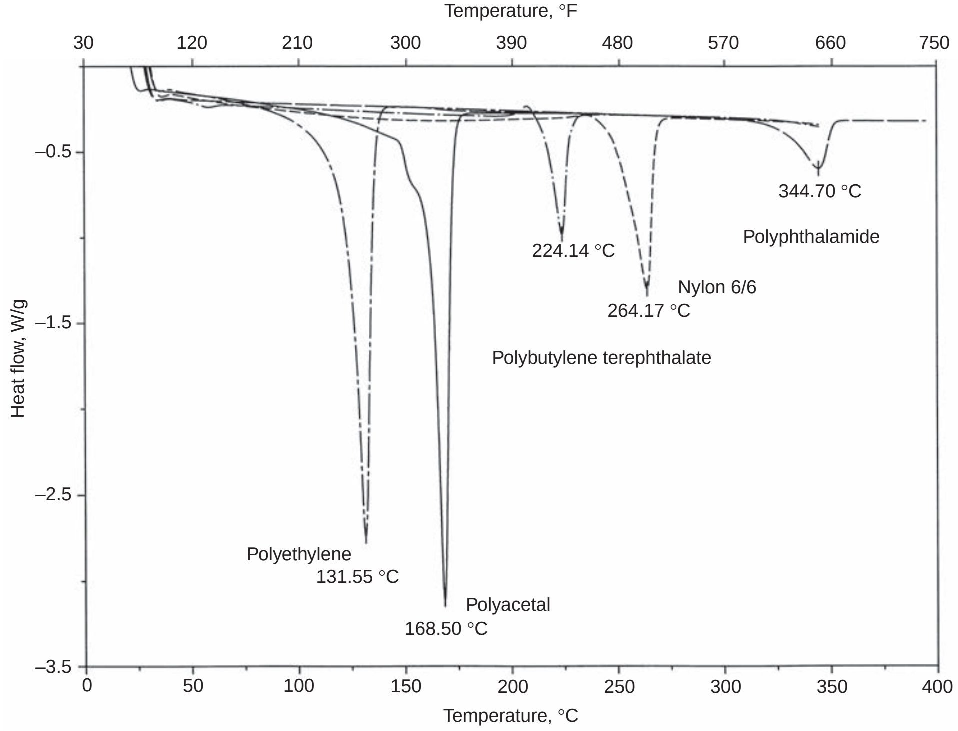


Fig. 7 Differential scanning calorimetry used to identify polymeric materials by determination of their melting point

This can be useful in identifying both the main resin and any contaminant materials. The material identification aspects of DSC are illustrated in Examples 4, 5, 7, 8, 10–12, and 15 in Ref 4. Additionally, Example 6 in this article shows how DSC identifies solvent-induced crystallization.

The heat of fusion represents the energy required to melt the material, and it is calculated as the area under the melting endotherm. The level of crystallinity is determined by comparing the actual as-molded heat of fusion with that of a 100% crystalline sample. The level of crystallinity that a material has reached during the molding process can be practically assessed by comparing the heat of fusion obtained during an initial analysis of the sample with the results generated during the second run, after slow cooling. The level of crystallinity is important because it impacts the mechanical, physical, and chemical resistance properties of the molded article. In general, rapid or quench cooling results in a lower crystalline state. This is the result of the formation of frozen-in amorphous regions within the preferentially crystalline structure. The magnitude of the heat of fusion obtained during the second heating run also provides insight into the inherent crystalline structure of the polymer. Higher heats of fusion correlate with increased levels of crystalline domains. Examples 11 and 12 in Ref 4 and Example 4 in this article show applications involving DSC as a means of assessing crystallinity.

Recrystallization, or the solidification of the polymer, is represented by the corresponding exothermic transition as the sample cools. The recrystallization temperature (T_c) is taken as the peak of the exotherm, and the heat of recrystallization is the area under the exotherm. Some slow-crystallizing materials, such as poly(ethylene terephthalate) and polyphthalamide, undergo low-temperature crystallization, representing the spontaneous rearrangement of amorphous segments within the polymer structure into a more orderly crystalline structure. Such exothermic transitions indicate that the as-molded material had been cooled relatively rapidly. Example 9 in Ref 4 shows how low-temperature crystallization was detected via DSC.

Glass Transition in Amorphous Plastics

Polymers that do not crystallize and semicrystalline materials that have a significant level of amorphous segments undergo a phase change referred to as a glass transition. The glass transition represents the reversible change from/to a viscous or rubbery condition to/from a hard and relatively brittle one (Ref 7). The glass transition is observed as a change in the heat capacity of the material. The glass transition temperature (T_g) can be defined in several ways but is most often taken as the inflection point of the step transition. A composite thermogram showing the glass transitions of several common plastic materials is presented in Fig. 8. The T_g of an amorphous resin has an important impact on the mechanical properties of the molded article because it represents softening of the material to the point that it loses load-bearing capabilities.

Aging, Degradation, and Thermal History

As noted by Sepe (Ref 6), "DSC techniques can be useful in detecting the chemical and morphological changes that accompany aging and degradation." Semicrystalline polymers may exhibit solid-state crystallization associated with aging that takes place at elevated temperatures. In some polymers, this may be evident as a second T_m at a reduced temperature. This second T_m represents the approximate temperature of the aging exposure. Other semicrystalline materials may show an increase in the heat of fusion and an increase in the T_m. The thermal aging of both the resin and the failed molded part is illustrated in Example 10 in Ref 4 and Example 2 in this article.

Amorphous resins exhibit changes in the glass transition as a result of aging. In particular, physical aging, which occurs through the progression toward thermodynamic equilibrium below the T_g, produces an apparent endothermic transition on completion of the glass transition.

Degradation and other nonreversible changes to the molecular structure of semicrystalline polymers can be detected as reduced values for the T_m, T_c, or heat of fusion. Similarly, degradation in amorphous resins can be observed as a reduction in the T_g or in the magnitude of the corresponding change in heat capacity. Instances of degradation detected by DSC are presented in Examples 7, 14, and 15 in Ref 4.

Further, the resistance of a polymer to oxidation can be evaluated via DSC by standard methods or experiments involving high-pressure oxygen or air exposure. Such evaluations usually measure the oxidative induction time or the temperature at which oxidation initiates under the experimental conditions. This can be used to compare two similar materials, to determine whether a plastic resin has undergone partial oxidation, or to comparatively assess the effectiveness of an antioxidant package. Example 6 in this article illustrates the use of DSC in evaluating oxidative resistance.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a thermal analysis technique that measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. The weight of the evaluated material can decrease due to volatilization or decomposition or increase because of gas absorption or chemical reaction. Thermogravimetric analysis

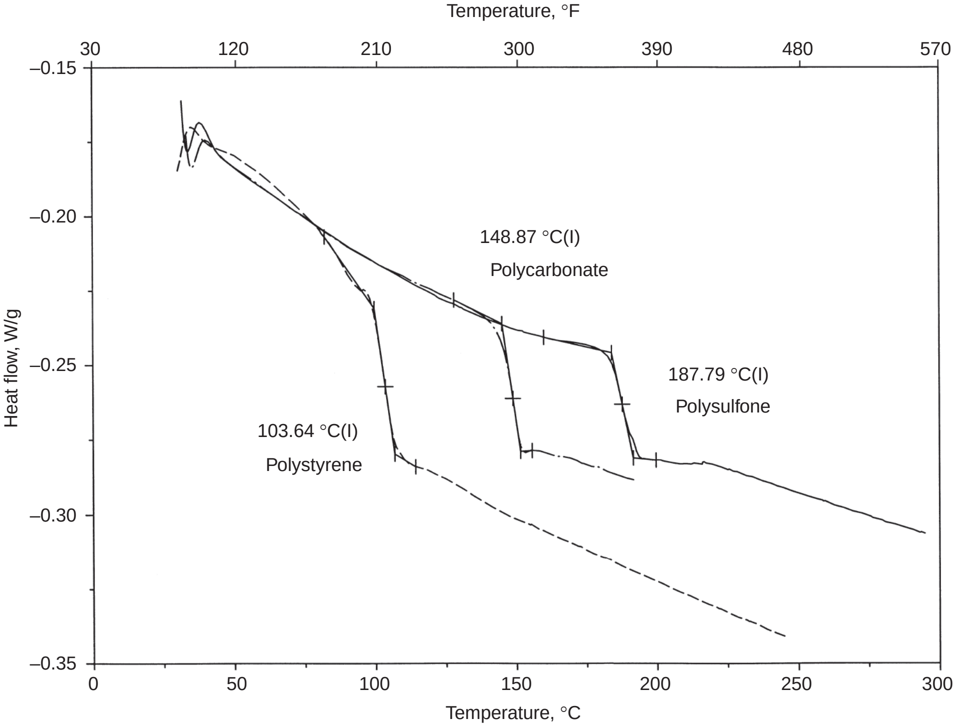


Fig. 8 Differential scanning calorimetry used to detect glass transitions within amorphous thermoplastic resins. The "(I)" indicates that the numerical temperature was determined as the inflection point on the curve.

can provide valuable information regarding the composition and thermal stability of polymeric materials. The obtained data can include the volatile content, inorganic filler content, glass-fiber level, carbon black content, the onset of thermal decomposition, and the volatility of additives such as antioxidants (Ref 5).

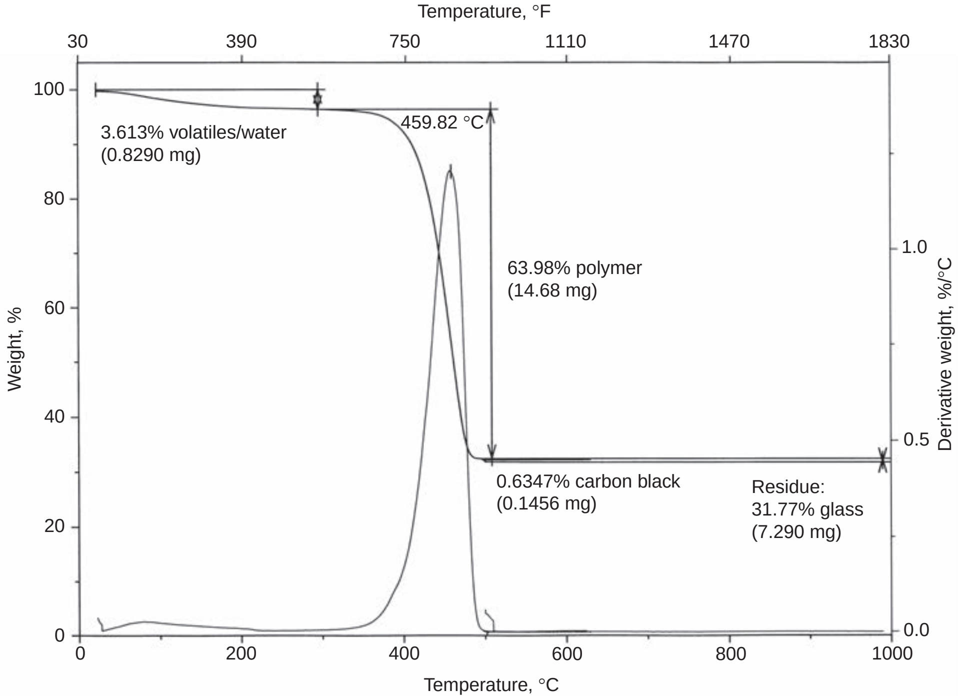


Fig. 9 Thermogravimetric analysis thermogram showing the weight-loss profile for a typical plastic resin

Method

Thermogravimetric analysis instruments consist of two primary components: a microbalance and a furnace. The sample is suspended from the balance while heated in conjunction with a thermal program. A ceramic or, more often, a platinum sample boat is used for the evaluation. As part of the TGA evaluation, the sample is usually heated from ambient room temperature to 1000 °C (1830 °F) in a dynamic gas purge of nitrogen, air, or a consecutive switch program. The composition of the purge gas can have a significant effect on the TGA results and, as such, must be properly controlled. The size of the sample evaluated usually ranges between 5 and 20 mg, but samples as large as 1000 mg are possible. Minimal sample preparation is required for TGA experiments.

Results

The graphical results obtained as part of a TGA evaluation are known as a thermogram. The TGA thermogram illustrates the sample weight, usually in percent of original weight, on the *y*-axis as a function of time or, more commonly, temperature on the *x*-axis. The weight-change transitions are often highlighted by plotting the corresponding derivative on an alternate *y*-axis.

Uses of TGA in Failure Analysis

Composition

Thermogravimetric analysis is a key analytical technique used to assess the composition of polymeric-based materials. The quantitative results obtained during a TGA evaluation directly complement the qualitative information produced by FTIR analysis. The relative loadings of various constituents within a plastic material—including polymers, plasticizers, additives, carbon black, mineral fillers, and glass reinforcement—can be determined. The assessment of a plastic resin composition is illustrated in Fig. 9. These data are important as part of a failure analysis in order to determine if the component was produced from the correct material. The weight-loss profile of the material is evaluated, and, ideally, the TGA results obtained on the material exhibit distinct, separate weight-loss steps. These steps are measured and associated with transitions within the evaluated material. A thorough knowledge of the decomposition and chemical reactions is required to properly interpret the obtained results. In most situations, however, distinct weight-loss steps are not obtained, and in these cases, the results are complemented by the corresponding derivative curve. Noncombustible material remaining at the conclusion of the TGA evaluation is often associated with inorganic fillers. Such residue is often further analyzed using EDS to evaluate its composition. The use of TGA in characterizing plastic composition is presented in Examples 8, 10, 12, and 15 in Ref 4 and in Example 5 in this article. Additionally, Example 11 in Ref 4 illustrates the quantification of an absorbed chemical within a failed plastic component.

Thermal Stability

Thermogravimetric analysis data can also be used to compare the thermal and oxidative stability of polymeric materials. The relative stability of polymeric materials can be evaluated by assessing the onset temperature of decomposition of the polymer. Quantitatively, these onset temperatures are not useful for comparing the long-term stability of fabricated products because the materials are generally molten at the beginning of decomposition (Ref 6). However, a comparison of the obtained TGA thermograms can provide insight into possible degradation of the failed component material. Example 6 in Ref 4 illustrates a comparison of the thermal stability of two polymeric materials, while Example 13 in Ref 4 and Example 2 in this article show the effects of molecular degradation. Degradation experiments involving polymeric materials can also provide information regarding the kinetics of decomposition. Such studies provide information regarding the projected lifetime of the material. These measurements, however, provide little information that is pertinent to a failure analysis.

Evolved Gas Analysis

Thermogravimetric analysis evaluations can also be performed whereby the evolved gaseous constituents are further analyzed using a hyphenated technique such as FTIR or mass spectroscopy (MS). Such TGA-FTIR or TGA-MS experiments are referred to as evolved gas analysis. The TGA is used not only to quantify transitions within the material but also to prepare volatiles for further qualitative analysis.

Thermomechanical Analysis

Thermomechanical analysis (TMA) is a thermal analysis method in which linear or volumetric dimensional changes are measured as a function of temperature, time, or force (Ref 2). Thermomechanical analysis is used to study the structure of a polymeric material by evaluating the implications of the material dimensional changes.

Method

Standard solid samples evaluated via TMA should be of regular shape, having two flat, parallel sides. Additionally, fiber and film samples can be tested with minimal preparation. Experiments conducted to evaluate expansion and contraction of solid materials are performed on a quartz stage. The sample is placed on the stage, with a quartz probe resting on the opposing end. Thermomechanical analysis data can be acquired in compression modes, including expansion, penetration, dilatometry, rheometry, and flexure or tension mode (Ref 2). The analysis of film and fiber samples requires special fixturing, similar in principle to a universal mechanical tester. For all analysis configurations, the stage assembly is surrounded by a furnace and a cooling device. The normal operating range for TMA experiments is −180 to 1000 °C (−290 to 1830 °F), with a 5 °C/min (9 °F/min) heating rate commonly used. A compressive force is normally applied to the probe configuration throughout the evaluation for purposes of preload and stability.

Results

Plotted results generated through a TMA, like the printed data obtained from all of the thermal analysis techniques, are referred to as a thermogram. The thermogram presents the sample dimension either as length or a percentage of original length on the *y*-axis and as a function of temperature, time, or force on the *x*-axis. Temperature is the standard independent variable. Changes in the sample are presented as expansion or contraction.

Uses of TMA in Failure Analysis

Coefficient of Thermal Expansion

The coefficient of thermal expansion (CTE) is the change in the length of a material as a response to a change in temperature. The CTE is represented by the derivative of the slope of the line showing the dimensional changes with respect to temperature. This is a significant property when plastic materials are used under highly constrained conditions. This is commonly the case when plastic parts are used in conjunction with components produced from other materials such as metals and ceramics. In general, the CTEs of polymeric materials are substantially greater than those of metals and ceramics. This is the case when plastic materials are overmolded onto metal inserts. Thus, comparative testing of mating materials can produce data used to illustrate and even calculate the potential interference stresses on the materials in a multimaterial design. The evaluation of the CTEs of mating plastic and metal components is illustrated in Examples 10 and 14 in Ref 4.

Material Transitions

According to Sepe (Ref 6), "The CTE is an important property in itself; however, it is of particular value in polymers, because sudden changes in CTE can signal important transitions in the material structure." Within semicrystalline polymers, the T_g, signaling the conversion from a hard, brittle material to a rubbery condition, is accompanied by an increase in the CTE. A thermogram representing a typical semicrystalline resin is shown in Fig. 10. The physical properties of the material can be expected to be significantly different across this transition. Amorphous resins soften at the T_g; because of this, samples undergo compression under the inherent load of the testing conditions. A thermogram showing the glass transition in an amorphous resin is shown in Fig. 11. The

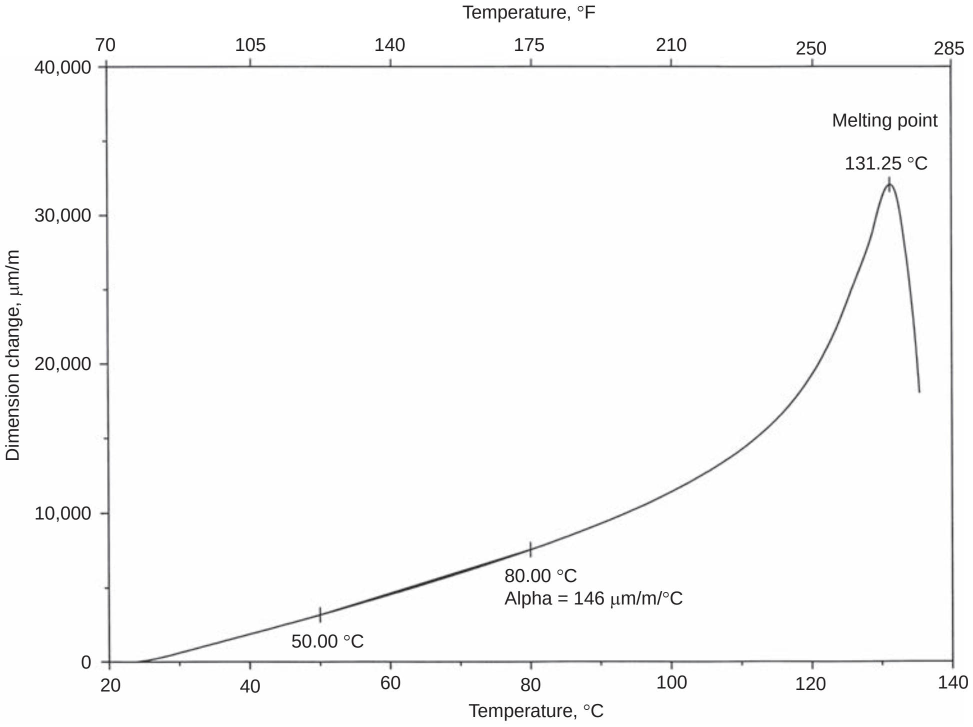


Fig. 10 Thermomechanical analysis thermogram representing a typical semicrystalline plastic resin

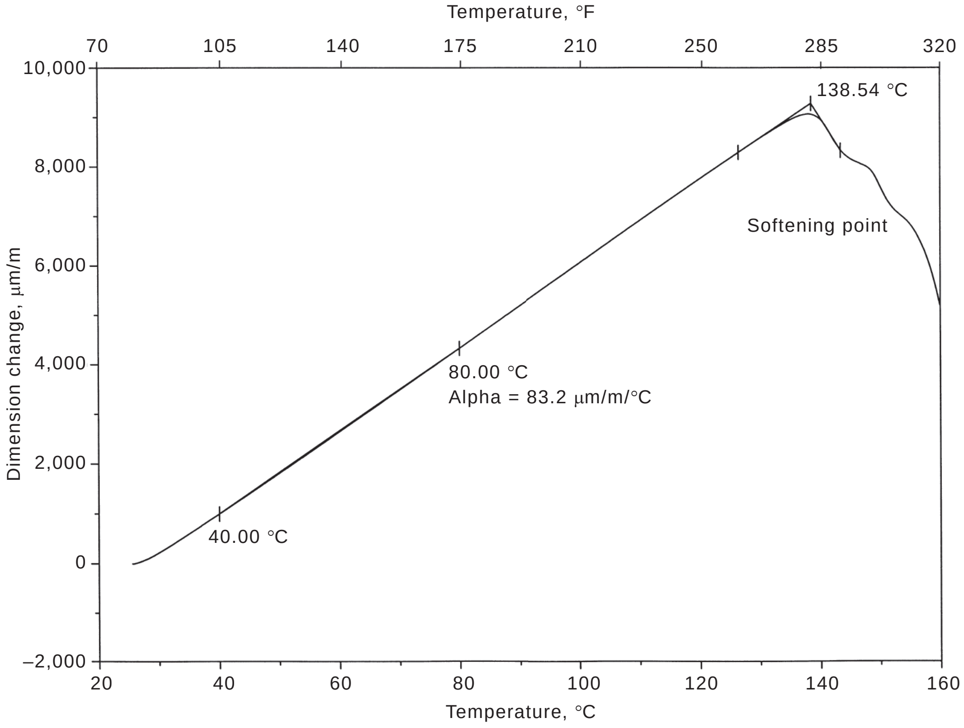


Fig. 11 Thermomechanical analysis thermogram representing a typical amorphous plastic resin

evaluation of the glass transition is presented in Example 14 in Ref 4. Thermomechanical analysis is generally accepted as a more accurate method for assessing the T_g of polymeric materials, relative to DSC. "By using the prescribed attachments and the appropriate force, TMA can be used to determine two commonly measured properties of plastic materials: the heat-deflection temperature and the Vicat softening temperature" (Ref 6).

Molded-In Stress

Internal molded-in stress is an important source of the total stress on a plastic component, and it is often sufficient to result in the failure of plastic materials. Such stresses are particularly important in amorphous resins, which are prone to environmental stress cracking. Molded-in stresses are commonly imparted through the forming process, especially injection molding and thermoforming. Molded-in stress is observed in amorphous resins as a marked expansion in the sample dimension at temperatures approaching the T_g, as illustrated in Fig. 12. This expansion is associated with rapid expansion as the internal stresses are relieved. This stress relief is due to molecular reorientation on attaining sufficient thermal freedom. In the absence of molded-in stress, the sample would compress due to the loss of load-bearing capabilities as the material undergoes glass transition.

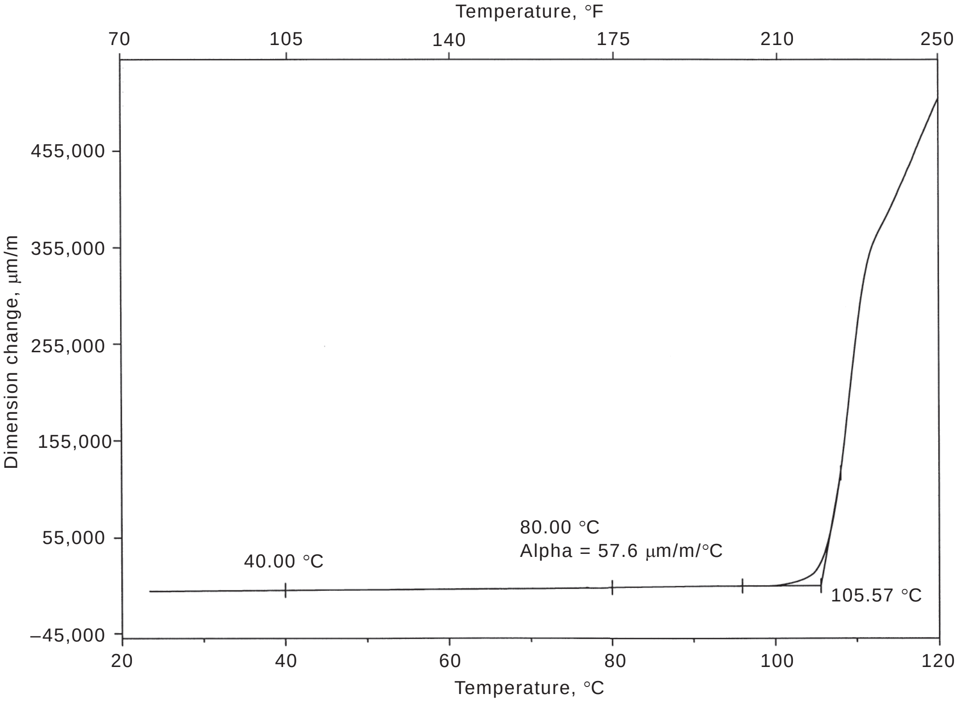


Fig. 12 Thermomechanical analysis thermogram showing a high level of residual stress in an amorphous plastic resin

Chemical Compatibility

The chemical compatibility of a plastic material with a particular chemical agent can be assessed using TMA. In particular, the volume swell of a polymeric material by a chemical can be tested. The sample material is constrained in a quartz vessel, and the chemical agent is added. Dilatometry is used to measure the volume expansion of the material over time.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) is a thermoanalytical technique that assesses the viscoelastic properties of materials. Dynamic mechanical analysis evaluates the stiffness, as measured by modulus, as a function of temperature or time. Polymeric materials display both elastic and viscous behavior simultaneously, and the balance between the elastic recovery and viscous flow changes with temperature, time, and frequency (Ref 6). Measurements can be made in several modes, including tension, shear, compression, torsion, and flexure. The results obtained as part of a DMA experiment provide the storage modulus, loss modulus, and the tangent of the phase-angle delta (tan delta). Dynamic mechanical analysis is not routinely used as a failure analysis technique, but it can provide valuable material information.

Method

Dynamic mechanical analysis experiments can be performed using one of several configurations. The analysis can be conducted to apply stress in tension, flexure, compression, shear, or torsion. The mode of the analysis determines which type of modulus is evaluated. The measurement of modulus across a temperature range is referred to as temperature sweep. Dynamic mechanical analysis offers an advantage over traditional tensile or flexural testing in that the obtained modulus is continuous over the temperature range of interest. In addition, special DMAs can also be conducted to evaluate creep through the application of constant stress or stress relaxation by using a constant strain. Dynamic mechanical analysis studies can be performed from −150 to 600 °C (−240 to 1110 °F), usually employing a 2 °C/min (4 °F/min) heating rate.

Results

The results obtained as part of a DMA evaluation are plotted to illustrate the elastic or storage modulus (E') and the viscous or loss modulus (E'') on the y-axis and as a function of temperature on the x-axis. Less frequently, time is used, depending on the type of experiment. Additionally, the tangent of the phase-angle delta (E''/E') is also calculated. A typical DMA thermogram is presented in Fig. 13.

Uses of DMA in Failure Analysis

Temperature-Dependent Behavior

The temperature-dependent behavior of polymeric materials is one of the most important applications of DMA. In a standard temperature-sweep evaluation, the results show the storage modulus, loss modulus, and the tan delta as a function of temperature. The storage modulus indicates the ability of the material to accommodate stress over a temperature range. The loss modulus and tan delta provide data on temperatures at which molecular changes produce property changes, such as the glass transition and other secondary transitions that are not detectable by other thermal analysis techniques. The superiority of DMA over DSC and TMA for assessing the glass transition is well documented (Ref 6). Secondary transitions of lesser magnitude are also important, because they can relate to material properties such as impact resistance. The ability of a plastic molded component to retain its properties over the service temperature range is essential and well predicted by DMA.

Time-Dependent Behavior

Time and temperature act on polymeric materials in the same way, due to their viscoelastic nature. When placed under conditions of continuous loading—even loads well below the yield point of the material—polymeric materials will exhibit time-dependent strain. This phenomenon is known as creep, and it is

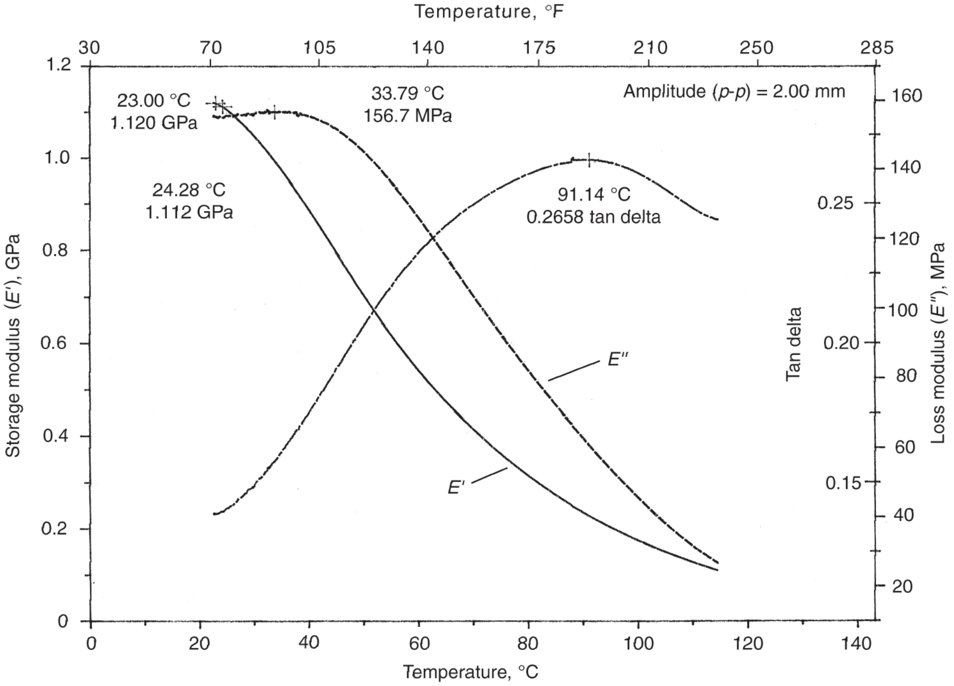


Fig. 13 Dynamic mechanical analysis thermogram showing the results obtained on a typical plastic resin. Tan delta is the ratio of the loss modulus to the storage modulus.

manifested as a reduction in the apparent modulus of the material over time. Dynamic mechanical analysis experiments can be run and evaluated using time-temperature superposition to project behavior over time. Example 3 in this article illustrates the use of creep modeling.

Aging and Degradation

Changes in the mechanical properties of plastic resins that arise from molecular degradation or aging can be evaluated via DMA. Such changes can significantly alter the ability of the plastic material to withstand service stresses. While the cause and type of degradation cannot be determined, DMA can assess the magnitude of the changes. This can provide insight into potential failure causes.

Solid and Liquid Interactions

Sepe (Ref 6) notes that "DMA is sensitive to structural changes that can arise when a solid polymer absorbs a liquid material." This effect can arise from the absorption of water or organic-based solvents. Dynamic mechanical analysis experiments can assess changes in the physical properties of a plastic material that can result from such absorption, including loss of strength and stiffness. Example 11 in Ref 4 shows the changes in mechanical properties of a plastic resin associated with chemical absorption. Experiments can also evaluate recovery after the removal or evaporation of an absorbed liquid.

Methods for Molecular Weight Assessment

The aspect of molecular structure, specifically molecular weight, makes polymeric materials unique among materials that are commonly used in engineering applications, including metals and ceramics. Molecular weight and molecular weight distribution are probably the most important properties for characterizing plastics (Ref 5). These parameters have a significant impact on the entirety of characteristics of a plastic resin, including mechanical, physical, and chemical resistance properties. Molecular weight assessment can be used to evaluate the inherent molecular weight of a base resin or to assess the effects of compounding, molding, or service on the material. Changes in molecular weight can occur throughout the material life cycle and significantly impact the performance of the molded part. Changes can result in molecular weight decreases through such mechanisms as chain scission, oxidation, and hydrolysis, or as increases through destructive cross linking. Because of this, the characterization of molecular weight is an important aspect of a thorough failure analysis.

Gel Permeation Chromatography

Gel permeation chromatography (GPC), which is also referred to as size exclusion chromatography, is an analytical method used to characterize the molecular weight distribution of a polymeric material. Similar to all chromatographic techniques, GPC uses a packed column to segregate various constituents. One or multiple columns are used to separate the polymeric and oligomeric materials within the plastic resin. The polymer is further separated by molecular weight, producing essentially a histogram representing the molecular weight distribution of the material. From these results, a numerical average molecular weight can be calculated. Detectors, based on refractive index or ultraviolet detection, are used to identify the changes in molecular weight.

Gel permeation chromatography offers the advantage, unlike melt viscosity and solution viscosity techniques, of producing results that directly represent the actual molecular weight and molecular weight distribution of the plastic resin, as illustrated in Fig. 14. Another advantage is that GPC requires a relatively small sample size, 30 to 120 μg, for a complete evaluation (Ref 8). The technique, however, is often complicated to perform, because it uses sophisticated instrumentation, and difficult to interpret. Example 10 in Ref 4 reviews the use of GPC in a failure investigation.

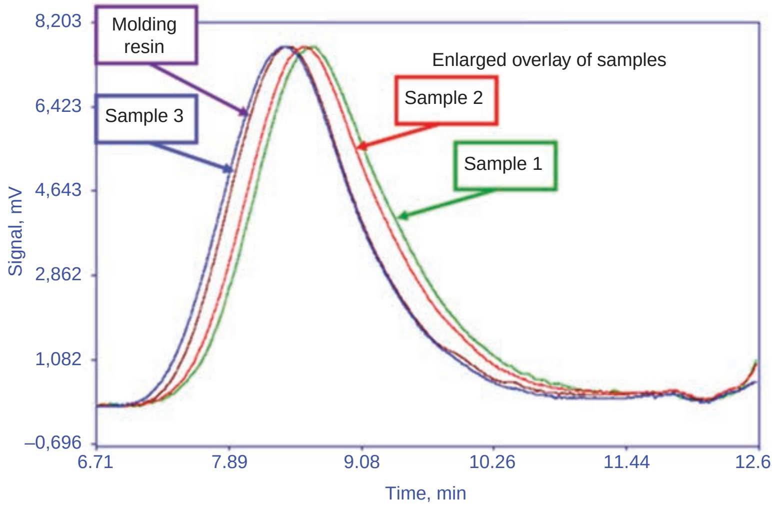
Melt Flow Index

The melt flow index or melt flow rate (MFR) describes the viscosity of a plastic material in the molten state. The sample material is heated through the melting or softening point and extruded through a die that has a standard-sized orifice. Different materials use various test conditions, including temperature and load. The method for determining the MFR is described in ASTM D1238. Melt flow rate is the simplest technique for assessing the molecular weight of a plastic material, and it is inversely proportional to the molecular weight of the polymer (Ref 5). Melt flow rate is widely used to describe the molecular weight of a plastic resin and is commonly cited by suppliers on a material data sheet. The units used to indicate MFR are grams per 10 min. Examples 7, 11, 12, and 14 in Ref 4 and Example 2 in this article describe the use of MFR in assessing molecular weight in a failure analysis.

While MFR is relatively easily determined and is commonly used to describe molecular weight, the technique has several negative aspects. Melt flow rate does not measure the molecular weight distribution of the analyzed material; it represents only the average molecular weight of the polymer. Because of this, the blending of polymers that have different molecular weight distributions and average molecular weights can result in equal determinations between very different materials that have distinct properties.

Solution Viscosity

The traditional approach for determining only the molecular weight of a resin, but not the molecular weight distribution, involves dissolving the polymer in a suitable solvent.



Gel permeation chromatography results
(Average molecular weight)

Sample	Run	M_n		M_w		M_z		M_w/M_n	
Molding resin	1	9,702	9,759	46,512	46,556	84,961	85,207	4.79	4.77
	2	9,816		46,601		85,093		4.75	
Sample 1	1	9,003	9,085	33,926	33,881	64,318	64,261	3.77	3.73
	2	9,167		33,835		64,204		3.69	
Sample 2	1	8,416	8,443	37,439	37,407	71,367	71,136	4.45	4.43
	2	8,470		37,375		70,905		4.41	

Fig. 14 Typical gel permeation chromatogram showing variation in the molecular weight distribution of polymer samples. The tabular data showing the molecular weight are also presented. mV, millivolts; M_n, number-average molecular weight; M_w, weight-average molecular weight; M_z, z-average molecular weight

However, the more structurally complicated macromolecules require the use of hostile solvents, tedious sample preparations, and costly time delays to obtain limited, single datapoint values. For example, the solution viscosity determination of polyvinyl chloride, according to ASTM D1243, requires either a 1 or 4% concentration in cyclohexanone or dinitrobenzene, while polyamides, or nylons, require formic acid. Other engineering polymers may require tetrahydrofuran, dimethylformamide, dimethyl sulfoxide, or other equally hostile solvents (Ref 9). The obtained solution viscosity values are only indications of molecular weight and do not reflect the absolute weight values (Ref 9). Example 9 in Ref 4 illustrates the use of solution viscosity in a failure investigation. Solution viscosity techniques are often preferred over MFR when the material of interest is glass-fiber reinforced. A correction factor can be used in solution viscosity to account for the weight of the glass, which is commonly determined through TGA.

Mechanical Testing

Because a wide range of mechanical tests are available to evaluate plastics and polymers, they initially do not seem to constitute a rational set. The totality of mechanical tests can be partitioned into logical groups in several distinct ways (Ref 10). One very useful way to classify the various mechanical test methods is to distinguish between tests that evaluate long-term properties and those that evaluate short-term properties. Short-term tests include those that assess what are generally considered to be material properties. These include tensile tests, flexural tests, and the evaluation of impact resistance. While short-term tests are generally easy to conduct and interpret, they lack the ability to predict or assess the long-range performance properties of a material. As such, short-term tests are frequently listed on material data sheets.

Tests for Short-Term Properties

The tensile test is the most commonly performed mechanical test for evaluating plastic material properties. This test is performed on a dumbbell-shaped specimen, and it is outlined in ASTM D638. Tensile testing provides data regarding the yield point in the form of yield strength and elongation at yield, the break properties as tensile strength at break and elongation at break, and the stiffness of the material as elastic modulus. Additionally, the tensile test generates information regarding the proportional limit.

A second short-term mechanical method that is used to evaluate plastic materials is flexural testing, which simulates bending of the test sample. The test specimen is evaluated on a universal mechanical tester, and the tests can be performed using a three- or four-point-bend configuration. Flexural testing provides two pieces of data: flexural modulus and break strength. This testing is performed in accordance with ASTM D790.

Several different types of tests are used to evaluate the impact properties of a plastic material. These include pendulum-based tests, such as Izod and Charpy tests, and falling weight tests, such as the dart penetration configuration. Unlike tensile and flexural testing, the results obtained from impact testing do not provide fundamental material properties. Instead, impact testing results are more performance-based. Given these different methodologies of assessing the impact properties of a plastic material, the falling weight or dart impact tests are generally considered to be superior to the pendulum configurations. Falling weight tests evaluate the sample material in two dimensions and not one, because the specimen is a plate rather than a beam. The data obtained during an instrumented falling weight impact test include the energy to maximum load, representing the energy required to initiate cracking, and the total energy to failure. The ratio of these two is an indication of the ductility of the material. Additionally, an examination of the test specimens is used to classify the failure mode from brittle to ductile. Falling weight impact testing is described as part of ASTM D3029.

Tests for Long-Term Properties

Fatigue testing of plastic materials exposes the samples to cyclic stresses in an attempt to evaluate the samples in a manner that would produce fatigue failure while in service. Testing procedures are used to simulate flexural fatigue and tensile fatigue. The analyses are normally conducted in a way that does not excessively heat the specimen, thus altering the failure mode. The results of a fatigue test are shown in the form of a stress/number of cycles curve.

A second long-term test methodology assesses the creep resistance of the material. Creep testing exposes the sample to a constant stress over a prolonged period of time. This is done to simulate the effects of static stresses on the performance of a material in service. The extension or strain of the sample over time is measured. Traditional creep testing can take an extended period of time. Similar results can, however, be obtained through a DMA creep study, which can be performed in the course of a few days.

Mechanical Testing as Part of a Failure Analysis

The use of mechanical testing in a failure analysis is limited. The preparation of specimens from the failed component may not be possible. Further, published standard mechanical data—including yield strength, elastic modulus, and flexural modulus—are very dependent on the specimen configuration and testing conditions. Given that most published data are generated on specially molded test specimens, the testing of samples excised from molded articles may not provide an adequate comparison. In some cases, it is not apparent whether observed differences are the result of material deficiencies or variations in test specimen configuration. Instead, mechanical testing is most useful in comparing a known good or control sample with a failed part. Many times, this is best accomplished through some sort of proof load testing. Proof load testing involves measuring the strength and dimensional changes as a function of an applied load. In most cases, this testing involves producing a catastrophic failure within the test sample. The use of proof load testing as part of a failure analysis is illustrated in Example 12 in Ref 4, while Example 3 in this article shows an application of tensile testing as a part of failure analysis.

Considerations in the Selection and Use of Test Methods

Through the application of analytical testing and a systematic engineering approach, it is possible to successfully ascertain the nature and cause of a plastic component failure. The testing, however, must be performed in a sound manner, because the data obtained are only as good as the analysis method. Further, the data presented by the analytical methods are often complicated; in many cases, they require an experienced analyst to properly interpret them.

The aforementioned analytical tests are not meant to be an all-encompassing list of the methods used to evaluate failed plastic components. Certainly, numerous testing methodologies provide data that are pertinent to a plastic component failure analysis. Other analysis techniques, including SEM, surface science techniques, and chromatographic methods, are important tools in a plastic component failure analysis. Scanning electron microscopy is covered in the article “Surface Examination and Analysis of Plastics” in this Volume. More specialized chromatographic methods, including gas chromatography and gas chromatography-mass spectroscopy, are extremely useful in assessing low-concentration additives within a plastic resin. Nuclear magnetic resonance spectroscopy is useful in polymeric analysis, because it provides information related to composition beyond FTIR. Nuclear magnetic resonance can provide data regarding stereoregularity, carbon content, chemical composition, and copolymer structure (Ref 11). Additionally, surface analysis spectroscopic techniques, such as secondary ion mass spectroscopy, x-ray photoelectron spectroscopy, and electron spectroscopy for chemical analysis, are specifically used to characterize very shallow surface layers. These techniques can be used to analyze material composition, but they are particularly suited to the analysis of surface contaminants (Ref 11). While these analytical techniques can provide valuable data as part of a plastics failure analysis, the tests described in this article are considered to be the most important in the majority of cases. Test methods used less often are not covered in this article. A summary showing both the treated and omitted analysis methods and the corresponding information gained is given in Table 1 (Ref 3).

Case Studies

Example 1: Brittle Performance of High-Impact Polystyrene Housings

Housings from two different production lots exhibited significant variation in performance during engineering testing. Specifically, the difference was detected during impact testing performed on the molded parts. One of the lots exhibited superior impact properties and ductile behavior, similar to that of previous production. The other lot demonstrated a marked reduction in the impact properties, as noted in the impact strength and relatively brittle behavior. The housings were specified to be injection molded from a high-impact polystyrene (HIPS) resin.

Tests and Results

Visual examination of the impacted housing specimens confirmed the reported property variation. Specimens representing the older, retained reference parts showed significant ductility in the form of stress whitening and deformation. Conversely, the new production lot samples exhibited characteristics of brittle fracture.

The two lot samples were analyzed using FTIR in the attenuated total reflectance mode. A comparison of the obtained results showed a general match. Both sets of spectra exhibited absorption bands that are characteristic of styrene and butadiene functionalities, as illustrated in Fig. 15. However, variation in the relative intensities of the styrene and butadiene bands was observed, as shown in Fig. 16. Band intensity measurements were taken for the butadiene and styrene functionalities at 964 and 751 cm^{-1}, respectively, for the two lot samples. The results, as shown in Table 2, clearly illustrated that the samples that performed in a brittle manner had a relatively lower level of butadiene content.

Conclusions

At the conclusion of this testing, the variation in performance observed within the housings was attributed to the use of two different resins to mold the parts. Both production lots were molded from HIPS; however, the relative level of butadiene functionality was significantly lower in the brittle parts. The butadiene is added as an impact modifier, and it enhances the ductility of the resin with increasing levels.

Table 1 Practical information derived from polymer analysis methods

Test method	Properties measured	Use in polymer failure analysis
Fourier transform infrared spectroscopy (FTIR)	Molecular bond structure	Material identification, contamination, degradation, chemical contact
Differential scanning calorimetry (DSC)	Heat of fusion, melting point, glass transition temperature, heat capacity	Material identification, level of crystallinity, aging/degradation, thermal history
Thermogravimetric analysis (TGA)	Weight loss over temperature or time	Composition, thermal stability, evolved gas analysis
Thermomechanical analysis (TMA)	Dimensional changes over temperature	Coefficient of thermal expansion, material transitions, molded-in stress, chemical compatibility
Dynamic mechanical analysis (DMA)	Elastic modulus, viscous modulus, tan delta	Temperature-dependent behavior, aging/degradation, solid-liquid interactions
Gel permeation chromatography (GPC)	Weight-average molecular weight, molecular weight distribution	Degradation, suitability of material for use
Melt flow rate (MFR)	Melt viscosity	Degradation, compliance with material specification
Solution viscosity	Intrinsic viscosity	Degradation
Mechanical testing	Strength and elongation properties, modulus	Compliance with material specification, mechanical properties
Scanning electron microscopy (SEM)	Surface and particle morphology	Fracture mode
Energy-dispersive x-ray spectroscopy (EDS)	Elemental concentrations	Material composition, fillers, additives
Nuclear magnetic resonance (NMR)	Molecular bond structure	Material identification
Mass spectroscopy (MS)	Molecular structure	Material identification, additives
X-ray photoelectron spectroscopy (XPS)	Elemental concentrations	Chemical composition of surfaces
Auger electron spectroscopy (AES)	Elemental concentrations	Chemical composition of surfaces

Source: Ref 3

Example 2: Failure of a Weather Monitor Housing

A housing for a weather-monitoring station failed while being used as part of an extended field-service product evaluation. Specifically, the failed unit had been installed outdoors at a coastal location within the southeastern United States. The housing had been injection molded from an unfilled, flame-retardant, ultraviolet-stabilized, weather-resistant grade of polycarbonate/poly(acrylonitrile-styrene-acrylate) (PC + ASA). The housing material was overmolded onto stainless-steel-profiled threaded inserts. After molding, the individual housing sections were assembled with the internal electrical components. The completed assembly was subsequently connected to a mating bracket with metal hardware, including M6 screws fastened into the overmolded stainless steel inserts. In addition to the failed housing, an as-molded housing, which had never been in service or tested, was also received for comparison purposes. A typical sample of the molding resin was also submitted as a reference.

Tests and Results

Examination of the failed housing confirmed the presence of individual parallel longitudinal fractures within several of the bosses. These cracks corresponded to the threaded metal inserts used to secure the housing to the mounting hardware. The cracking within the bosses exhibited features characteristic of brittle fracture and lacked features associated with significant macroductility. The exterior surface of the boss surrounding the cracks exhibited an orange-brown coloration. In particular, the material adjacent to the stainless steel insert exhibited mud cracking characteristic of localized molecular degradation of the boss material, as shown in Fig. 17. Microscopic examination of the exposed fracture surfaces revealed features indicative of the initiation and subsequent coalescence of multiple individual cracks, which produced the longitudinal fractures. The fracture surfaces lacked signs of significant macroductility. Further evidence

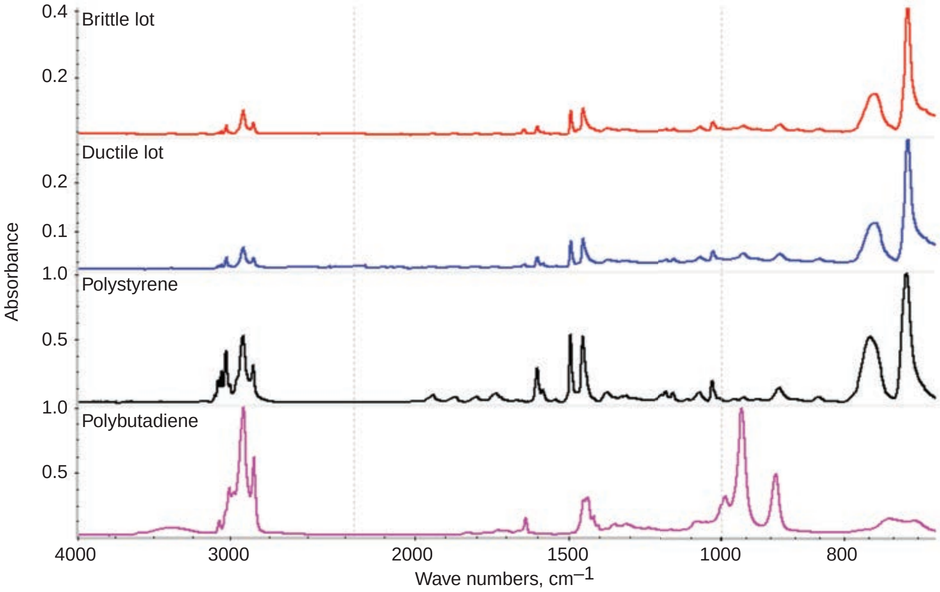


Fig. 15 Fourier transform infrared spectroscopy spectral comparison showing generally good agreement between the brittle lot and ductile lot materials. Both spectra contained absorbances that are associated with styrene and butadiene functionalities.

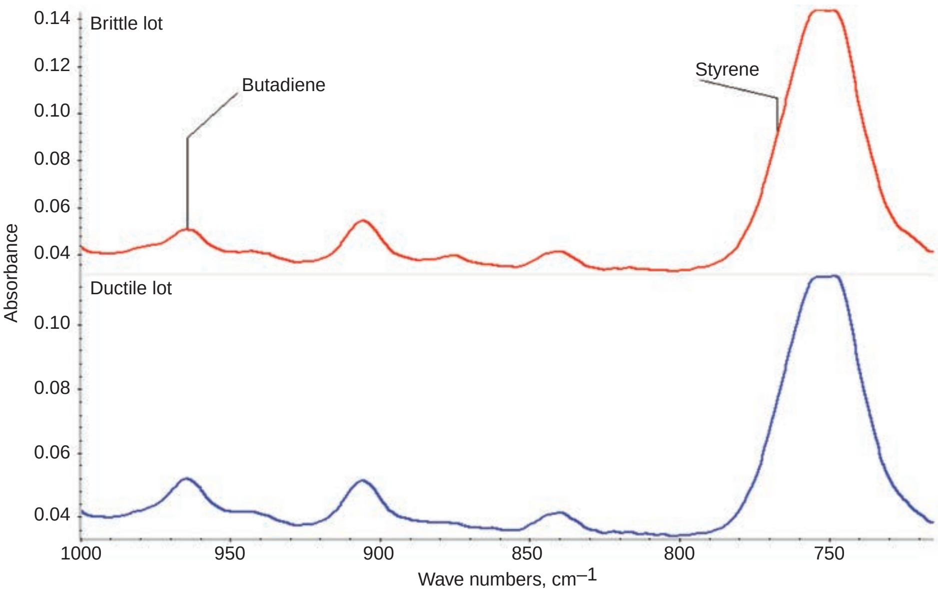


Fig. 16 Fourier transform infrared spectroscopy spectral comparison illustrating a relatively lower level of absorption associated with butadiene functionality in the brittle lot material compared with the ductile lot material

Table 2 Spectral band intensities for a ductile sample and a brittle sample, illustrating variation in the ratio in content between butadiene and styrene

Sample	Butadiene 964 cm^{-1}	Styrene 751 cm^{-1}	Ratio of butadiene/styrene
Ductile lot			
1	0.0130	0.0780	0.167
2	0.0110	0.0660	0.167
3	0.0099	0.0570	0.174
Brittle lot			
1	0.0068	0.0685	0.099
2	0.0130	0.1320	0.098
3	0.0110	0.1040	0.106

Fig. 17 Micrograph showing cracking on the failed housing boss. A localized zone of mud cracking and discoloration characteristic of molecular degradation is present.

of the orange-brown coloration was also present.

The SEM inspection of the fracture surfaces revealed features associated with brittle fracture through a slow crack-initiation mechanism. The origin zone displayed signs of localized molecular degradation. Evidence of adherent debris was also present within the crack origins. This debris was thought to correspond to the orange-brown coloration that was noted during the visual and microscopic examinations. After initiating, the cracking extended longitudinally down the wall of the boss.

Compositional analysis was performed using FTIR on the molding resin, exemplar part, and the failed housing. The results were characteristic of a PC + ASA resin blend. The FTIR analysis found no evidence to indicate the presence of bulk contamination or other anomalies within the failed housing material.

The housing samples were further analyzed using EDS in conjunction with the SEM examination (Table 3). The analysis of the molding resin showed relatively high concentrations of carbon and oxygen; moderate levels of bromine, titanium, and antimony; and trace amounts of silicon and sulfur. The carbon and oxygen were associated with the base polymer. The bromine and the antimony were thought to be present as flame-retardant additives. The titanium was likely titanium dioxide. Analysis of a core sample representing the failed housing produced a very similar elemental profile.

An analysis was also conducted on the orange-brown residue present on one of the boss fracture surfaces. Elements associated with the plastic resin were present. However, the residue sample contained a much higher level of oxygen relative to carbon, as compared to the resin and housing core materials. Additionally, the residue contained a relatively high concentration of iron as well as significant levels of chromium and nickel. Importantly, the presence of chlorine was also identified. Accounting for the elements associated with the base plastic, the results that were obtained on the orange-brown residue were consistent with corrosion products of a stainless steel component. Chlorine-base compounds are known to cause corrosion within stainless steel alloys.

The molding resin and the failed housing material were analyzed via DSC, producing relatively similar thermograms (Fig. 18). A review of the second heating results showed that the molding resin underwent a dual shift in heat flow associated with two individual glass transitions within the material. Glass transition temperatures (T_g) of 110 and 135 °C (230 and 275 °F) were obtained, representing the ASA and PC constituents, respectively. A disturbance in the thermogram baseline was observed at approximately 300 °C (570 °F), representing partial material degradation, likely within the flame-retardant package. The second heating DSC thermogram representing the failed housing material also showed the dual glass transitions. While the glass transition associated with the ASA remained relatively consistent, the glass transition corresponding to the PC was somewhat lower, 132 °C (270 °F). A comparison showing this is included in Fig. 18. This reduction in T_g was thought to represent variation in molecular structure between the molding resin and the failed housing material, within the polycarbonate domain. Given the DSC results, it was evident that some molecular structural differences existed between the molding resin and the failed part material.

The samples were also analyzed using TGA, and the molding resin and failed part material produced generally similar weight-loss profiles. Under the dynamic nitrogen purge, the samples underwent a multistage weight loss, with combined losses of approximately 86%. These weight losses were associated with the initial stages of thermal decomposition of the polymers. Further heating under an air

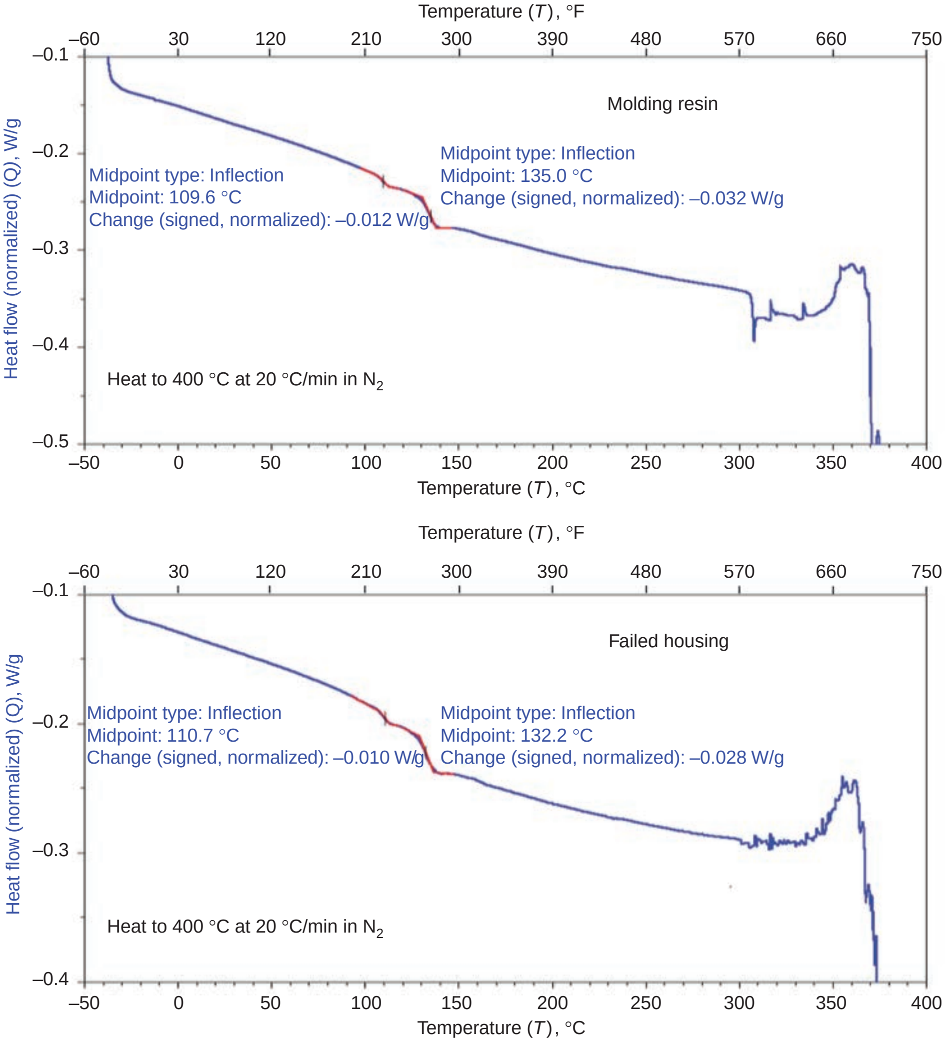


Fig. 18 Differential scanning calorimetry thermogram comparison showing a reduction in the glass transition associated with the polycarbonate in the results obtained on the failed housing material

Table 3 Energy-dispersive x-ray spectroscopy analysis showing differences in the elements composing a sample of molding resin, a failed housing, and a fracture-surface deposit

Element, relative wt%	Molding resin	Failed part core	Fracture-surface deposit
Carbon	77.2	75.9	26.7
Oxygen	15.3	16.9	48.5
Titanium	1.5	2.1	0.8
Antimony	1.4	1.2	0.6
Bromine	4.4	3.5	1.2
Silicon	0.1	0.1	0.3
Sulfur	0.1	0.2	0.6
Chlorine	...	0.1	0.6
Sodium	...	0.1	...
Iron	...	...	18.1
Chromium	...	...	2.1
Nickel	...	...	0.7
Magnesium	...	...	0.1

atmosphere resulted in a weight loss of 11%, which corresponds with the combustion of carbonaceous char formed during the initial thermal decomposition of the polymer. This pattern of weight loss was consistent with the expected results for a PC + ASA resin. Upon completion of the analysis, a noncombusted residue content of approximately 4% remained, which indicates that the material was not formulated with a significant level of fillers.

While the two materials produced similar quantitative results, a direct comparison of the weight-loss profiles revealed that the failed housing material underwent weight loss at a significantly lower temperature, as illustrated in Fig. 19. This variation in thermal decomposition suggested that the failed part material was less thermally stable. Specifically, the weight loss corresponding to the polycarbonate was shifted to a substantially lower temperature. This was also supported by a review of the localized maximum in the weight-loss derivative curve. The molding resin showed the polycarbonate weight loss to be centered at 507 °C (945 °F), while the temperature was reduced to 469 °C (876 °F) in the failed part material. The identification of molecular differences in the materials through TGA was consistent with the results obtained during the DSC analysis. This type of variation is often associated with molecular degradation. Importantly, the level of char was in good agreement between the resin and the failed part material, which indicates a consistent ratio of PC and ASA.

The MFR testing of the supplied molding resin produced an MFR of 45.8 g/10 min. This was on the high side of the nominal range that is indicated for the resin used to produce the housings. The results obtained on the as-molded and failed housings were notably higher than that obtained on the molding resin: 102.8 and 75.9 g/10 min, respectively. This represented a significant reduction in average molecular weight compared with the molding resin. Typically, for unfilled resins, shifts greater than 40% in molded part results relative to molding resin represent excessive molecular degradation. The results obtained on the two molded parts were indicative of severe and excessive molecular degradation of the housing material.

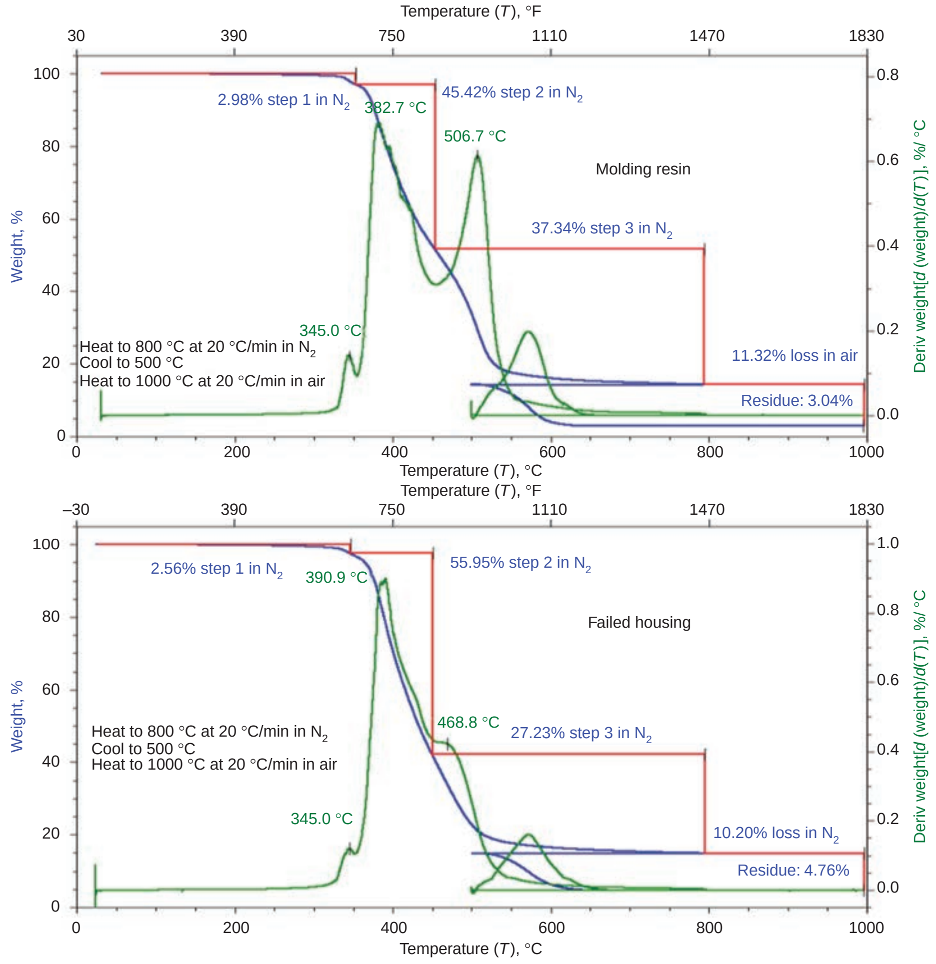


Fig. 19 Thermogravimetric analysis thermogram comparison showing a difference in the weight-loss profiles of the molding resin and the failed housing material

Conclusions

It was the conclusion of the failure analysis that the cracking within the housing bosses occurred as a result of localized molecular degradation of the plastic, adjacent to the stainless steel inserts. The form of cracking observed during the fractographic evaluation was characteristic of a chemical reaction that resulted in significant molecular weight reduction of the polymer at isolated locations on the boss. Based on the EDS analysis, the chemical agent thought to be responsible for the molecular degradation was identified as ferrous chloride. Ferrous chloride is produced as a corrosion by-product of ferrous alloys, including stainless steel. Given the installation location, it is likely that salt spray from the coastal installation produced this corrosion. The stress that precipitated the cracking is likely interference between the stainless steel insert and the overmolded boss.

A primary factor in the failure was identified as molecular degradation associated with the injection molding process. Melt flow rate testing indicated a significant decrease in the average molecular weight of the molded parts compared with the molding resin. Such degradation will considerably reduce the mechanical integrity as well as the chemical resistance of the molded part. The results obtained during the DSC and TGA testing supported the conclusion that the housing materials had been substantially degraded.

Example 3: Failure of Automotive Aftermarket Components

Cracking was observed within a number of automotive aftermarket components after approximately 2 years in service. The parts were used on the exterior of the vehicle but not under the hood. They were molded from a 30% glass-fiber-reinforced nylon 6/6 resin. Based on finite-element analysis, the load on the parts was identified as approximately 60 MPa (9 ksi), applied continuously.

Tests and Results

Fractographic examination of the failed components, including visual, microscopic, and SEM examinations, identified partial cracking at a design corner within the component Although the design included an adequate radius, the cracking evidenced a lack of significant macro- and microductility. However, substantial ductility was present within the laboratory fracture and isolated locations outside of the crack origins. The fracture characteristics were indicative of stresses that exceeded the long-term strength of the material through a creep-rupture mechanism. The glass fibers within the cracked area appeared to be randomly distributed, and they were well bonded to the polymer matrix.

Analytical testing performed on the failed parts produced results that are characteristic of a 30% glass-fiber-reinforced nylon 6/6 resin with no evidence of contamination. Results obtained through DSC indicated that the material had been properly crystallized during the injection molding process. Further, no evidence was found that indicated molecular degradation.

Given the results of the failure analysis, the failures appear to be related to improper materials selection. Tensile testing of the incumbent nylon 6/6 resin showed that the anticipated continuous load of 60 MPa (9 ksi) was well below the tensile strength of the material, 172 MPa (25 ksi), as illustrated in Fig. 20. However, this load was still significantly along the stress-strain curve, given the effects of time on plastic materials. An alternate material was proposed: a 30% glass-fiber-reinforced polyarylamide (PARA) resin. Comparative DMA temperature sweeps showed that the PARA resin had a higher modulus as well as an elevated T_g compared with the nylon 6/6, as shown in Fig. 21. A series of DMA time-temperature superposition creep experiments were conducted that compared the effects of time on the apparent modulus of the two materials. Consistent with the temperature sweeps, the apparent modulus of the PARA was higher across the projected time range to 200,000 h at 25 °C (77 °F), as demonstrated in Fig. 22. Finally, plots of strain versus time were created using the apparent modulus plots and the 60 MPa (9 ksi) constant load. This is included in Fig. 23. While the nylon 6/6 was predicted to fail after approximately 25,000 h (2.85 years), no cracking was projected through 200,000 h (20+ years) at 25 °C (77 °F).

Conclusions

It was the conclusion of the failure analysis that the creep rupture of the automotive aftermarket components was the result of improper materials selection. Evaluation of an alternate material, a 30% glass-fiber-reinforced PARA resin, projected a service lifetime exceeding 20 years. Further testing was recommended to model the creep performance at additional temperatures above 25 °C (77 °F). Also, additional testing to assess the effects of glass-fiber orientation, knit lines, and moisture content would be beneficial.

Example 4: Failure of Storage Buckets

A recent increase in the failure rate of storage buckets was noted within a 6 month time period. The failures were observed after the buckets had been filled and subsequently stacked onto pallets. The failures correlated with a particular production lot of the buckets. The buckets were specified to be injection molded from a high-density polyethylene (HDPE) resin. No processing changes were reported by the molder for the production lot of failed buckets. Older retained buckets with a demonstrated low failure rate were available for comparative testing.

Tests and Results

Visual and microscopic examination of the buckets revealed a combination of longitudinal

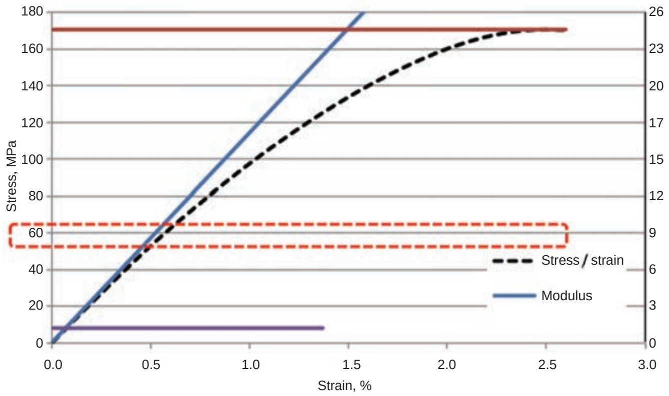


Fig. 20 Tensile stress/strain at 23 °C (73 °F) for nylon 6/6 30% glass fiber. Stress-strain curve represents the nylon 6/6 resin that was used to produce the failing aftermarket automotive components. The identified level of stress inherent to the application is indicated.

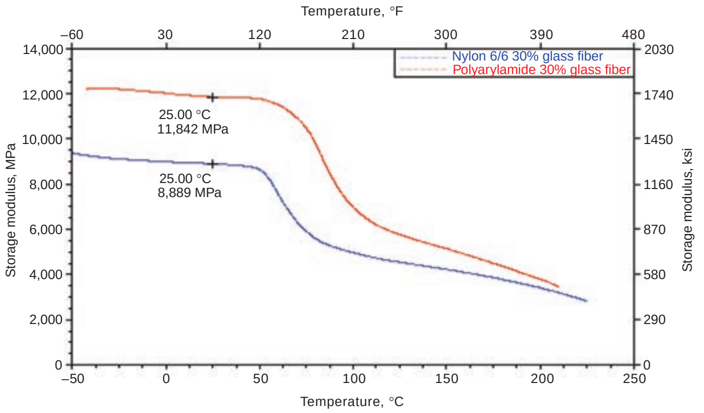


Fig. 21 Dynamic mechanical analysis thermogram overlay comparing the storage moduli of the failing and proposed materials. The proposed material exhibited a higher modulus and elevated glass transition.

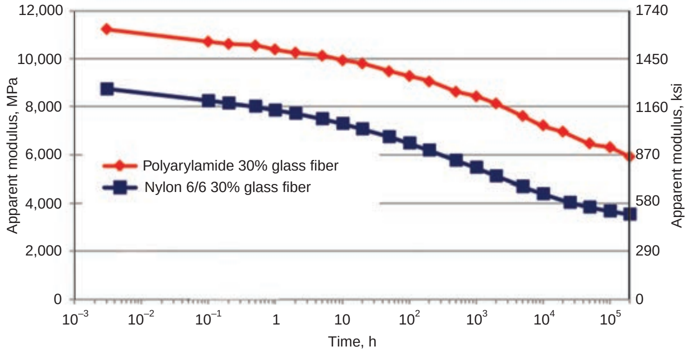


Fig. 22 Comparison of the apparent creep moduli of the failing and proposed materials at 25 °C (77 °F). The proposed material exhibits superior performance.

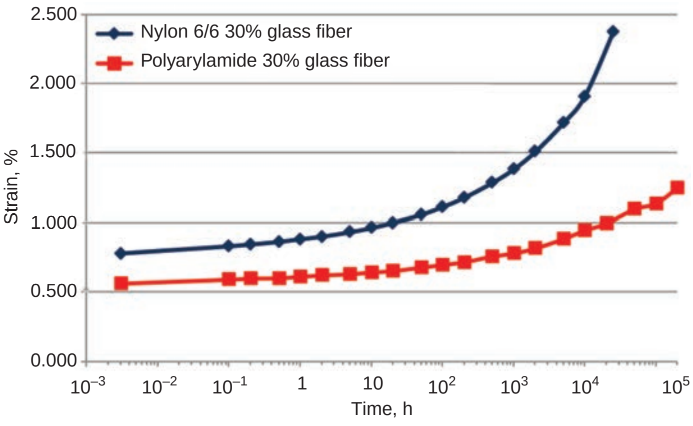


Fig. 23 Comparison of projected strain over time for the failing and proposed materials at 25 °C (77 °F). The proposed material exhibits a longer projected lifetime.

cracking on the buckets and circumferential cracking at the bottom. The samples also showed significant deformation in the form of buckling within the side wall. No signs of significant macro- or microductility were apparent, aside from the permanent deformation that is shared with the buckling. The fractographic examination revealed a single point of crack initiation on the longitudinal fractures. The origin was positioned along the outer diameter of the sidewall at the proximal apex of the bend associated with the buckling. This was consistent with the area on the pail that would be under the greatest level of tensile stress from the static loading. A comparison of the profiles of the failed and older retained buckets showed a distinct difference. The failed buckets exhibited a sink mark at the intersection of the bucket sidewall and the bottom wall, associated with molded-in residual stress, as shown in Fig. 24.

The failed and reference bucket materials were analyzed by FTIR. The obtained results produced an excellent match, and both spectra were characteristic of polyethylene. No signs of contamination or degradation were present.

The bucket materials were analyzed via DSC using a heat/cool/heat thermal profile. The initial heating run on the failed part material showed results consistent with an HDPE resin. Specifically, a melting point of 133 °C (271 °F) and a heat of fusion of 194 J/g were obtained. The heat of fusion obtained during the second heating run was significantly higher, 236 J/g. The difference in heat of fusion between the first and second runs indicated that the material was undercrystallized as-molded. The obtained thermograms are included in Fig. 25. The magnitude of the heat of fusion of the second heating run characterizes a relatively high-crystalline structure of the HDPE resin. The results of the second heating run obtained on the reference bucket material showed a significantly lower heat of fusion, 206 J/g. A comparison between the second heating runs is shown in Fig. 26. This was consistent with an HDPE resin that has a moderate crystalline structure. Specific gravity measurements were taken on the two materials, and they supported the DSC findings. The failed bucket material had a specific gravity of 0.959, while the retained bucket material was 0.951.

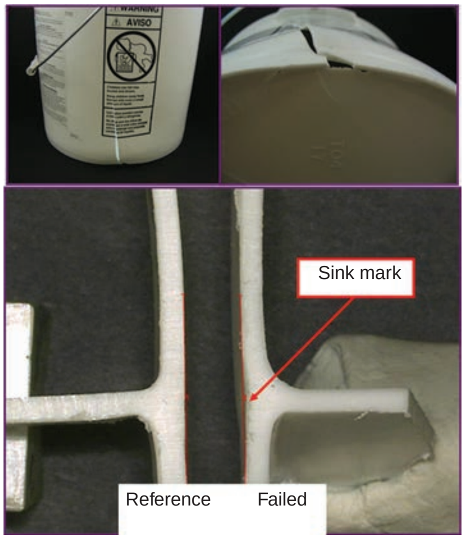


Fig. 24 Micrographs showing the buckling within a failed bucket. A sink mark within the sidewall is also illustrated.

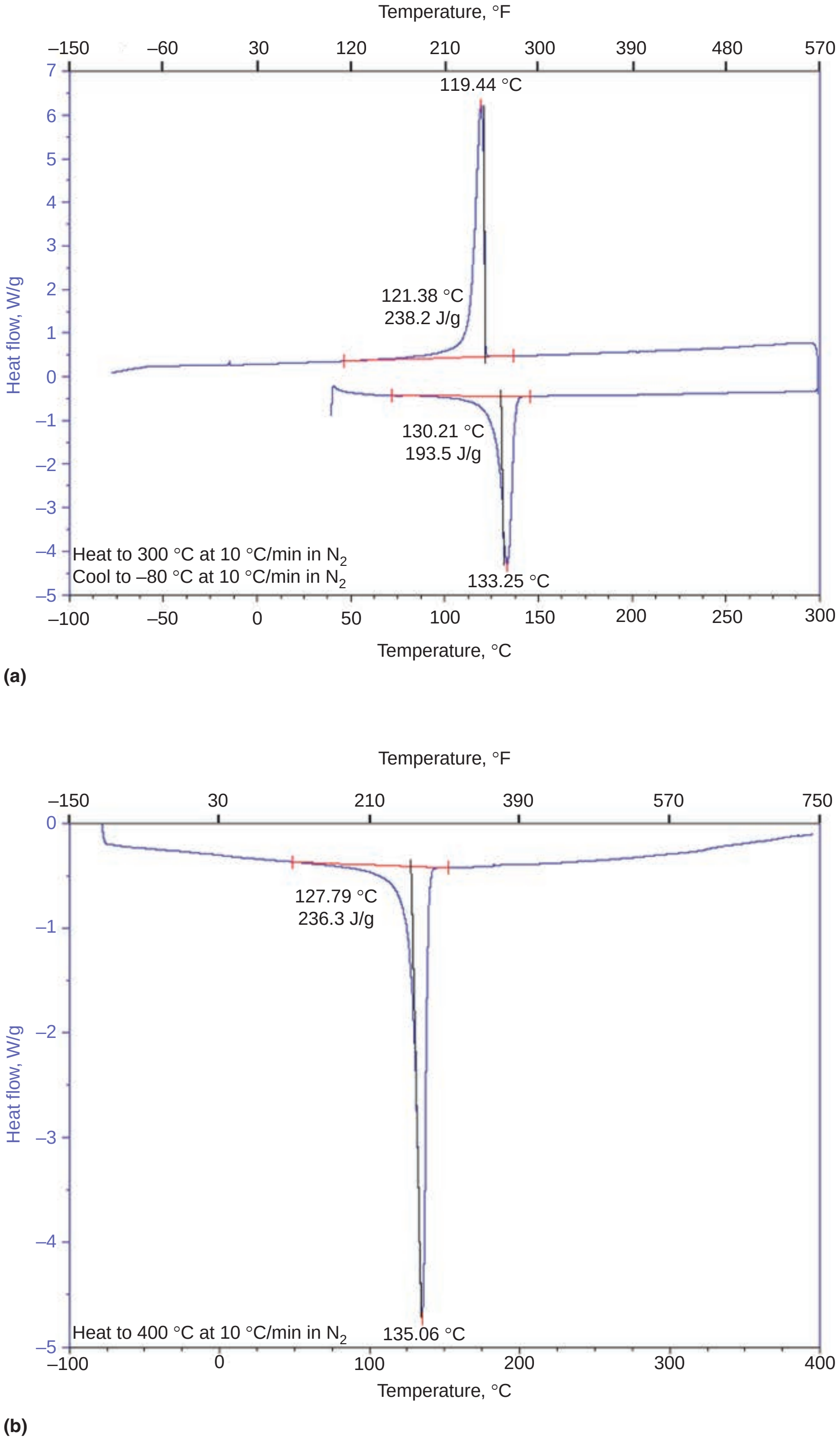


Fig. 25 Differential scanning calorimetry thermograms representing (a) the first and (b) the second heating runs obtained on the failed bucket material. A comparison of the heats of fusion shows that the material is undercrystallized as-molded.

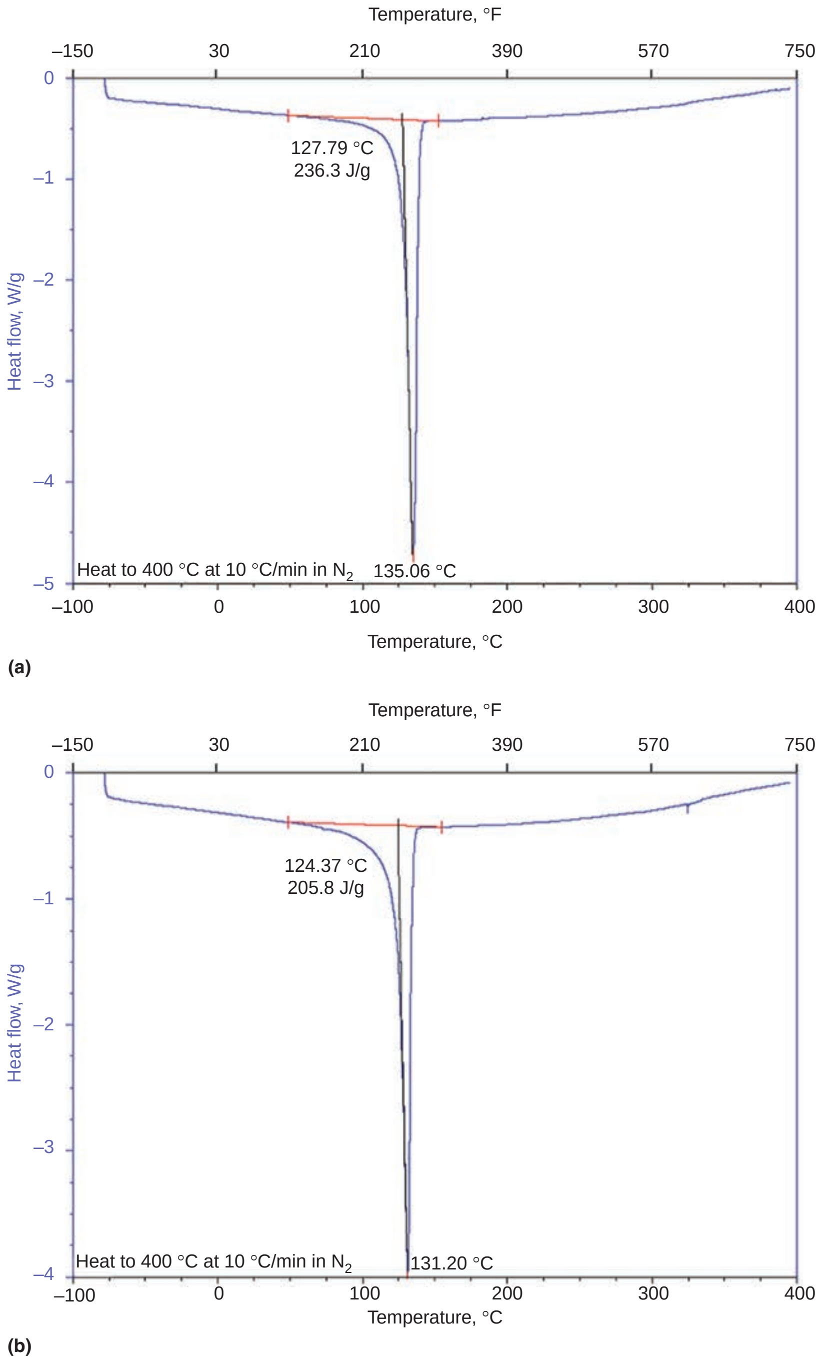


Fig. 26 Differential scanning calorimetry thermogram comparison showing the second heating runs for (a) the failed bucket material and (b) the reference bucket material. The failed bucket material has a substantially higher heat of fusion, indicating a greater level of crystallinity.

Melt flow rate testing performed on the two bucket materials produced comparable results, both approximately 6.0 g/10 min. This indicated that the materials had relatively consistent average molecular weight.

Conclusions

It was concluded through this analysis that the buckets failed by creep rupture associated with stresses that exceeded the long-term strength of the material. The stresses associated with the failure emanated from the stacking loads. Over time, longitudinal cracking initiated within the bucket sidewall, which subsequently extended until buckling occurred. The root cause of the failure, and the variation in performance demonstrated by the older buckets and the most recent production lot, was identified as a difference in the materials used to produce the buckets. Specifically, the two HDPE materials had different crystalline levels. This was verified through DSC and specific gravity testing. The more crystalline material corresponded with increased stiffness and reduced ductility in the molded part. This combination made the material more susceptible to creep-rupture failure.

Example 5: Radiation Penetration of an Instrument Housing

Housings for a piece of scientific equipment were failing engineering testing. Specifically, the housings allowed the penetration of ultraviolet (UV) radiation, which affected the internal workings of the instrumentation. It was indicated that the parts from a particular production run exhibited this phenomenon, while previously produced parts performed satisfactorily. The housings were specified to be injection molded from an unfilled grade of polycarbonate/poly(acrylonitrile-butadiene-styrene) (PC + ABS). The material was formulated with titanium dioxide to achieve UV opacity. A retained housing representing previous production was available for comparative analysis.

Tests and Results

Samples representing the two housing production lots were analyzed using FTIR in the attenuated total reflectance mode. A direct comparison of the spectra yielded an excellent match without significant spectral variation. Subsequent library searching and interpretation indicated that the spectra exhibited absorption bands that were characteristic of PC + ABS. One difference observed was that the results obtained on the retained reference housing exhibited a relatively broad absorption pattern between 750 and 400 cm^{-1}. This observance was also present in the failed housing but to a distinctly lesser degree, as illustrated in Fig. 27. Bands in this region of the infrared spectrum are often associated with metallic oxides.

The housing materials were further analyzed using TGA. The two materials produced very similar weight-loss profiles. Both samples underwent a major weight loss of approximately 78% while heating under the dynamic nitrogen purge. This weight loss was bimodal, with individual weight-loss maxima at 445 and 529 °C (833 and 984 °F). The bimodal nature of the weight loss was associated with individual decomposition mechanisms of the ABS and PC functionalities, respectively. Upon conversion to an air atmosphere, the two samples underwent a weight loss corresponding to the combustion of char remaining from the initial thermal decomposition of the polymers. The relative ratio of the weight loss under nitrogen and the weight loss under air was generally consistent across the two samples, which suggests that the materials contained similar ratios of PC to ABS. Upon completion of the evaluation, the samples showed a difference in the noncombusted residue content. The housing that had performed well produced a residue content of 5.4%, while the failed housing material had a residue content of 2.2%. The TGA weight-loss comparison is presented in Fig. 28.

The TGA residues were analyzed via EDS, and the results were consistent regarding the elements present, as shown in Table 4. Both samples showed relatively high concentrations of oxygen and titanium, with moderate levels of aluminum, silicon, phosphorus, and antimony. The oxygen and titanium were present as titanium dioxide. The phosphorus and antimony were likely present as flame-retardant additives, with the silica and aluminum present as a minor amount of a silicate-based mineral such as aluminum silicate. Significantly, the residue from the failed housing material exhibited relatively higher amounts of the aluminum, silicon, phosphorus, and antimony, which indicates that the titanium dioxide was present at a lower level. This was in agreement with the results obtained during the TGA analysis.

Conclusions

It was the conclusion of this analysis that the observed variation in UV opacity between the instrument housings was the result of a significant difference in the level of titanium dioxide formulated into the resins. The housing that performed well was formulated with a titanium dioxide content of approximately 5%, while the housings that allowed UV radiation penetration had a titanium dioxide content of approximately 2%.

Example 6: Accelerated Aging Failures in HDPE Tubing

Tubing from two different production lots performed significantly differently during an accelerated aging evaluation. The tubing was used in a water supply application, and it was manufactured from HDPE that was specially formulated with an antioxidant package. The accelerated aging was performed on an audit basis to assess incoming production lots for proper oxidative resistance. One of the lots performed as expected, consistent with previous production. The other lot exhibited signs of improvement and cracking as a result of the aging test.

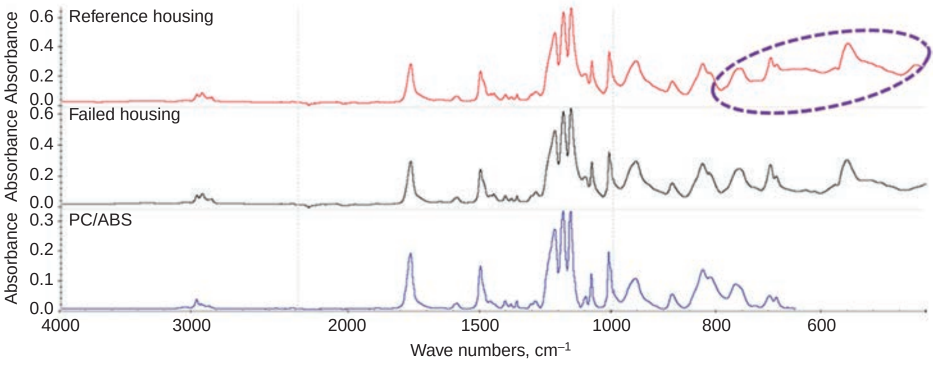


Fig. 27 Fourier transform infrared spectroscopy spectral comparison showing a subtle difference in absorption features between 750 and 400 cm^{-1}. The reference housing shows a higher relative level of absorptivity within this region. PC/ABS, polycarbonate/poly(acrylonitrile-butadiene-styrene)

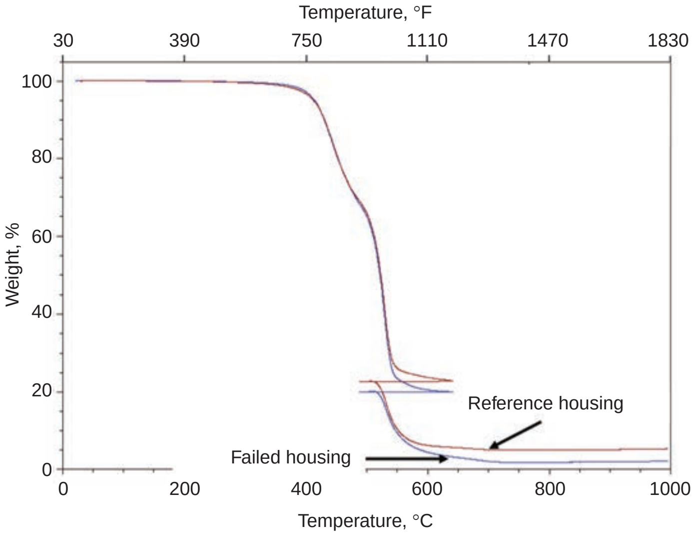


Fig. 28 Overlay showing thermogravimetric analysis weight-loss profile comparison. The reference housing material contains a higher level of noncombustible residual material compared with the failed housing material.

Tests and Results

Based upon the variation in performance identified during the accelerated aging test, compositional analysis was performed on the two lots of materials in the as-manufactured condition. The FTIR analysis of the two tubing lot materials produced results characteristic of a polyethylene resin, with no identifiable differences. Standard DSC analysis showed that both materials underwent a single endothermic transition at approximately 134 °C (273 °F), consistent with HDPE. Very similar heats of fusion were obtained for the two lot samples: 184 J/g for the exemplar lot and 180 J/g for the failed lot material. Melt flow rate testing showed further evidence of consistency, with the two materials producing values of 6.1 and 6.9 g/min. These analytical results indicated that the materials had similar crystalline structures and average molecular weights, important characteristics for polyethylene resins. Further, no evidence of contamination or other material anomalies was identified.

The two materials were comparatively evaluated for resistance to oxidation through DSC oxidative induction time (OIT). Triplicate specimens representing each production lot were analyzed. A review of the results showed excellent agreement between the three individual specimens from each lot. However, a distinct difference was apparent between the two lots. The exemplar lot had an OIT that was approximately twice that of the failed lot material. A comparison of the OIT performance is presented in Fig. 29.

Conclusions

It was the conclusion of this analysis that the tubing from the two individual production lots

Table 4 Energy-dispersive x-ray spectroscopy analysis indicating that a failed housing sample contained a lower level of titanium dioxide compared to a housing sample from a previous production

Element, relative wt%	Reference housing	Failed housing
Oxygen	40.3	62.7
Titanium	51.2	27.1
Sodium	0.9	···
Aluminum	1.3	2.5
Silicon	1.1	1.5
Phosphorus	3.7	5.9
Antimony	1.5	4.8

was manufactured from two different resins. While the two materials had similar crystallinity levels and average molecular weights, the level of oxidative protection was distinctly different. This variation in performance was likely associated with a significantly lower level of antioxidant formulated into the failed lot material compared with the exemplar lot. Further testing through gas chromatography/mass spectroscopy could be beneficial to confirm the antioxidant qualitatively and quantitatively.

Example 7: Cracking of Plastic Site-Gage Windows

Several site-gage windows that were used as part of a piece of industrial manufacturing equipment cracked while in service. The failures had taken place at one specific installation, with no other reported instances of cracking. While in service, the interior surface of the window comes in contact with commercial lubricants. The exterior surface may experience incidental contact with lubricants as part of the machine operation. Additionally, the exterior surface is occasionally cleaned. The windows are injection molded from an unfilled, transparent aromatic polyamide. Unused, as-molded parts as well as molding resin were also available for comparative analysis.

Tests and Results

The cracked site-gage windows were inspected visually, microscopically, and with the aid of an SEM. The fractographic examination indicated that the windows failed via brittle fracture precipitated by chemical interaction with the plastic material. The cracking initiated along the exterior surface and extended radially through the part wall as well as transversely and longitudinally through the part, as illustrated in Fig. 30. The fracture surface presented macro features characteristic of brittle fracture without apparent ductility. At higher magnification, isolated locations on the fracture surfaces exhibited a white flaky appearance. Additionally, distinct features, including pores, localized microstretching, a woody grainlike texture, and isolated material loss, were observed, as represented in Fig. 31. The fracture-surface characteristics were indicative of a combination of plasticization, solvation, dissolution, and environmental stress cracking, associated with extensive plastic-chemical interaction. The stress associated with the cracking may emanate from internal sources, such as molded-in residual stress, or externally from assembly stress.

The site-gage window samples were analyzed via FTIR, and the spectra obtained on the failed parts, as-molded parts, and molding resin produced an excellent match. The results were characteristic of a polyphthalamide (PPA) resin. No signs of contamination or degradation were evident in the FTIR results.

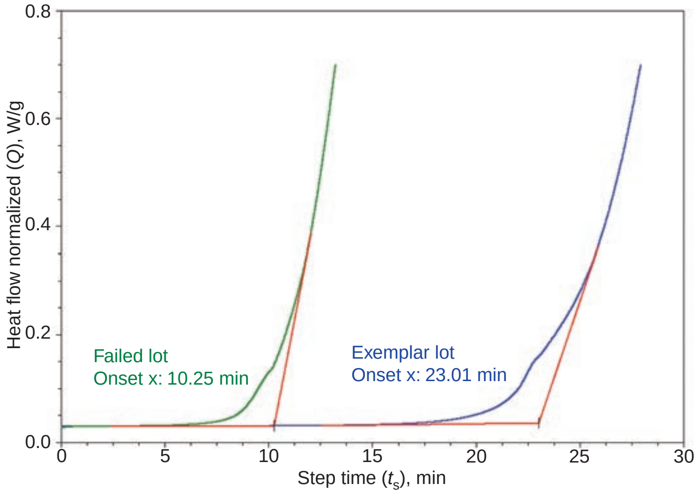


Fig. 29 Differential scanning calorimetry thermogram comparison showing a substantially higher oxidative induction time for the exemplar lot compared with the failed lot

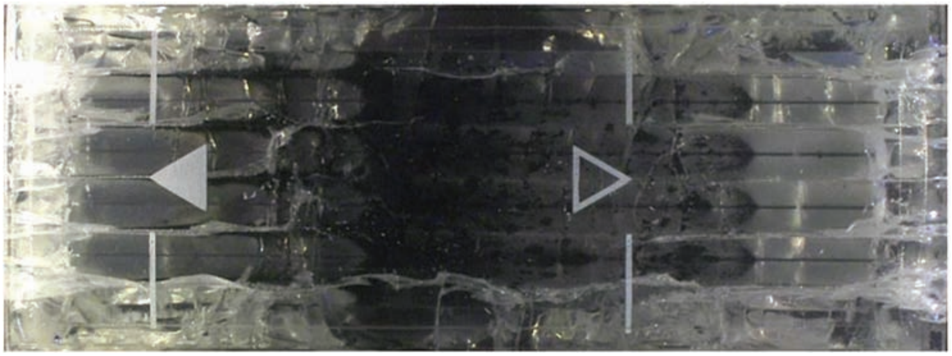


Fig. 30 Micrograph showing final cracking within the failed site-gage window. The cracking exhibits features that are characteristic of brittle fracture with no apparent ductility.

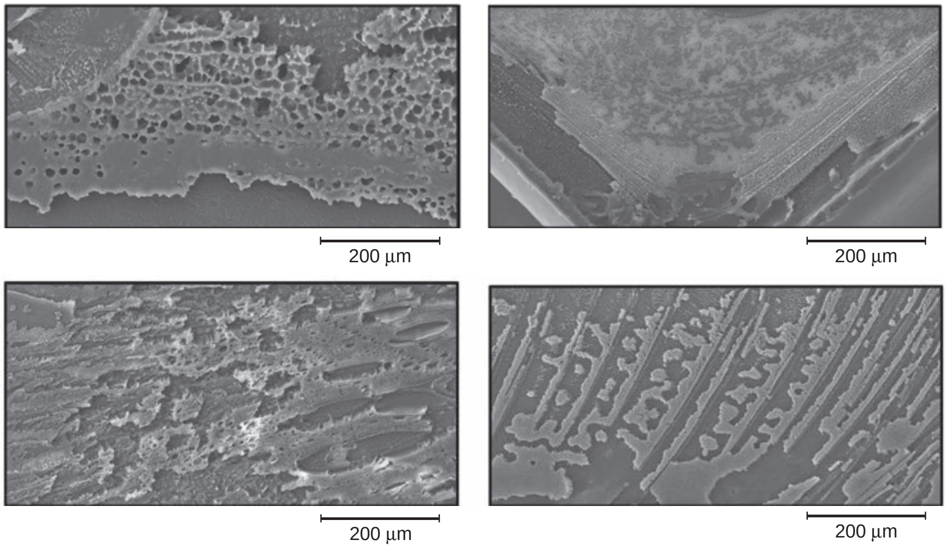


Fig. 31 Scanning electron micrographs showing features characteristic of substantial chemical interaction with the site-gage window material, magnification 500×

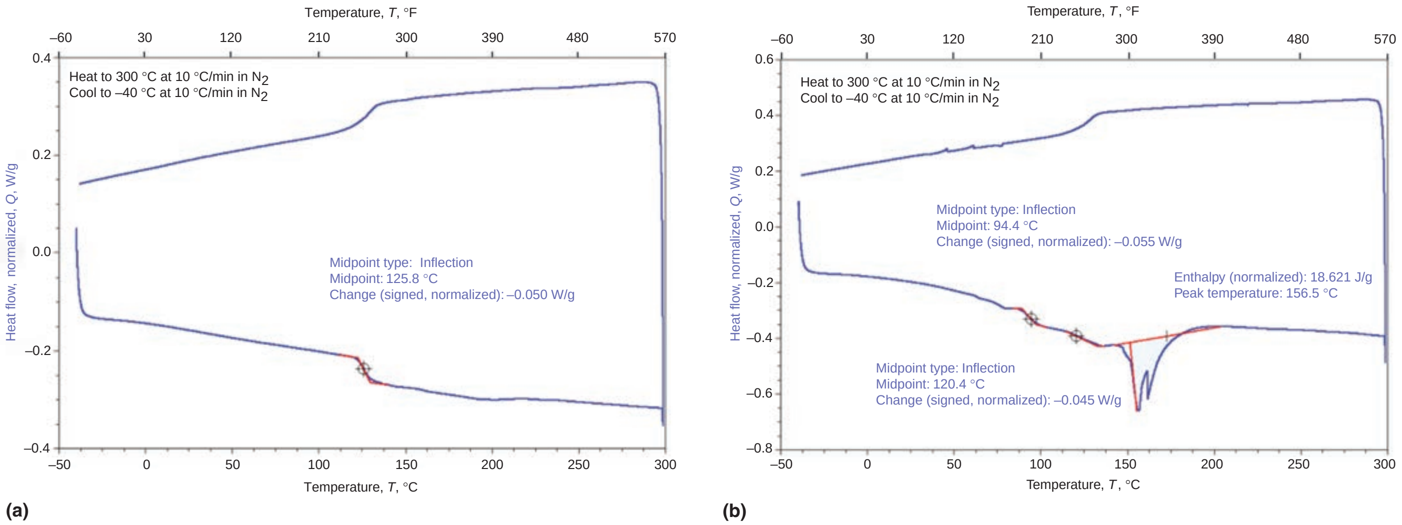


Fig. 32 Differential scanning calorimetry thermogram comparison of first heating results for the (a) molding resin and (b) failed part. An endotherm is present in the results obtained on the failed window material. The endotherm is characteristic of the melting of crystalline structure within the polyphthalamide material created through solvent-induced crystallization.

The molding resin and part materials were also analyzed using DSC. The thermograms obtained on the molding resin and the as-molded part material were very similar. The materials underwent a single shift in heat flow associated with the glass transition of the material during both the first and second heating runs. A T_g of 134 °C (273 °F) was obtained, which is consistent with the designation of the material as PPA. Analysis of the failed part material produced a very different response during the initial heating run, as presented in Fig. 32. The material underwent two shifts in heat flow, with identified glass transitions at 94 and 120 °C (201 and 248 °F). The material also showed a significant bimodal endothermic transition centered at 157 °C (315 °F). This was thought to represent the melting of crystalline content within the material. The crystal structure within the material formed through solvent-induced crystallization. During the controlled cooling phase of the analysis, the material underwent a single shift in heat flow with no recrystallization. During the second heating run, the results were very similar to those obtained on the resin and as-molded part materials, and a T_g of 133 °C (271 °F) was determined.

Melt flow rate testing was performed on the molded window samples and the molding resin. The testing produced an MFR of 23.1 g/10 min for the molding resin and 35.6 and 39.8 g/10 min for the as-molded and failed parts, respectively. This shift in MFR indicated excessive molecular degradation as a result of the injection molding process.

Conclusions

The analysis concluded that the site-gage windows cracked through brittle fracture that was precipitated by severe chemical interaction with the plastic material. The magnitude of the chemical interaction was indicated by characteristic features observed during the fractographic examination as well as the formation of solvent-induced crystallization within the window material. The grade of PPA material used to mold the windows does not form a crystalline structure through heat processing. The DSC results indicated that the failed part material had formed crystalline content within the preferentially amorphous material. It is possible to achieve crystalline structure within amorphous materials if the polymer dissolves in a solvent and then the solvent evaporates slowly. The source of the chemical agent is likely aggressive solvents used to clean the manufacturing equipment.

ACKNOWLEDGMENT

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REFERENCES

1. J.A. Jansen, Conducting a Plastic Component Failure Investigation: Examples from the Appliance Industry, *International Appliance Technology Conference*, March 2002, p 2
2. J.A. Jansen, Plastic Component Failure Analysis, *Adv. Mater. Process.*, May 2001, p 56, 58, 59
3. A.T. Riga and E.A. Collins, Analysis of Structure, *Engineering Plastics*, Vol 2, *Engineered Materials Handbook*, ASM International, 1988, p 825, 826
4. Characterization of Plastics in Failure Analysis, *Characterization and Failure Analysis of Plastics*, Steven Lampman, Ed., ASM International, 2003, p 368–382
5. J. Scheirs, *Compositional and Failure Analysis of Polymers*, John Wiley & Sons, 2000, p 109, 138, 153, 393, 415
6. M.P. Sepe, *Thermal Analysis of Polymers*, RAPRA Technology, Shawbury, U.K., 1997, p 3, 4, 8, 17, 19, 22, 24, 33
7. L.C. Roy Oberholtzer, General Design Considerations, *Engineering Plastics*, Vol 2, *Engineered Materials Handbook*, ASM International, 1988, p 21
8. *Polymer Characterization: Laboratory Techniques and Analysis*, Noyes Publications, 1996, p 15
9. S.B. Driscoll, Physical, Chemical, and Thermal Analysis of Thermoplastic Resins, *Engineering Plastics*, Vol 2, *Engineered Materials Handbook*, ASM International, 1988, p 533
10. S. Turner, Mechanical Testing, *Engineering Plastics*, Vol 2, *Engineered Materials Handbook*, ASM International, 1988, p 545
11. M. Ezrin, Plastics Analysis: The Engineer's Resource for Troubleshooting Product and Process Problems and for Competitive Analysis, *Plast. Eng.*, Feb 2002, p 45, 46

SELECTED REFERENCES

- W. Brostow and R.D. Corneliussen, *Failure of Plastics*, Hanser Publishers, 1986

- T.R. Crompton, *Practical Polymer Analysis*, Plenum Press, 1993
- T.R. Crompton, *Manual of Plastics Analysis*, Plenum Press, 1998
- M. Ezrin, *Plastics Failure Guide*, Hanser Publishers, 2013
- *G.E. Engineering Thermoplastics Design Guide*, G.E. Plastics, 1997
- J.W. Gooch, *Analysis and Deformulation of Polymeric Materials*, Plenum Press, 1997
- W. Grellmann and S. Seidler, *Polymer Testing*, Hanser Publishers, 2007
- E. Kaiserberger, S. Knappe, H. Mohler, and S. Rahner, *TA for Polymer Engineering*, Vol 1, Vol 2, and Vol 3, Netzsch, 1994
- F. Kurr, *Handbook of Plastics Failure Analysis*, Hanser Publishers, 2015
- J. Moalli, Ed., *Plastics Failure: Analysis and Prevention*, Plastics Design Library, 2001
- T.A. Osswald and G. Menges, *Materials Science of Polymers for Engineers*, Hanser Publishers, 1995
- R.C. Portney, Ed., *Medical Plastics: Degradation Resistance and Failure Analysis*, Plastic Design Library, 1998
- B.C. Smith, *Fundamentals of Fourier Transform Infrared Spectroscopy*, CRC Press, 1996
- E.A. Turi, Ed., *Thermal Characterization of Polymeric Materials*, Academic Press, Inc., 1981
- D. Wright, *Failure of Plastics and Rubber Products*, RAPRA Technology, Shawbury, U.K., 2001