

Characterization of Plastics in Failure Analysis

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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 general steps required to conduct a comprehensive failure investigation are the same, and these are outlined in Fig. 1. In general, 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 a broad knowledge of polymeric materials.

Plastic components can fail via many different modes, including catastrophic mechanisms, such as brittle fracture, ductile overload, creep rupture, environmental stress cracking, molecular degradation, and fatigue. In the case of failure involving fracture, the determination of the failure mode involves identifying how the crack initiated and how it subsequently extended. This is usually ascertained using a number of visual-based techniques, such as stereomicroscopy, scanning electron microscopy (SEM), and the preparation of mounted cross sections. Noncatastrophic failure modes are also relevant, and these include discoloration, distortion, and contamination. Assessing the mode of the failure is often not as difficult as establishing why the part failed. Evaluating why the part failed 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 of the factors that affect the performance of a plastic component can be classified into one of four categories: material, design, processing, and service conditions (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 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 molecular weight, crystallinity, and orientation, and this has a significant impact on the properties of the molded article. Additionally, plastic resins usually contain 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 most commonly used in plastic component failure analysis. The description of the techniques is not designed to be a comprehensive review and tutorial but instead is intended to make the reader familiar with the general principles and benefits of the methodologies. The descriptions of the analytical techniques are supplemented by a series of case studies. The technique descriptions refer to the case studies, and the two are written in a complimentary manner to illustrate the significance of the 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 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, revealing the structure of the sample. Fourier transform infrared spectroscopy produces a unique spectrum, which is comparable to the fingerprint of the material. It is the principle analytical technique used to qualitatively identify polymeric materials.

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, transmittance, reflectance, and attenuated total reflectance (ATR) are the most common sampling techniques. 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 of the sample and directed to a detector. The obtained spectrum shows those frequencies that the material has absorbed and those that have been transmitted, as illustrated in Fig. 3. The spectrum can be interpreted manually, or more commonly, compared with voluminous library references with the aid of a computer.

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 wavenumbers. The discrete spectral features present with a FTIR spectrum are known as absorption bands.

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 used to produce the sample. The determination of the composition of the failed component is an essential part of the investigation. Because different polymers have a wide variation in their physical, me-

chanical, 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 having different molecular structures, and this is illustrated in Fig. 4. Confirming that the failed article was produced from the specified material is the 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 this article. One area where FTIR is inadequate is in differentiating between polymers having similar molecular structures, such as the members of the nylon family, and poly(ethylene terephthalate) and poly(butylene terephthalate). 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 is used to characterize 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 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

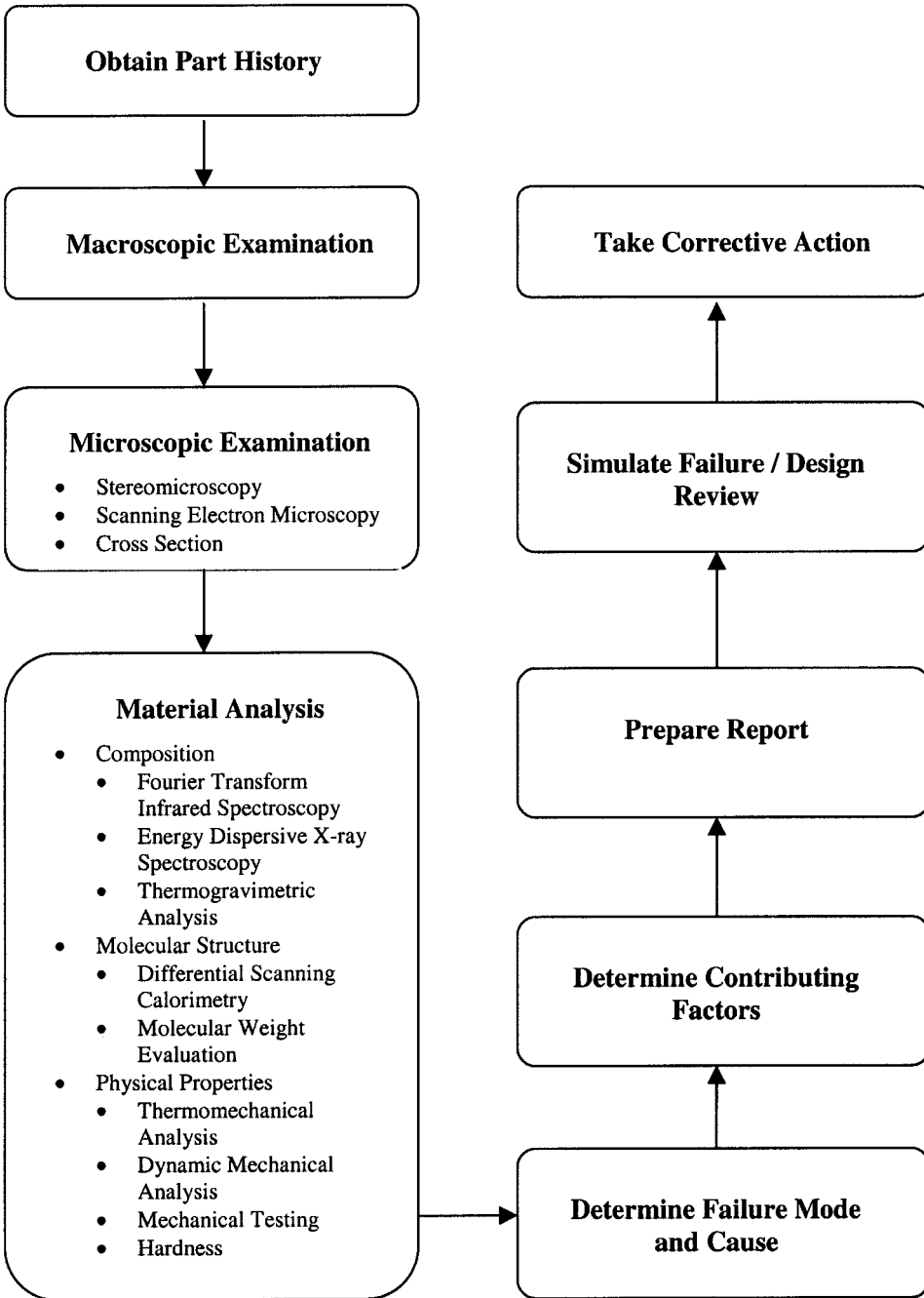


Fig. 1 Steps for performing failure analysis. The steps are the same regardless of the material

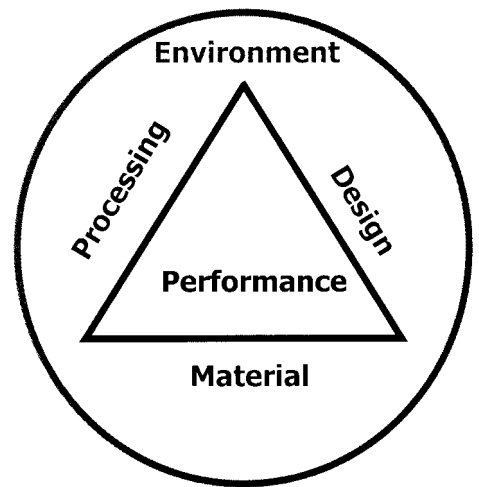


Fig. 2 Graphical representation of the four factors influencing plastic part performance

absorption spectra. Example 6 in this article shows the analysis of plastic-resin formulation constituents.

Contamination. Similar to its ability to identify the plastic formulation constituents, FTIR is extremely useful in the determination of contaminant materials within the failed part material. While contamination is never an intended part of a plastic compound, its presence certainly can have a tremendous impact on the properties of the molded component. Through the electronic manipulation of the obtained FTIR results, including spectral subtraction, extraneous absorption bands 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 discussed in examples 3 and 8 in this article.

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 product 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 determining the mechanism of the degradation. Specifically, several spectral bands and the corresponding molecular structure can be ascertained, including carbonyl band formation representing oxidation, vinylidene group formation as an indication of thermal oxidation, vinyl, vinylene functionality for photooxidation, and hydroxyl group formation indicating hydrolysis (Ref 4). Case studies showing the effectiveness of FTIR in assessing molecular degradation are presented in examples 1, 13, and 15 in this article.

Chemical Contact. Parallel 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, 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 4).

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 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 this article illustrate the identification of chemicals that had been in contact with a failed plastic component.

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

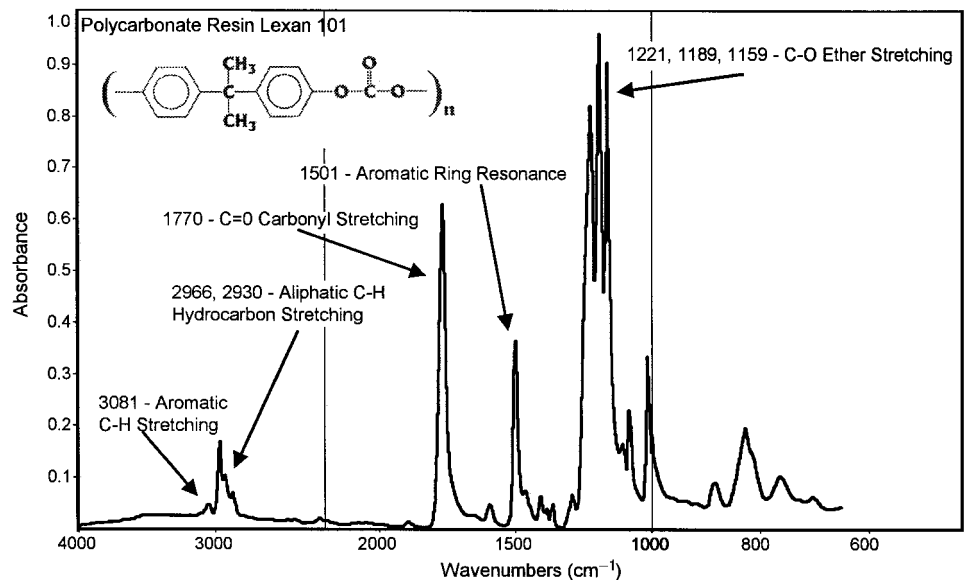


Fig. 3 A typical FTIR spectrum illustrating the correlation between structure and absorption bands

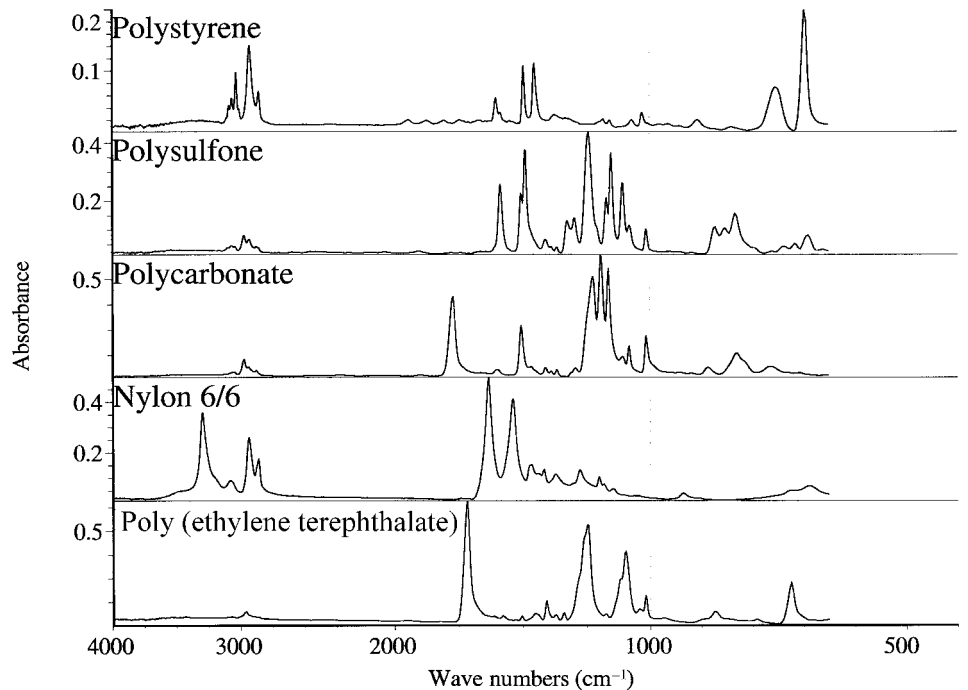


Fig. 4 Fourier transform infrared spectral comparison showing distinct differences between the results obtained on various plastic materials

2). Differential scanning calorimetry monitors the difference in heat flow between a sample and a reference as the material is heated or cooled (Ref 5). The technique is used to evaluate thermal transitions within a material. Such transitions include melting, evaporation, crystallization, solidification, cross linking, chemical reactions, and decomposition. A typical DSC result is presented in Fig. 5. 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 5), the limitation being that commercially available equipment may not be able to detect transitions within materials that are present at concentrations below 5% (Ref 4).

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, either in the form of an empty pan of the same type or an inert material having the same weight as the sample, is used. 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, with thermocouples used to measure the differential heat flow (Ref 5). 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 in order to eliminate 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 de-

tection 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 5). The melting point (T_m) of a semi-

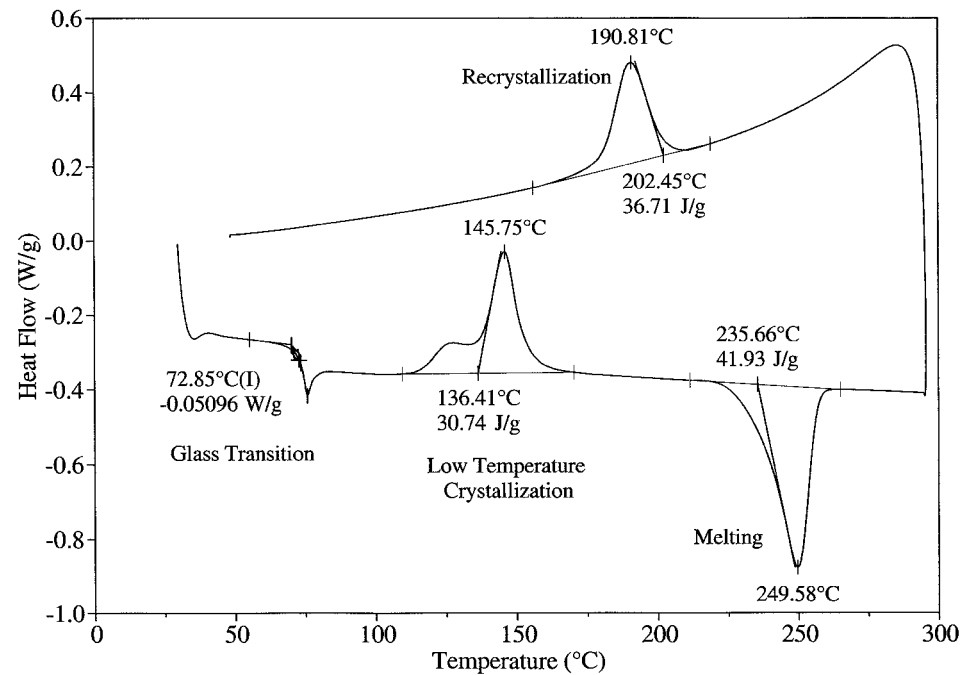


Fig. 5 Differential scanning calorimetry thermogram showing various transitions associated with polymeric materials. The (I) indicates that the numerical temperature was determined as the inflection point on the curve.

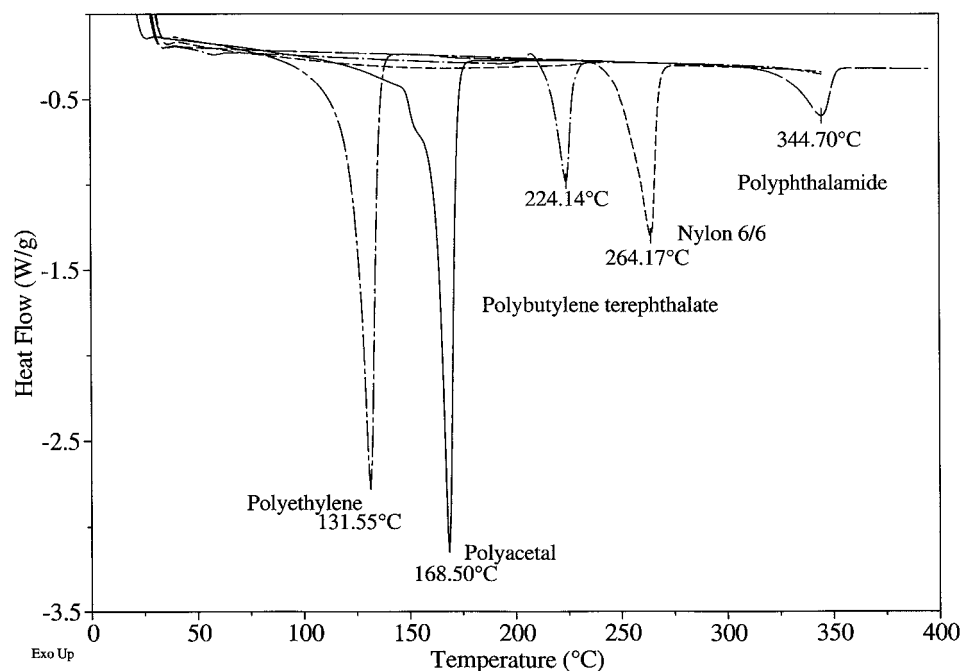


Fig. 6 Differential scanning calorimetry used to identify polymeric materials by determination of their melting point.

crystalline 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. 6. The T_m is used as a means of identification, particularly when other techniques, such as FTIR, cannot distinguish between materials having similar structures. 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 this article.

The heat of fusion represents the energy required to melt the material and 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. Examples 11 and 12 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 this article shows how low-temperature crystallization was detected via DSC.

Glass Transition in Amorphous Plastics. Polymers that do not crystallize and semicrystalline materials having 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 6). 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. 7. 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 5), "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 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. Instances of degradation detected by DSC are presented in examples 7, 14, and 15 in this article. 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.

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 or to determine whether a plastic resin has undergone partial oxidation.

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 can provide valuable information regarding the composition and thermal stability of polymeric materials. The obtained data can include the volatiles content, inorganic filler content, carbon black content, the onset of thermal decomposition, and the volatility of additives such as antioxidants (Ref 4).

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 com-

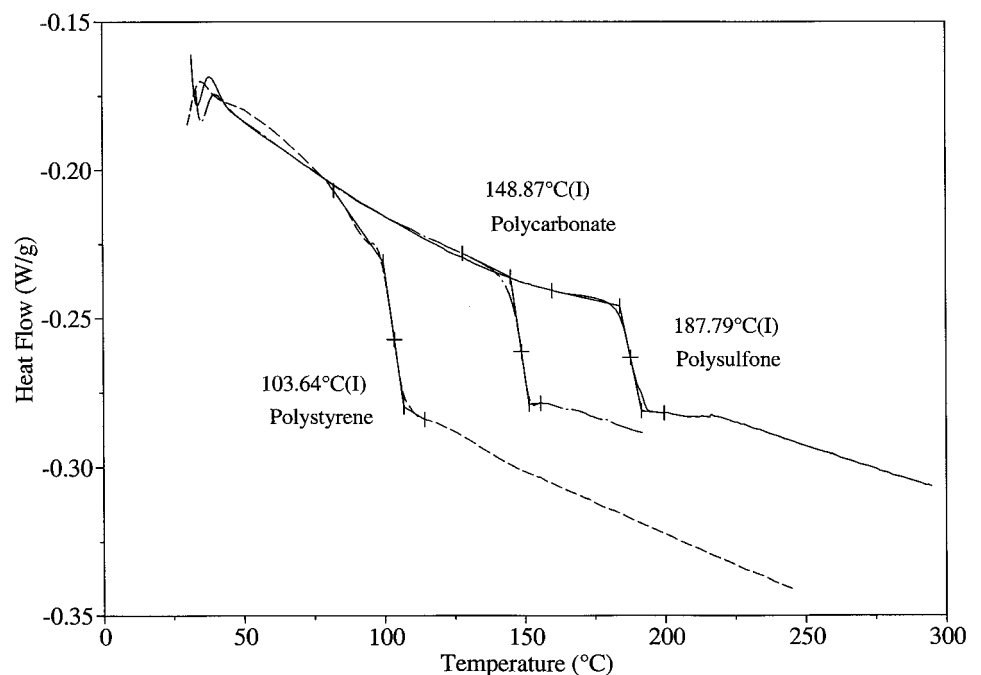


Fig. 7 Differential scanning calorimetry used to detect glass transitions within amorphous thermoplastic resins. The (I) indicates that the numerical temperature was determined as the inflection point on the curve.

position 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 100 mg, with samples as large as 1000 mg possible. Minimal sample preparation is required for TGA experiments.

Results

The results obtained as part of 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 in the assessment of 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 assessed. The assessment of a plastic resin composition is illustrated in Fig. 8. This data is 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 energy-dispersive x-ray spectroscopy (EDS) in order to evaluate its composition. The use of TGA in characterizing plastic composition is presented in examples 8, 10, 12, and 15 in this article. Additionally, example 11 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 5). However, a comparison of the obtained TGA thermograms can provide insight into possible degradation of the failed component material. Example 6 in this article illustrates a comparison of the thermal stability of two polymeric materials, while example 13 shows 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. Such measurements, however, provide little information 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.

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, par-

allel sides. Additionally, fiber and film samples can also 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 analysis, similar to 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

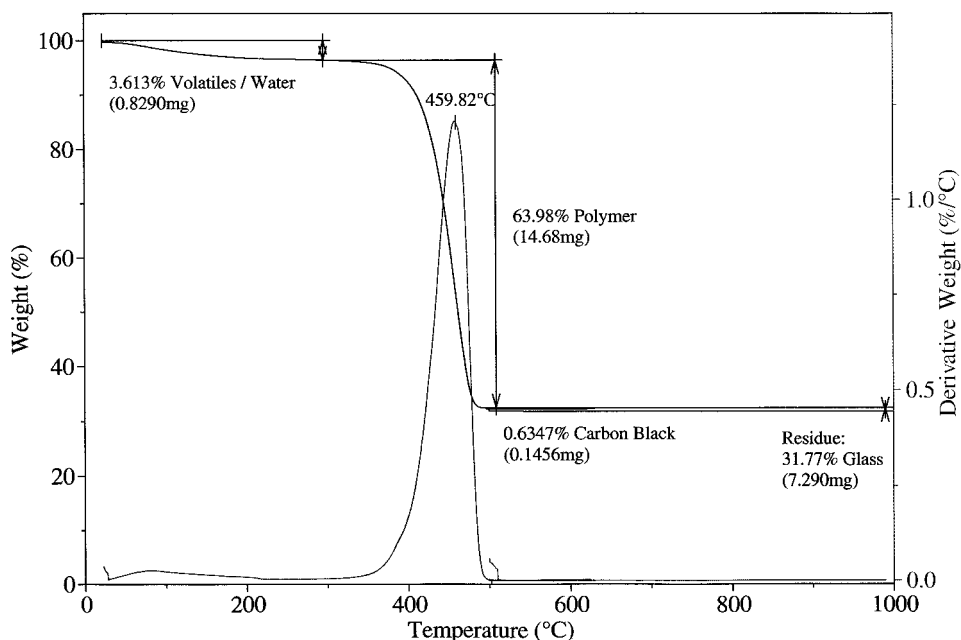


Fig. 8 Thermogravimetric analysis thermogram showing the weight-loss profile for a typical plastic resin

change in the length of a material as a response to a change in temperature. The derivative of the slope of the line showing the dimensional changes with respect to temperature represents the CTE. 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. 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 this article.

Material Transitions. According to Sepe (Ref 5). "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. 9. The physical properties of the material can be expected to be significantly different across this transition. Amorphous resins soften at the T_g , and 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. 10. The evaluation of the glass transition is presented in example 14 in this article. Thermo-mechanical 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 5).

Molded-In Stress. Internal molded-in stress is an important source of the total stress on a plastic component and 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. 11. 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.

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. Dynamical 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 and time (Ref 5). 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 mea-

surement 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-axes 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. 12.

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

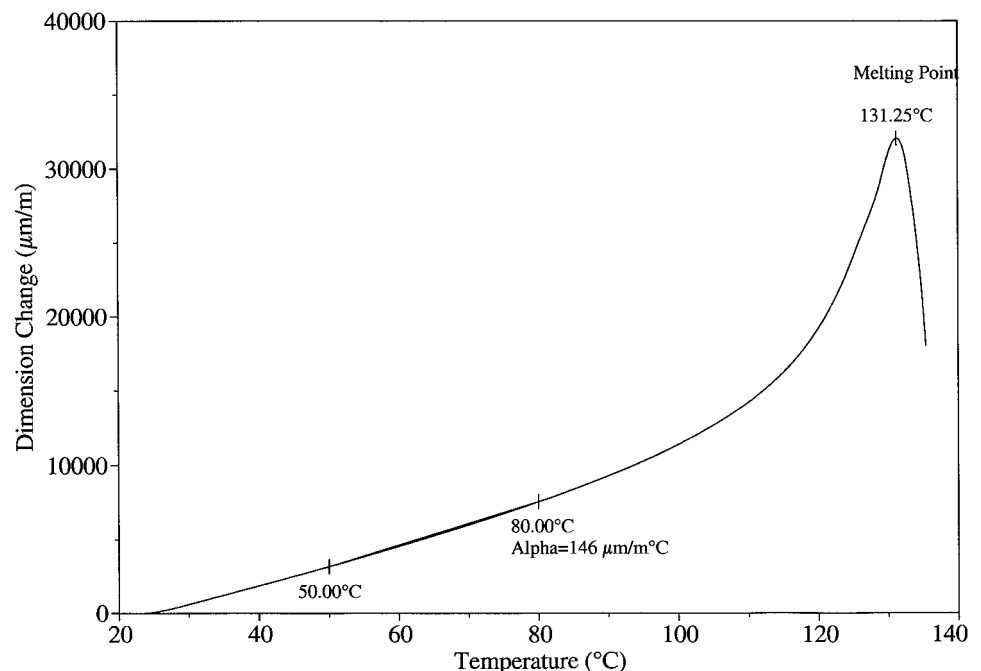


Fig. 9 Thermogravimetric analysis thermogram representing a typical semicrystalline plastic resin

over a temperature range. The loss modulus and tan delta provide data on temperatures where molecular changes produce property changes, such as the glass transition and other secondary transitions not detectable by other thermal analysis techniques. The superiority of DMA over DSC and TMA for assessing the glass transition is well documented (Ref 5). 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 is well predicted by DMA.

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 5) 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 this article shows the changes in mechanical properties of a plastic resin associated with chemical absorption. The experiments can also evaluate the recovery after the removal or evaporation of the absorbed liquid.

Methods for Molecular Weight Assessment

The aspect of molecular structure, and specifically molecular weight, makes polymeric materials unique among materials 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 4). 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 characteristics 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 can 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 (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 used in conjunction 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 di-

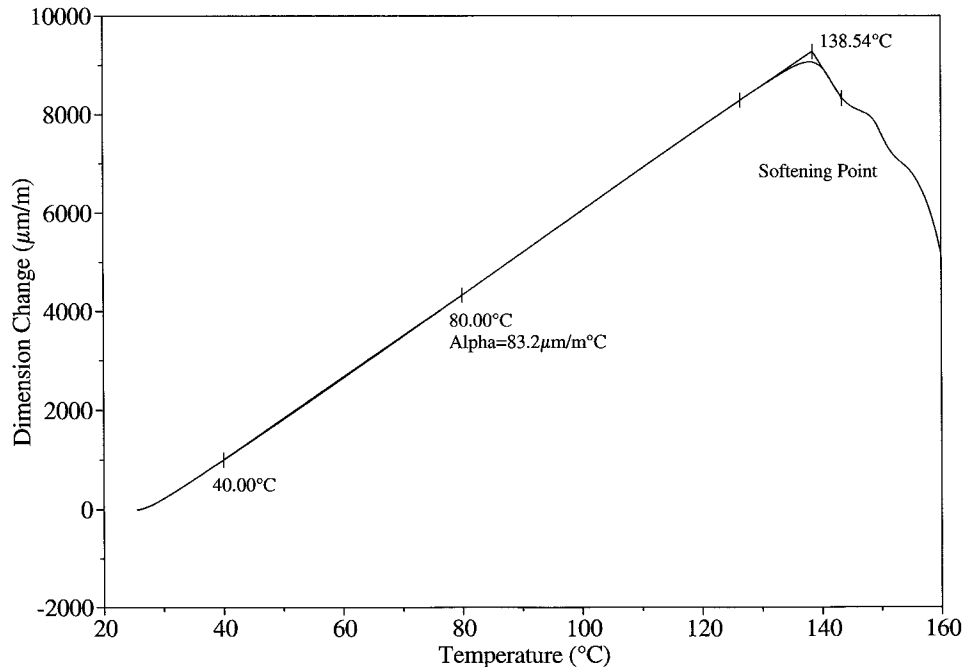


Fig. 10 Thermogravimetric analysis thermogram representing a typical amorphous plastic resin

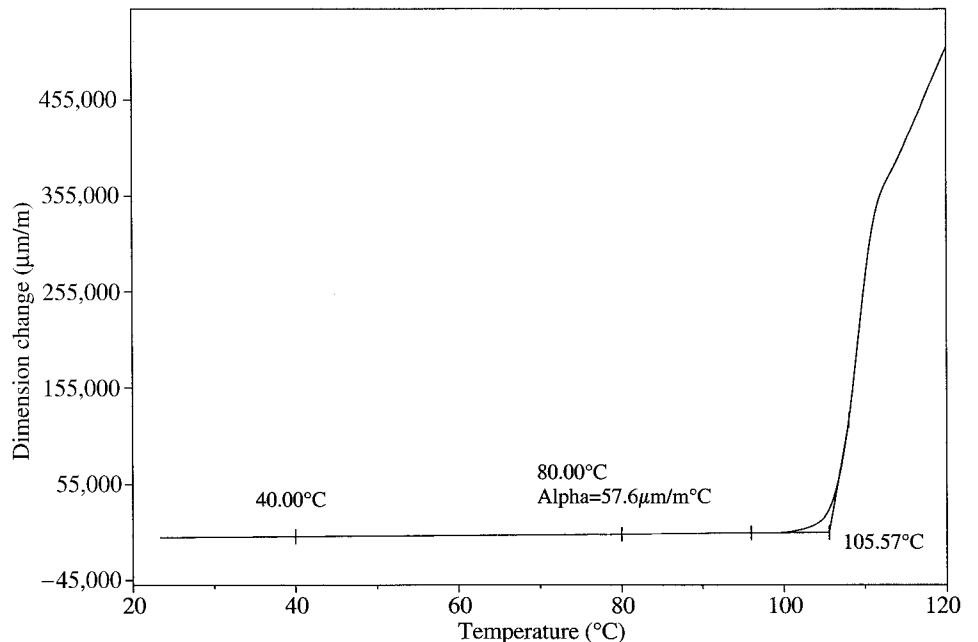


Fig. 11 Thermogravimetric analysis thermogram showing a high level of residual stress in an amorphous plastic resin

rectly represent the actual molecular weight and molecular weight distribution of the plastic resin. Another advantage is that GPC requires a relatively small sample size, 30 to 120 μg , for a complete evaluation (Ref 7). The technique, however, is often complicated to perform, using sophisticated instrumentation, and difficult to interpret. Example 10 in this article 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 having a standard-sized orifice. Different materials use various test conditions, including temperature and load. The method for determining the MFR is described in ASTM D 1238. Melt flow rate is the simplest technique for assessing the molecular weight of a plastic material and is inversely proportional to the molecular weight of the polymer (Ref 4). 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 this article describe the use of melt flow 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 and represents only the average molecular weight of the material. Because of this, the blending of polymers having different molecular weight distributions and average molecular weights can result in equal determinations between very different materials having 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. 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 (PVC), according to ASTM D 1243, requires either a 1 or 4% concentration in cyclohexanone or dinitrobenzene, while polyamides, or nylons, require formic acid. Other engineering polymers might require tetrahydrofuran, dimethylformamide, dimethylsulfoxide, or other equally hostile solvents (Ref 8). The obtained solution viscosity values are only indications of molecular weight and do not reflect the absolute weight values (Ref 8). Example 9 in this article illustrates the use of solution viscosity in a failure investigation.

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 9). One very useful way to classify the various mechanical test methods is to distinguish between tests that evaluate long-term properties, as opposed to 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. Short-term tests, while generally easy to conduct and interpret, 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 most commonly performed mechanical test used to evaluate plastic material properties is the tensile test. This testing is performed on a dumbbell-shaped specimen and is outlined in ASTM D 638. 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. Flexural testing 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 D 790.

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 D 3029.

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.

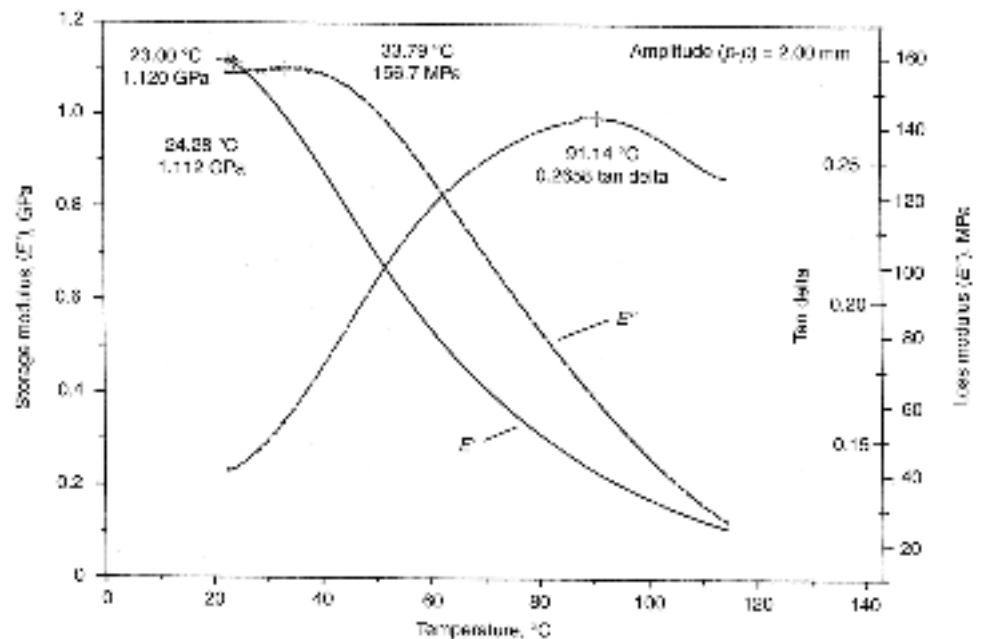


Fig. 12 Dynamic mechanical analysis thermogram showing the results obtained on a typical plastic resin. Tan delta is ratio of the loss modulus to the storage modulus.

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 this article.

scopy is useful in polymeric analysis, providing information related to composition beyond FTIR. Nuclear magnetic resonance can provide data regarding stereoregularity, carbon content, chemical composition, and copolymer structure (Ref 10). 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 are particularly suited for the analysis of surface contaminants (Ref 10). While these analytical techniques can

Table 1 Practical information derived from polymer analysis methods

Test method	Properties measured	Use in 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

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, with the obtained data only being as good as the analysis method. Further, the data presented by the analytical methods are often complicated and, in many cases, require an experienced analyst to be properly interpreted.

The aforementioned analytical tests are not meant to be an all-encompassing list of the methods used to evaluate failed plastic components. Certainly, there are numerous testing methodologies that provide data pertinent to a plastic component failure analysis. Other analysis techniques, including EDS and SEM, are important tools in a plastic component failure analysis. Scanning electron microscopy and EDS methods are covered elsewhere 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 spec-

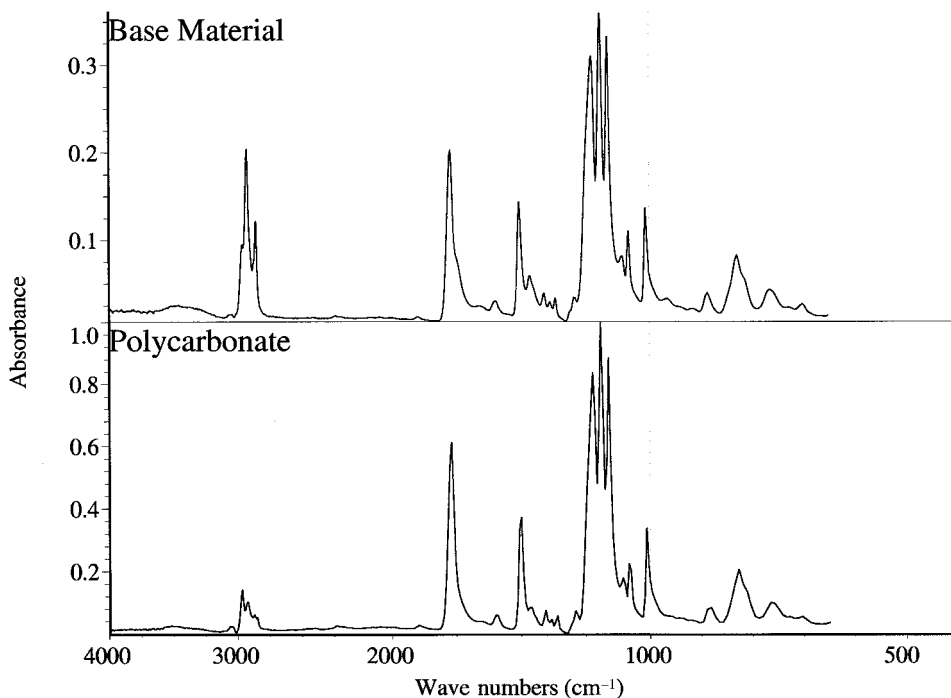


Fig. 13 The FTIR spectrum obtained on the bracket base material, exhibiting absorption bands characteristic of polycarbonate

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. Given the charge that this article be treated in a practical manner, test methods used less often were omitted. A summary showing both the treated and omitted analysis methods and the corresponding information gained is included in Table 1 (Ref 3).

Case Studies

Example 1: Embrittlement of a Polycarbonate Bracket. A plastic bracket exhibited relatively brittle material properties, which ultimately led to catastrophic failure. The part had been injection molded from a medium-viscosity polycarbonate resin and had been in service for a short duration prior to the failure.

Tests and Results. A visual examination of the bracket revealed a series of surface anomalies, and it was suspected that the presence of the defects was related to the premature failure. The component base material was analyzed using micro-FTIR in the attenuated total reflectance (ATR) mode. The obtained spectrum exhibited absorption bands characteristic of polycarbonate, as shown in Fig. 13. No evidence of material contamination was found. A similar analysis was performed on the part surface in an area that showed the anomalous surface condition. The spectrum representing the surface was generally similar to the results obtained on the base material. However, the surface spectrum showed a

relative increase in the intensity of a spectral band between 3600 and 3350 cm^{-1} , indicative of hydroxyl functionality. Additionally, the spectrum also showed changes in the relative intensities of several bands, as compared to the results representing the base material. A spectral subtraction was performed, and the results produced a good match with a library reference of diphenyl carbonate. This is illustrated in the spectral comparison presented in Fig. 14. Diphenyl carbonate is a common breakdown product produced during the decomposition of polycarbonate.

Conclusions. Overall, the obtained results suggested that the anomalous surface condition observed on the bracket represented molecular degradation of the polycarbonate. This is consistent with the brittle properties exhibited by the component. The most likely cause of the molecular degradation was improper drying and/or exposure to excessive heat during the injection molding process.

Example 2: Chemical Attack of Acrylonitrile-Butadiene-Styrene Grips. A set of plastic grips from an electric consumer product failed while in service. The grips had been injection molded from a general-purpose grade of an acrylonitrile-butadiene-styrene (ABS) resin. The parts had cracked while in use after apparent embrittlement of the material.

Tests and Results. An examination of the grips confirmed a severe level of cracking, covering the majority of the grip surface. Handling of the parts revealed that the grip material exhibited very little integrity, unlike the usual ductility associated with ABS resins. A white discoloration

was also observed on the otherwise red grips. The surface of the grips was evaluated using SEM, revealing isolated areas that showed significant degradation in the form of material loss, as shown in Fig. 15. The observed morphology suggested selective degradation of the polybutadiene domains within the ABS resin.

Micro-FTIR in the ATR mode was used to analyze the base material and the surfaces of the grips. The results obtained on the base material were characteristic of an ABS resin. Analysis of the surface of the part produced a somewhat different result. The spectrum representing the grip surface contained absorption bands associated with ABS; however, the results contained additional bands of significant intensity. A spectral subtraction was performed, thereby removing the bands associated with the ABS resin. The obtained subtraction spectrum produced a very good match with glyceride derivatives of fats and oils. This identification is illustrated in Fig. 16.

Conclusions. It was the conclusion of the analysis that the grips failed via brittle fracture associated with severe chemical attack of the ABS resin. A significant level of glyceride derivatives of fatty acids, known to degrade ABS resins, was found on the part surface. The glyceride derivatives selectively attacked the polybutadiene domains within the molded ABS part, leading to apparent embrittlement and subsequent failure.

Example 3: Inclusion within an ABS Handle. The handle from a consumer product exhibited an apparent surface defect. The handle had been injection molded from a medium-viscosity-grade ABS resin. The anomalous appearance was objectionable to the assembler of the final product and resulted in a production lot being placed on quality-control hold.

Tests and Results. The surface of the part was examined using an optical stereomicroscope. The defect appeared as a localized area of lightened color, and the zone immediately surrounding the anomaly was slightly recessed. A mounted and polished cross section was prepared through the part, revealing distinct inclusions within the base molding resin.

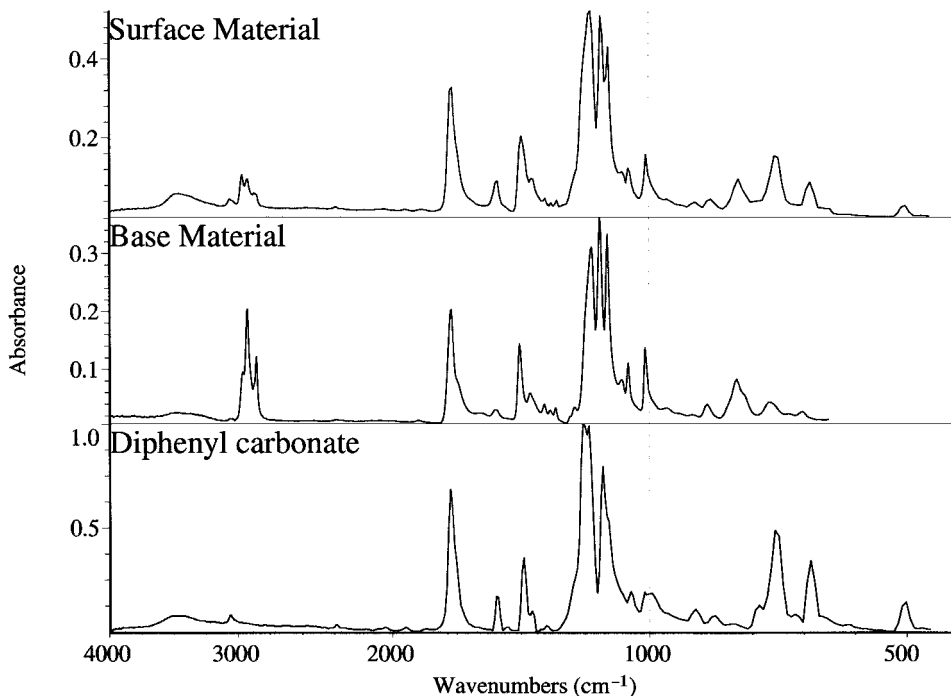


Fig. 14 Spectral comparison showing differences between the base material and surface spectra, attributed to diphenyl carbonate

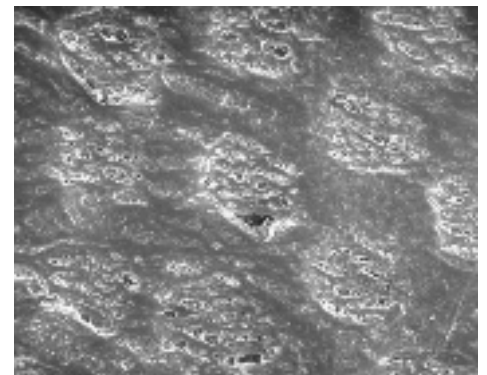


Fig. 15 Scanning electron image showing isolated degradation of the grip material. 30 \times

The inclusion, as shown in Fig. 17, did not appear to contain a significant level of the blue pigment, as present in the base material.

The preparation of the cross section not only allowed a thorough inspection of the defect but also served to facilitate further analysis of the material. The sample was initially analyzed using EDS. The results obtained on the included material showed exclusively carbon and oxygen, precluding an inorganic contaminant. The base resin and the included material were further analyzed using FTIR in the reflectance mode. The spectrum representing the base material contained absorption bands indicative of an ABS resin. Analysis of the included material produced distinctly different results. The spectrum obtained on the included material was characteristic of polybutadiene, the rubber-modifying agent present in ABS. This identification is presented in Fig. 18.

Conclusions. It was the conclusion of the evaluation that the handle contained an inclusion, which produced the apparent surface anomaly. The included material was identified as polybutadiene. The most likely source of the included polybutadiene was an undispersed gel particle formed during the production of the molding resin.

Example 4: Relaxation of Nylon Wire Clips. A production lot of plastic wire clips was failing after limited service. The failures were characterized by excessive relaxation of the clips, such that the corresponding wires were no longer adequately secured in the parts. No catastrophic failures had been encountered. Parts representing an older lot, which exhibited

satisfactory performance properties, were also available for reference purposes. The clips were specified to be injection molded from an impact-modified grade of nylon 6/6. However, the part drawing did not indicate a specific resin.

Tests and Results. A visual examination of the clips showed that the failed parts were off-white in color, while the control parts had a pure white appearance. An analysis of both sets of parts was performed using micro-FTIR in the ATR mode. A direct comparison of the results produced a good match, with both sets of spectra exhibiting absorption bands that were characteristic of a nylon resin. The comparison, however, revealed subtle differences between the two sets of clips. The spectrum representing the reference parts showed a relatively higher level of a hydrocarbon-based impact modifier, while the results obtained on the failed parts showed the presence of an acrylic-based modifier. The differences in the spectra suggested that the two sets of clips were produced from resins having different formulations, particularly regarding the impact modifier.

The clip materials were further analyzed using DSC. The thermogram representing the reference part material, as shown in Fig. 19, exhibited an endothermic transition at 264 °C (507 °F), characteristic of the melting point of a nylon 6/6 resin. Additionally, the results contained a second melting point, of lesser magnitude, at 95 °C (203 °F). This transition was indicative of a hydrocarbon-based impact modifier, as indicated by the FTIR results. The thermogram obtained on the failed clip material also showed a melting point characteristic of a nylon 6/6 resin. However, no evidence was found to indicate a tran-

sition corresponding to the hydrocarbon-based modifier found in the control clip material.

Conclusions. It was the conclusion of the analysis that the control and failed clips had been produced from two distinctly different resins. While both materials satisfied the requirements of an impact-modified nylon 6/6 resin, differences in the impact modifiers resulted in the observed performance variation. From the results and the observed performance, it appeared that the material used to produce the failed clips had different viscoelastic properties, which produced a greater predisposition for stress relaxation.

Example 5: Embrittlement of Nylon Couplings. Molded plastic couplings used in an industrial application exhibited abnormally brittle properties, as compared to previously produced components. The couplings were specified to be molded from a custom-compounded glass-filled nylon 6/12 resin. An inspection of the molding resin used to produce the discrepant parts revealed differences in the material appearance, relative to a retained resin lot. Specifically, physical sorting resulted in two distinct sets of molding resin pellets from the lot that had generated the brittle parts. Both of these sets of pellets had a coloration that varied from that of the retained reference resin pellets. A sample of retained molding resin, which had produced parts exhibiting satisfactory performance, was available for comparative analysis.

Tests and Results. Micro-FTIR in the ATR mode was used to analyze the molding resin samples. The results obtained on the three molding resin samples were generally similar, and all of the spectra exhibited absorption bands characteristic of a nylon resin. Further analysis of the resin samples using DSC indicated that the control material results exhibited a single endothermic transition at 218 °C (424 °F), consistent with the melting point of a nylon 6/12 resin, as specified.

The DSC thermograms obtained on the two resin samples that produced brittle parts also exhibited melting point transitions associated with nylon 6/12. However, additional transitions were

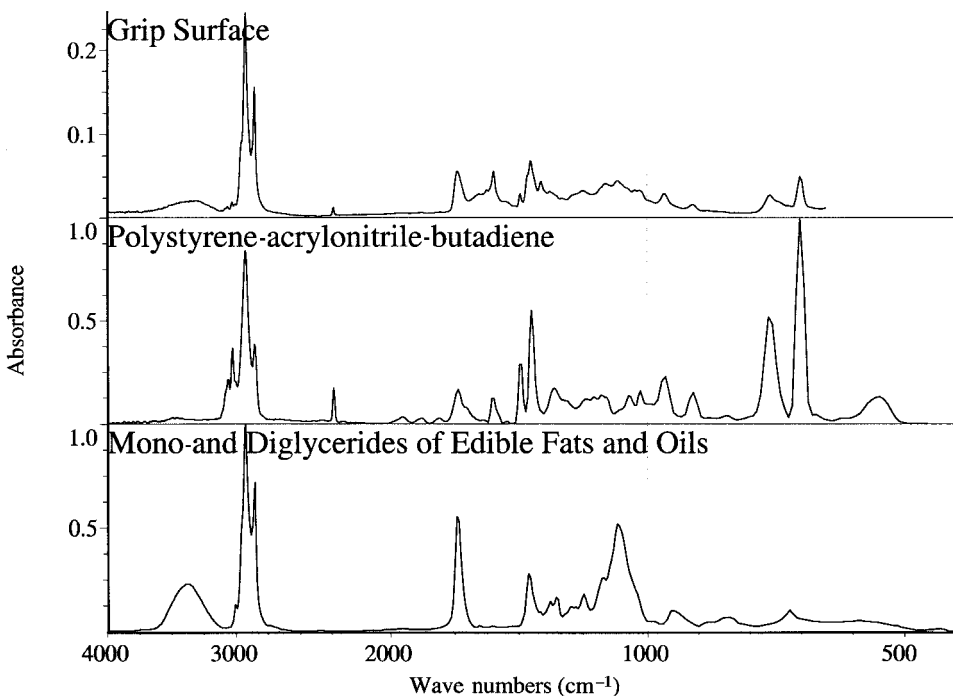


Fig. 16 The FTIR spectrum obtained on the grip surface. The spectrum contains absorption bands indicative of glyceride derivatives of fats and oils in addition to bands associated with the base ABS resin.

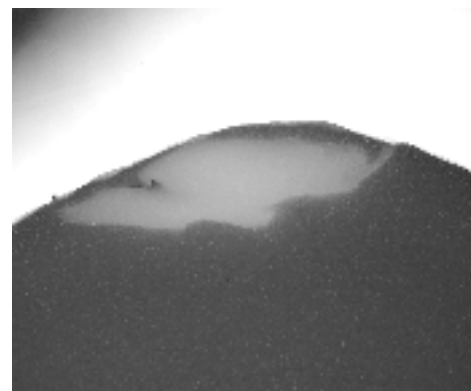


Fig. 17 Micrograph showing the included material within the handle. 24 ×

also apparent in the results, indicative of the presence of contaminant materials. The results obtained on one of the resin samples, as presented in Fig. 20, showed a secondary melting point at 165 °C (330 °F), indicative of polypropylene. The thermogram representing the second resin sample, as included in Fig. 21, displayed a second melting transition at 260 °C (500 °F), characteristic of a nylon 6/6 resin.

Conclusions. It was the conclusion of the analysis that the molding resin used to produce the brittle couplings contained a significant level of contamination, which compromised the mechanical properties of the molded components. Two distinct contaminants were found mixed into the molding pellets. The contaminant materials were identified as polypropylene and nylon 6/6. The source of the polypropylene was likely the purging compound used to clean the compounding extruder. The origin of the nylon 6/6 resin was unknown but may represent a previously compounded resin.

Example 6: Failure of Plasticized Poly(vinyl chloride) Tubing. A section of clear polymeric tubing failed while in service. The failed sample had been used in a chemical transport application. The tubing had also been exposed to periods of elevated temperature as part of the operation. The tubing was specified to be a poly(vinyl chloride) (PVC) resin plasticized with trioctyl trimellitate (TOTM). A reference sample of the tubing, which had performed well in service, was also available for testing.

Tests and Results. The failed and reference tubing samples were analyzed using micro-FTIR in the ATR mode, and the results representing the reference tubing material were consistent with the stated description: a PVC resin containing a trimellitate-based plasticizer. However, the spectrum representing the failed tubing material was noticeably different. While the obtained spectrum contained absorption bands characteristic of PVC, the results indicated that the material had been plasticized with an adipate-based material, such as dioctyl adipate. This identification is shown in Fig. 22.

In order to assess their relative thermal stability, the two tubing materials were analyzed via thermogravimetric analysis (TGA). Both sets of results were consistent with those expected for plasticized PVC resins. The thermograms representing the reference and failed sample materials showed comparable plasticizer contents of 28 and 25%, respectively. The results also showed that the reference material, containing the trimellitate-based plasticizer, exhibited superior thermal resistance relative to the failed material, containing the adipate-based material. This was indicated by the elevated temperature of weight-loss onset exhibited by the reference tubing material.

Conclusions. It was the conclusion of the evaluation that the failed tubing had been produced from a formulation that did not comply with the specified material. The failed tubing was identified as a PVC resin with an adipate-based plas-

ticizer, not TOTM. The obtained TGA results confirmed that the failed tubing material was not as thermally stable as the reference material because of this formulation difference, and that this was responsible for the observed failure.

Example 7: Cracking of Poly(butylene terephthalate) Automotive Sleeves. A number of plastic sleeves used in an automotive application cracked after assembly but prior to installation into the mating components. The sleeves were

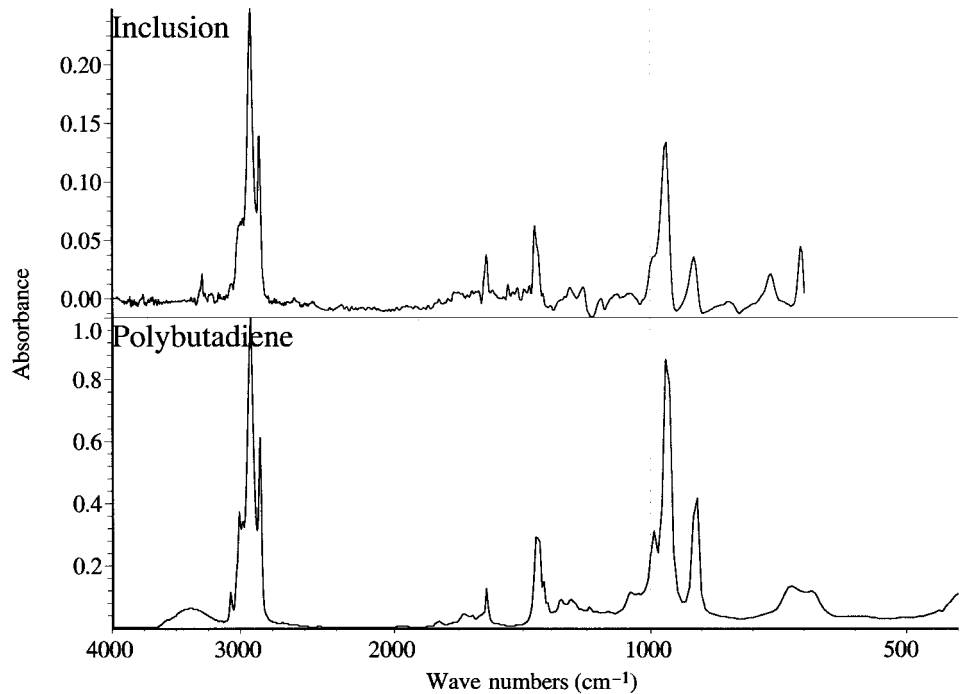


Fig. 18 The FTIR spectrum obtained on the included particle, characteristic of polybutadiene

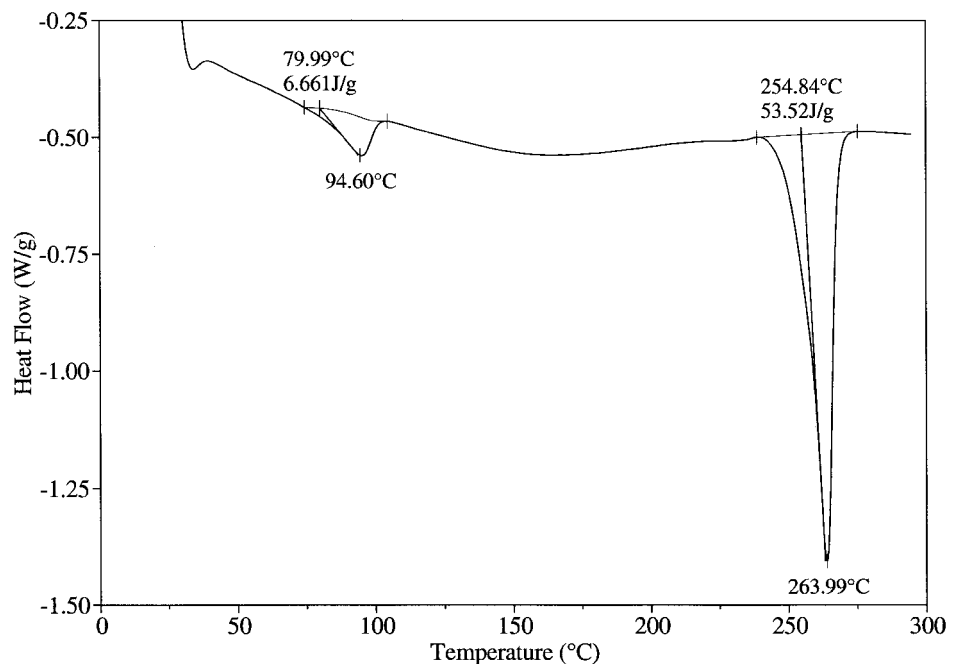


Fig. 19 The DSC thermogram representing the reference clip material, exhibiting an endothermic transition characteristic of the melting of a nylon 6/6 resin. The results also showed a second melting transition attributed to a hydrocarbon-based impact modifier.

specified to be injection molded from a 20% glass-fiber-reinforced poly(butylene terephthalate) (PBT) resin. After molding, electronic components are inserted into the sleeves, and the assembly is filled with a potting compound. A retained lot of parts, which had not cracked, were available for reference purposes.

Tests and Results. The reference and failed parts were analyzed using micro-FTIR in the ATR mode. The spectra obtained on both sets of parts contained absorption bands characteristic of a thermoplastic polyester, such as PBT or poly(ethylene terephthalate) (PET). Different types of polyester resins cannot be distinguished spectrally, because of the similar nature of their structures. However, subtle but distinct differences were apparent in the results, suggestive of degradation of the failed part material.

Differential scanning calorimetry was performed on the sleeve materials using a heat/cool/heat methodology. Testing of the reference material produced initial heating results indicative of a PBT resin, as illustrated by the melting point at 224 °C (435 °F). Analysis of the failed sleeve samples produced a melting transition at a significantly reduced temperature, 219 °C (426 °F). Additionally, the failed material transition was broader, and overall, the results suggested molecular degradation of the failed sleeve material. A comparison of the initial heating thermograms is presented in Fig. 23.

The identification of degradation was supported by the second heating DSC results, obtained after slow cooling. The second heating thermogram representing the failed sleeve material showed additional differences relative to the results obtained on the reference material. The failed material did not produce the bimodal melting endothermic transition normally associated with PBT after slow cooling. This was thought to be the result of molecular degradation, which produced shorter polymer chain lengths, therefore reducing steric hindrance. A comparison of the second heating thermograms is included in Fig. 24.

The sleeve materials were further analyzed using TGA. The thermograms obtained on the reference and failed samples were generally consistent, including equivalent glass contents. Additionally, the results were in agreement with those expected for a PBT resin.

The melt flow rates (MFRs) of the reference and failed sleeve materials were determined. Because no molding resin was available for comparison purposes, the nominal range from the specification sheet, 14 to 34 g/10 min, was used. The testing showed that the failed sleeve material had been severely degraded, producing a MFR of 128 g/10 min. This was in agreement with the DSC data and indicated severe molecular degradation of the PBT resin. A review of the results generated by the reference parts also showed significant molecular degradation. While the extent of the degradation was less, the obtained melt flow rate, 50 g/10 min, still demonstrated a substantial reduction in the average molecular weight.

Conclusions. It was the conclusion of the evaluation that the failed sleeves had cracked due to embrittlement associated with severe degradation and the corresponding molecular weight reduction. The degradation was clearly illustrated by the reduced melting point and uncharacteris-

tic nature of the associated endothermic melting transitions as well as the substantial increase in the MFR of the molded parts. The reduction in molecular weight significantly reduced the mechanical properties of the sleeves. The cause of the degradation was not evident, but the likely

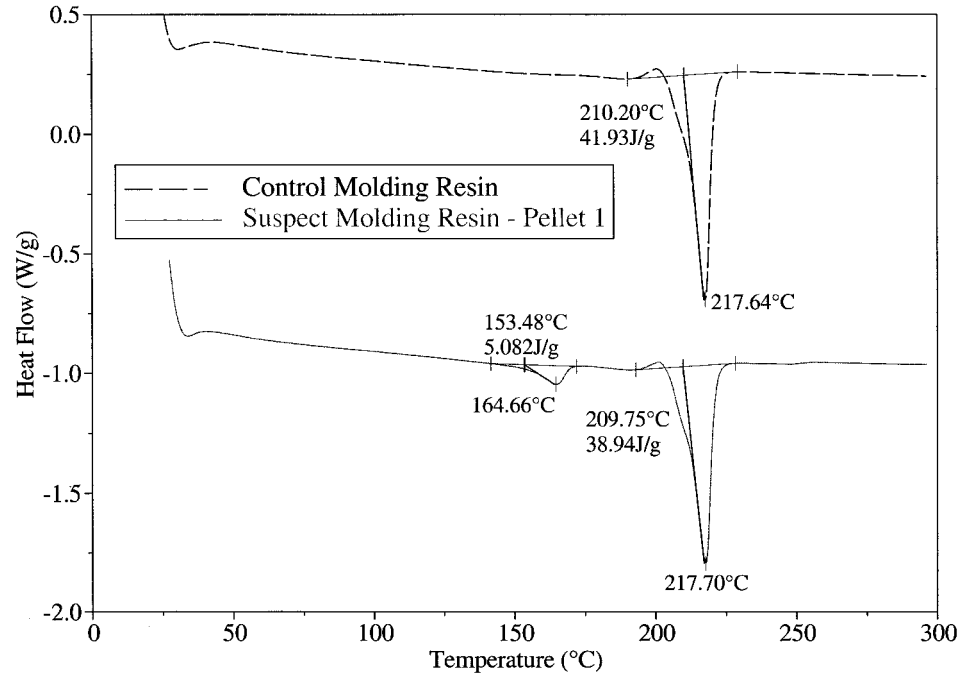


Fig. 20 The DSC thermogram representing a molding resin pellet that had produced brittle parts. The thermogram shows a major melting transition associated with nylon 6/12 and a weaker transition attributed to polypropylene.

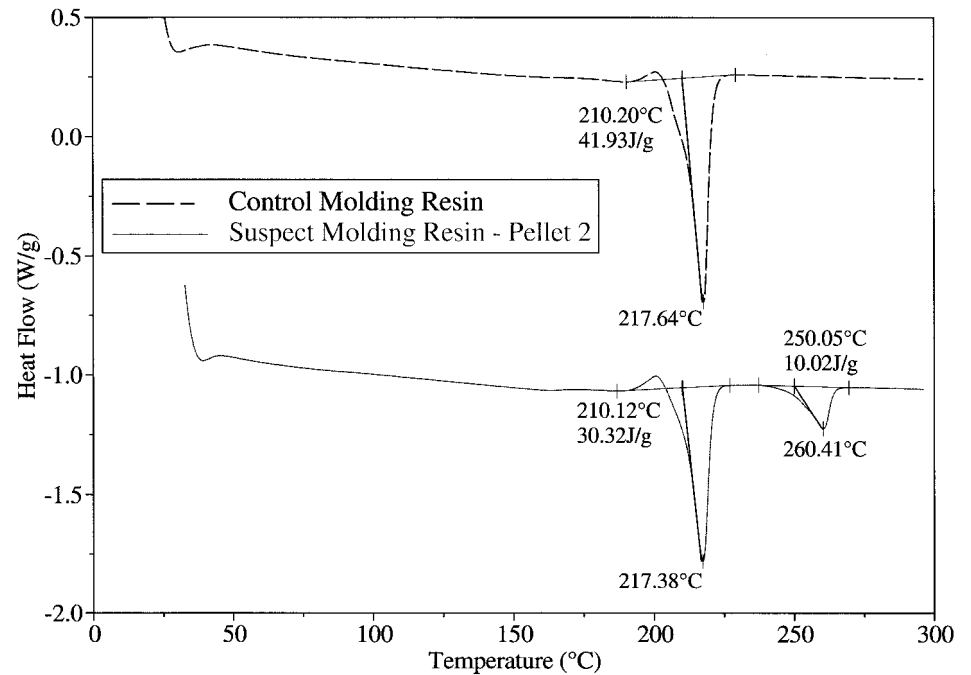


Fig. 21 The DSC thermogram representing a second molding resin pellet that had produced brittle parts. The thermogram shows a major melting transition associated with nylon 6/12 and a weaker transition attributed to nylon 6/6.

source appears to be the molding operation and exposure to elevated temperature for an extended period of time. It is significant to note that the reference parts also showed a moderate level of molecular degradation, rendering them susceptible to failure over a longer duration.

Example 8: Cracking of ABS Protective Covers. Numerous protective covers, used in conjunction with an electrical appliance, failed during assembly with the mating components. The failures were traced to a particular production lot of the covers and occurred during insertion of the screws into the corresponding bosses. The parts had been injection molded from an ABS resin to which regrind was routinely added. Retained parts, which exhibited normal behavior during assembly, were available for comparative analysis.

Tests and Results. A visual examination of the failed parts revealed relatively brittle fracture features, without significant ductility, as would be apparent as stress whitening or permanent deformation. Core material taken from the reference and failed parts was analyzed using micro-FTIR in the ATR mode. Both obtained spectra exhibited absorption bands associated with an ABS resin. However, the spectrum representing the failed part showed additional absorption bands. A spectral subtraction was performed, thereby removing the absorbances attributed to the ABS resin from the spectrum obtained on the failed part. The spectral subtraction results were consistent with a thermoplastic polyester, such as PET or PBT. However, these two materials cannot be distinguished spectrally, because of similarities in their structures. As such, the melting point is usually used to differentiate between these materials. The FTIR results indicated the presence of contaminant material exclusively within the ABS resin used to mold the failed covers.

In order to further identify the contaminant material, a sample taken from the failed part was analyzed via DSC. The obtained DSC thermogram, as presented in Fig. 25, showed a glass transition at approximately 101 °C (214 °F), consistent with the expected results for an ABS resin. The results also showed an additional endothermic transition at 222 °C (432 °F), indicative of a PBT resin. The failed cover material was also analyzed using TGA in order to assess the level of the contamination. The TGA analysis was performed using high-resolution temperature programming, and the results revealed adequate separation of the ABS and PBT resins. Based on the results, the contamination was estimated to account for approximately 23% of the failed cover material.

Conclusions. It was the conclusion of the evaluation that the appliance covers failed via brittle fracture associated with stress overload. The failures, which occurred under normal assembly conditions, were attributed to embrittlement of the molded parts, due to contamination of the ABS resin with a high level of PBT. The source of the PBT resin was not positively identified, but a likely source appeared to be the use of improper regrind.

Example 9: Failure of Polycarbonate/PET Appliance Housings. Housings from an electrical appliance failed during an engineering evaluation. The housings had been injection molded from a commercial polycarbonate/PET (PC/PET) blend. The parts were being tested as

part of a material conversion. Parts produced from the previous material, a nylon 6/6 resin, had consistently passed the testing regimen. The housing assembly included a spring clip, which applied a static force on a molded-in boss extending from the main body of the housing.

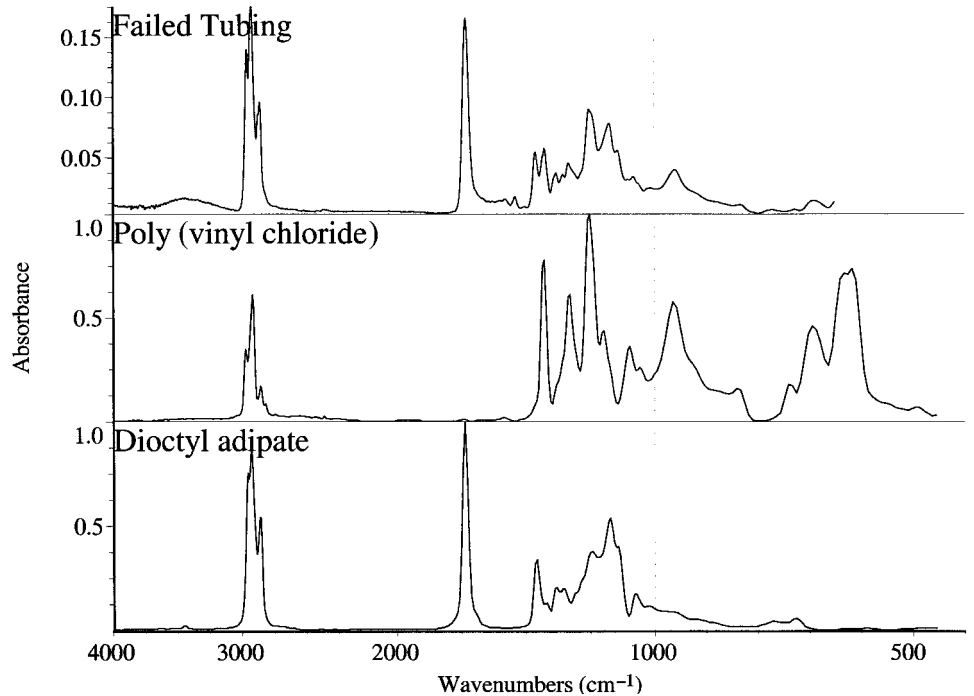


Fig. 22 The FTIR spectrum obtained on the failed tubing material. The spectrum exhibits absorption bands indicative of a PVC resin containing an adipate-based plasticizer.

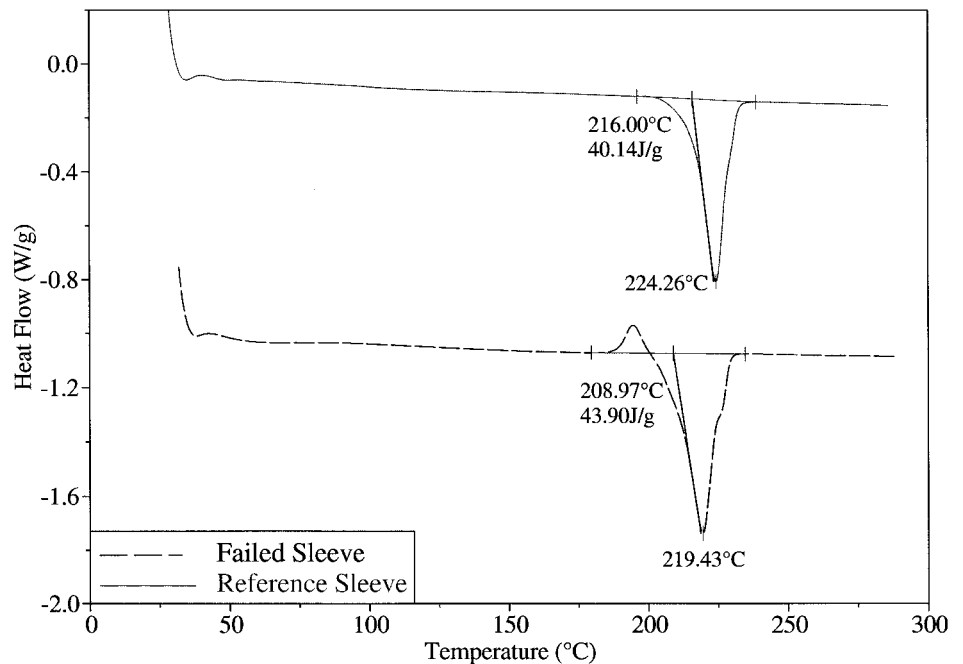


Fig. 23 A comparison of the initial heating run results, suggesting degradation of the failed sleeve material

Grease was applied liberally within the housing assembly during production.

Tests and Results. A visual inspection of the tested parts showed catastrophic failure within the molded-in boss. The failures were consistent across all of the parts and were located at an area where the spring clip contacted the housing boss. While the final fracture zone ex-

hibited limited features associated with ductility in the form of stress whitening, no such characteristics were apparent at the locations corresponding to the crack origins. The fracture surfaces were further examined via SEM. The SEM inspection showed the presence of multiple crack initiation sites along the side of the boss that had mated with the spring clip. No

evidence of significant ductility was found with the crack initiation locations, as represented in Fig. 26. The overall features observed on the fracture surface were indicative of environmental stress cracking.

Micro-FTIR in the ATR mode was performed on the housing material, and the resulting spectrum was in agreement with the stated resin description, a blend of PC and polyester. No signs of material contamination were found. The housing material was further evaluated using DSC. The thermogram obtained during the initial heating run, as shown in Fig. 27, exhibited an endothermic transition at 253 °C (487 °F), characteristic of the melting point of a PET resin. The initial heating run results also showed a low-temperature exothermic transition associated with the crystallization of the PET resin. These results indicated that the material had not been fully crystallized during the molding process. The results generated during the second heating run, after slow cooling, did not show the low-temperature crystallization. The glass transition associated with the PC resin was observed in the second heating run.

In order to assess the molecular weight of the housing material, the intrinsic viscosity of the resin was measured. A comparison of the results with historical data revealed a substantial reduction in the viscosity of the failed part material. This indicated that the housing material had undergone significant molecular degradation during the injection molding process.

The grease present within the housing assembly was analyzed using micro-FTIR. The FTIR test results indicated that the grease was composed of a relatively complex mixture. The lubricant contained a hydrocarbon-based oil, a phthalate-based oil, lithium stearate, and an amide-based additive. These results were significant, because phthalate esters are known to be incompatible with PC resins.

Conclusions. It was the conclusion of the analysis that the appliance housings failed through environmental stress cracking. The required chemical agent was identified as a phthalate-based oil present within the grease used to lubricate the assembly. Specifically, the phthalate

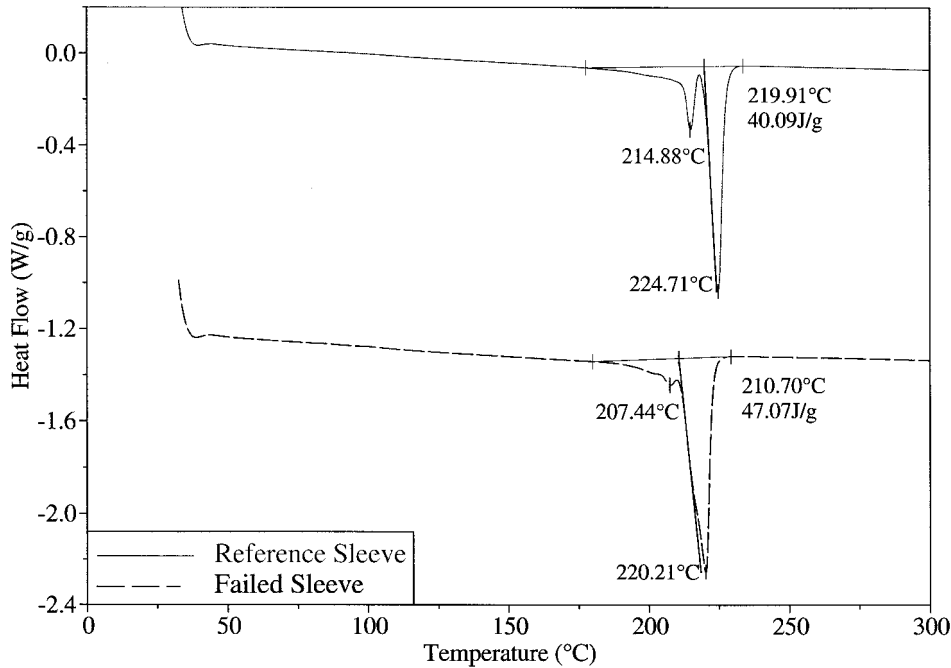


Fig. 24 A comparison of the second heating run results, further suggesting degradation of the failed sleeve material

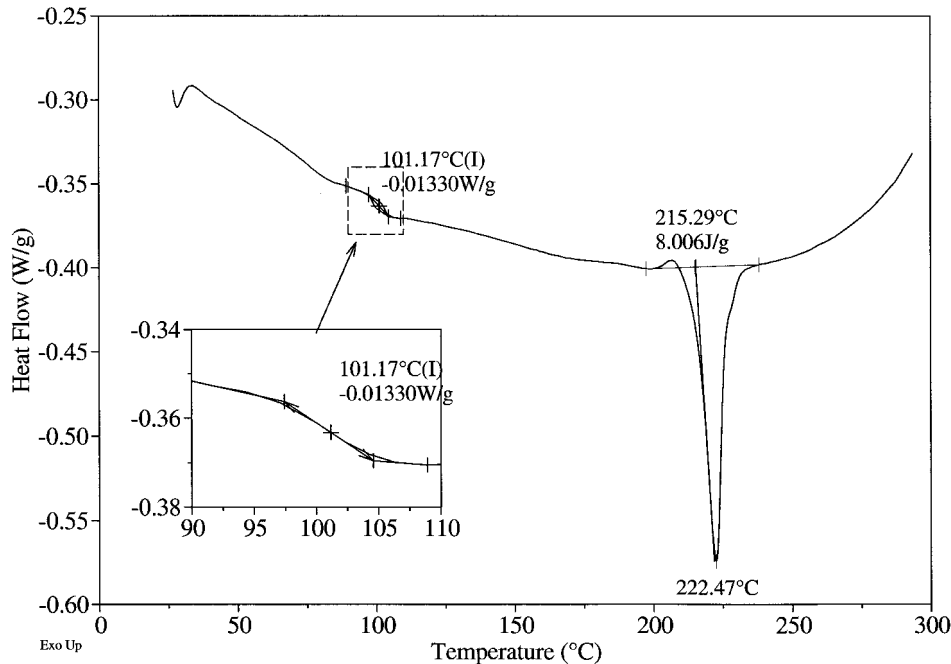


Fig. 25 The DSC thermogram obtained on the failed cover material. The thermogram shows an endothermic transition associated with PBT. The (I) indicates that the numerical temperature was determined as the inflection point on the curve.

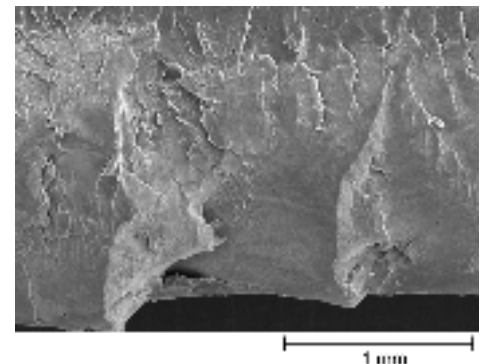


Fig. 26 Scanning electron image showing brittle fracture features at the crack initiation site, characteristic of environmental stress cracking. 24×

oil was not compatible with the PC portion of the resin blend. The source of the stress responsible for the cracking appears to be the interference related to the spring clip. While the previous parts, produced from the nylon 6/6 resin, were also under similar stresses, this resin was not prone to stress cracking in conjunction with the lubricant. Thus, the resin conversion was the root cause of the failures. Additionally, the test results also showed that the injection molding process left the material susceptible to failure. Specifically, the molded parts had been under-crystallized, reducing the mechanical strength of the molded articles, and, more importantly, the resin had been degraded, producing a reduction in the molecular weight and reducing both the

mechanical integrity and chemical-resistance properties of the parts.

Example 10: Failure of PET Assemblies. Several assemblies used in a transportation application failed during an engineering testing regimen. The testing involved cyclic thermal shock, immediately after which cracking was observed on the parts. The cracking occurred within the plastic jacket, which had been injection molded from an impact-modified, 15% glass-fiber-reinforced PET resin. The plastic jacket had been molded over an underlying metal coil component. Additionally, a metal sleeve was used to house the entire assembly. Prior to molding, the resin had reportedly been dried at 135 °C (275 °F). The drying process usually lasted 6

h, but occasionally, the material was dried overnight. The thermal shock testing included exposing the parts to alternating temperatures of -40 and 180 °C (-40 and 360 °F). The failures were apparent after 100 cycles. Molding resin and non-failed parts were also available for analysis.

Tests and Results. The failed assemblies were visually and microscopically examined. The inspection showed several different areas within the overmolded jacket that exhibited cracking. The cracked areas were located immediately adjacent to both the underlying metal coil and the outer metal housing. The appearance of the cracks was consistent with brittle fracture, without significant signs of ductility. The examination also revealed design features, including relatively sharp corners and nonuniform wall thicknesses, that appeared to have likely induced molded-in stress within the plastic jacket.

The fracture surfaces were further inspected using SEM, and the examination revealed features generally associated with brittle fracture, as shown in Fig. 28. No evidence of microductility, such as stretched fibrils, was found. The fracture surface features indicated that the cracking had initiated along the outer jacket wall and subsequently extended through the wall and circumferentially around the wall. Throughout the examination, no indication of postmolding molecular degradation was found.

Micro-FTIR was performed in the ATR mode on a core specimen of the jacket material. The resulting spectrum was consistent with a thermoplastic polyester resin. Such materials, including PET and PBT, cannot be distinguished spectrally, and a melting point determination is usually used to distinguish these materials. The failed jacket material and reference molding resin were analyzed using TGA, and the results obtained on the two samples were generally consistent. This included relatively comparable levels of volatiles, polymer, carbon black, and glass reinforcement. Further, the results were in excellent agreement with those expected for the stated PET material.

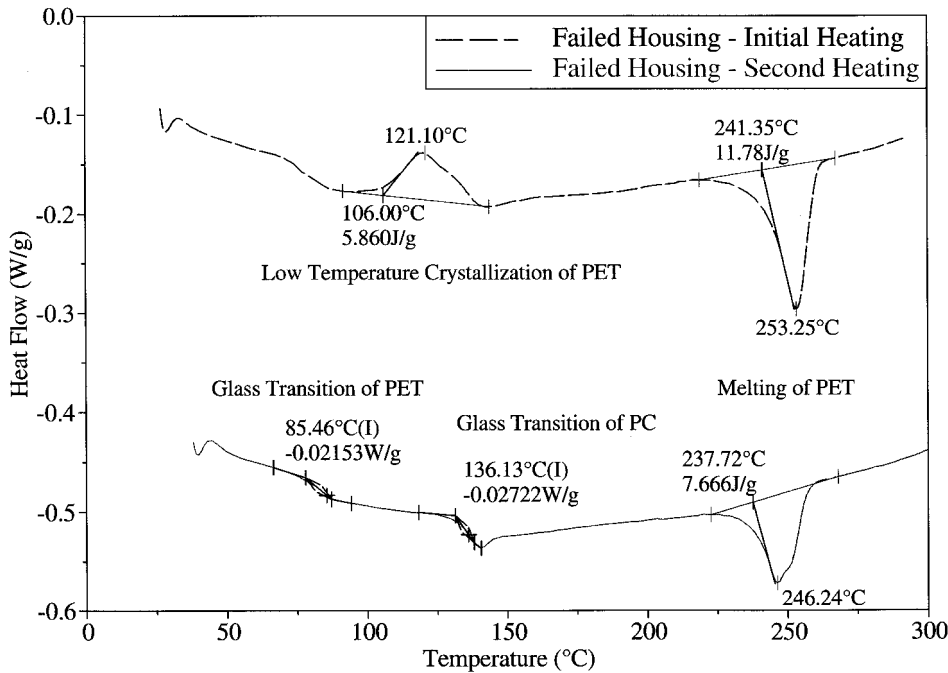


Fig. 27 The initial heating DSC thermogram, exhibiting a melting transition consistent with a PET resin. A low-temperature crystallization exothermic transition was also apparent. The (I) indicates that the numerical temperature was determined as the inflection point on the curve.

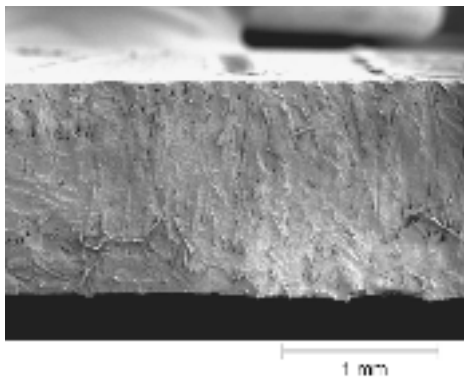


Fig. 28 Scanning electron image showing brittle fracture features on the failed jacket crack surface. 20×

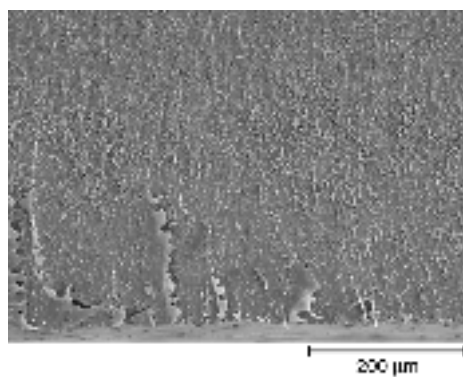


Fig. 29 Scanning electron image showing features associated with brittle fracture and slow crack growth within the crack initiation site. 100×

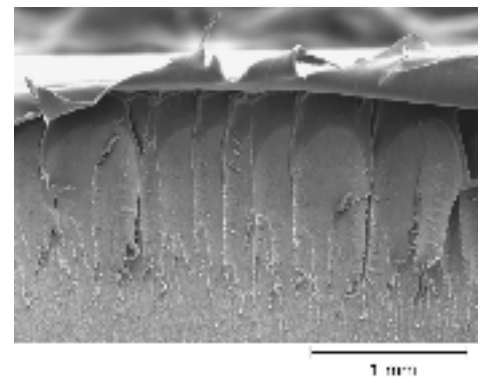


Fig. 30 Scanning electron image showing features indicative of rapid crack extension within the final fracture zone. 20×

The failed jacket and reference materials were evaluated via DSC. Analysis of the failed jacket material produced results that indicated a melting transition at 251 °C (484 °F), consistent with a PET resin. However, a second endothermic transition was also present. This transition, at 215 °C (420 °F), suggested the melting of annealed crystals, indicating that the part had been exposed to a temperature approaching 215 °C (420 °F). The thermal shock testing appeared to be the only possible source of this thermal exposure.

Analysis of the molding resin also produced results consistent with a PET resin. The results also exhibited a second melting endotherm at 174 °C (345 °F). Again, this transition was associated with melting of annealed crystals for material exposed to this temperature. The apparent source of the exposure was the drying process. This was well in excess of the stated drying temperature.

Further analysis of the assembly materials using thermomechanical analysis (TMA) produced significantly different results for the PET jacket and the steel housing material. Determination of the coefficients of thermal expansion (CTEs) showed approximately an order of magnitude difference between the two mating materials.

An assessment of the molecular weight of the failed jacket samples as well as a non-failed part and the molding resin samples was performed using several techniques. A combination of MFR, intrinsic viscosity, and finally, gel permeation chromatography (GPC) was used, because of conflicting results. The MFR determinations showed that the drying process produced a considerable increase in the MFR of the resin, corresponding to molecular degradation in the form of chain scission. This was contrasted by the results generated by the intrinsic viscosity testing. These results showed an increase in the viscosity of the dried resin relative to the virgin resin. This increase was suggestive of an increase in molecular weight, possibly through partial cross linking. Testing of the resin samples and the molded parts via GPC produced results that reconciled the discrepancy. The GPC results showed that the drying process produced competing reactions of chain scission and cross linking. The net result was severe degradation of the dried resin, which predisposed the molding material to produce jackets having poor mechanical properties. The GPC testing showed that the molded jackets were further degraded during the injection molding process.

Conclusions. It was the conclusion of the investigation that the assemblies failed via brittle fracture associated with the exertion of stresses that exceeded the strength of the resin as-molded. The stresses were induced by the thermal cycling and the dimensional interference caused by the disparity in the CTEs of the PET jacket and the mating steel sleeve. However, several factors were significant in the failures. It was determined that the resin drying process had exposed the resin to relatively high temperatures, which caused substantial molecular

degradation. The drying temperature was found to be approximately 173 °C (344 °F), well in excess of the recommendation for the PET resin. Further degradation was attributed to the molding process itself, leaving the molded jacket in a severely degraded state. This degradation limited the ability of the part to withstand the applied stresses. Additionally, the testing itself exposed the parts to temperatures above the recognized limits for PET, and this may have significantly lowered the mechanical properties of the part.

Example 11: Cracking of a Polyethylene Chemical Storage Vessel. A chemical storage vessel failed while in service. The failure occurred as cracking through the vessel wall, resulting in leakage of the fluid. The tank had been molded from a high-density polyethylene (HDPE) resin. The material held within the vessel was an aromatic hydrocarbon-based solvent.

Tests and Results. A stereomicroscopic examination of the failed vessel revealed brittle fracture surface features. This was indicated by the lack of stress whitening and permanent deformation. Limited ductility, in the form of stretching, was found exclusively within the final fracture zones. On cutting the vessel, significant stress relief, in the form of distortion, was evident. This indicated a high level of molded-in stress within the part. The fracture surface was further inspected using SEM. The observed features included a relatively smooth morphology within the crack origin location, which was indicative of slow crack initiation. This area is shown in Fig. 29. Features associated with more rapid crack extension, including hackle marks and river markings, were found at the midfrac-

ture and final fracture areas, as represented in Fig. 30. The entirety of the fracture surface features indicated that the cracking had initiated along the exterior wall of the vessel. The cracking extended transversely through the wall initially, and subsequently, circumferentially around the wall. Throughout the examination, no signs of postmolding molecular degradation or chemical attack were found.

The failed vessel material was analyzed using micro-FTIR in the ATR mode. The obtained spectrum exhibited absorption bands characteristic of a polyethylene resin. No evidence was found to indicate contamination or degradation of the material.

Material excised from the failed vessel was analyzed using DSC. The results showed a single endothermic transition associated with the melting point of the material at 133 °C (271 °F). The results were consistent with those expected for a HDPE resin. The results also showed that the HDPE resin had a relatively high level of crystallinity, as indicated by the elevated heat of fusion.

Thermogravimetric analysis was performed to further evaluate the failed vessel material. The TGA testing showed that the HDPE absorbed approximately 6.3% of its weight in the aromatic hydrocarbon-based solvent. Overall, the TGA results were consistent with those expected for a HDPE resin.

The MFR of the vessel material was evaluated, and the testing produced an average result of 3.8 g/10 min. This is excellent agreement with the nominal value indicated on the material data sheet, 4.0 g/10 min. As such, it was apparent that the vessel material had not undergone molecular

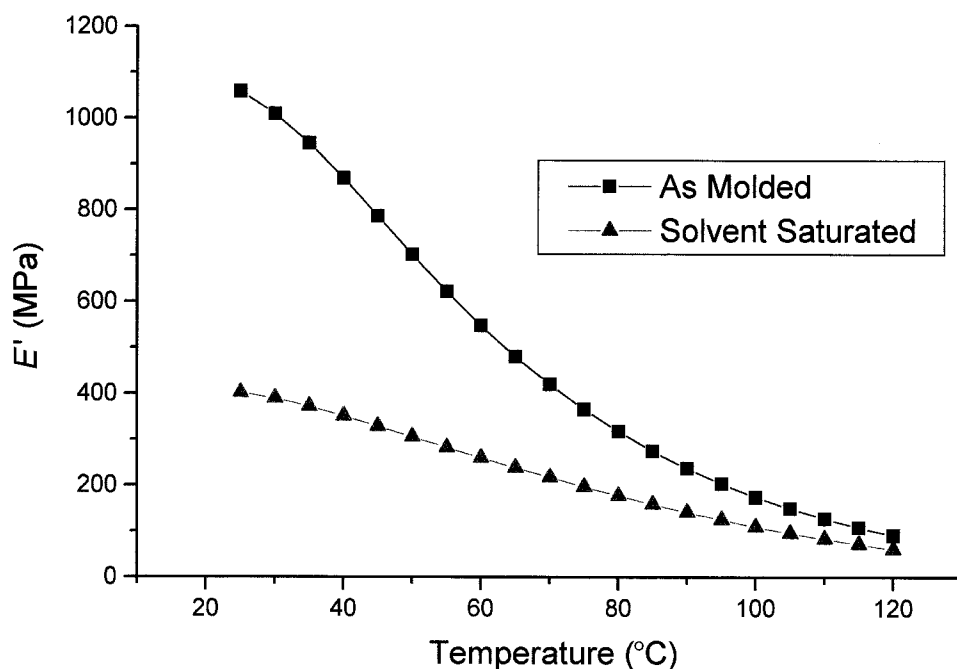


Fig. 31 A comparison of the DMA results, showing a loss of over 60% in the elastic modulus as a result of the effects of the solvent

degradation. The specific gravity of the resin was measured. The material produced a result of 0.965. This indicated that the material had a relatively high level of crystallinity, as suggested by the DSC results.

In order to assess the effects of the hydrocarbon-based solvent on the HDPE vessel, the material was evaluated using dynamic mechanical analysis (DMA). The vessel material was analyzed in two conditions. Material samples representing the vessel material in the as-molded condition as well as material from the failed vessel were evaluated. A comparison of the DMA results showed that in the saturated, equilibrium state, the HDPE resin lost over 60% of its elastic modulus at room temperature, because of the plasticizing effects of the solvent. A comparison of the DMA results, indicating the reduction in mechanical properties, is shown in Fig. 31.

Conclusions. It was the conclusion of the investigation that the chemical storage vessel failed via a creep mechanism associated with the exertion of relatively low stresses. Given the lack of apparent ductility, the stresses responsible for the failure appear to have been below the yield strength of the material. The source of the stress was thought to be molded-in residual stresses associated with uneven shrinkage. This was suggested by the obvious distortion evident on cutting the vessel. The relatively high specific gravity and the elevated heat of fusion are indicative that the material has a high level of crystallinity. In general, increased levels of crystallinity result in higher levels of molded-in stress and the corresponding warpage. The significant reduction in the modulus of the HDPE material, which accompanied the saturation of the resin with the aromatic hydrocarbon-based solvent, substantially decreased the creep resistance of the material and accelerated the failure. The dramatic effects of the solvent had not been anticipated prior to use.

Example 12: Failure of Polyacetal Latch Assemblies. Components of a latch assembly used in a consumer device exhibited a relatively high failure rate. The latches are used as a safety restraint, and failure in the field could result in severe injury. The failures were occurring after installation but prior to actual field use. Specifically, the failures occurred as cracking within retaining tabs used to secure a metal slide. The cracking was limited to an older design, with newer components showing no signs of failure. The latch assembly components were injection molded from an unfilled commercial grade of a polyacetal copolymer. As part of the evaluation, both failed parts representative of the older design and newer components were available for testing.

Tests and Results. A visual examination of the failed parts confirmed cracking within the retaining tab adjacent to the metal slide. The failures were present at consistent locations on all of the parts. The crack surfaces showed evidence of macroductility in the form of stress whitening within the final fracture zone exclusively. Throughout the visual examination, it was also

apparent that the parts exhibited a very sharp corner formed by the retaining tab and the main body of the latch assembly body. Sharp corners are considered a poor design feature in plastic components, because they can result in severe stress concentration and can produce areas of localized poor fusion.

The fracture surface was further evaluated using SEM. The SEM examination showed a clear crack origin at the corner formed by the retaining tab. The crack origin areas exhibited brittle fracture features without signs of significant microductility. Secondary crazing was also apparent at the crack origin location. A typical crack initiation site is shown in Fig. 32. The overall features were suggestive of cracking caused by a relatively high strain rate event and/or very high stress concentration. The midfracture surface showed an increase in the apparent ductility, as evidenced by an overlapping morphological structure. The final fracture zone showed significant deformation and stretching, indicative of ductile overload. A laboratory failure was created by overloading the tab from a nonfailed part in a manner consistent with the insertion of the corresponding metal slide. The laboratory fractures exhibited surface features that were in excellent agreement with those exhibited by the failed parts, as apparent in Fig. 32.

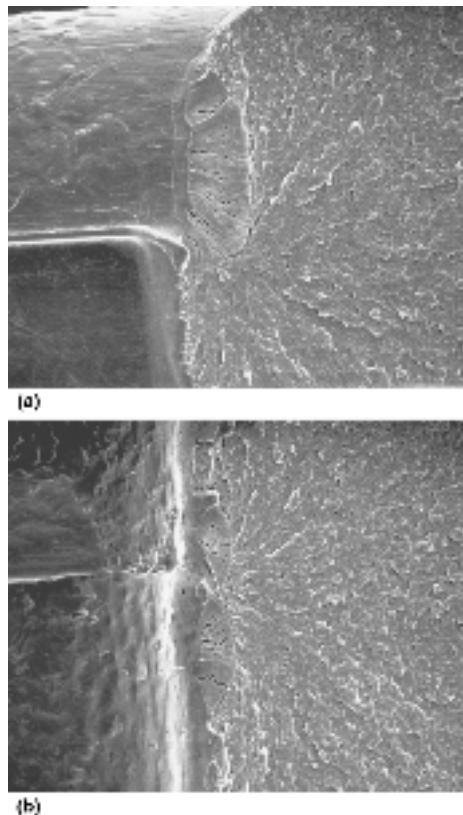


Fig. 32 Scanning electron images showing excellent agreement between the features present within the crack initiation sites of (a) the failed latch assembly and (b) the laboratory fracture. Both surfaces showed relatively brittle fracture features. 59×

The failed latch assembly material was analyzed using micro-FTIR in the ATR mode, and the obtained spectrum exhibited absorption bands characteristic of a polyacetal resin. It is significant to note that polyacetal copolymers and homopolymers cannot be differentiated spectrally, and a melting point determination is often used to distinguish between these materials.

Differential scanning calorimetry was used to analyze the latch material. The obtained results showed that the material underwent a single endothermic transition at approximately 165 °C (330 °F), characteristic of the melting point of a polyacetal copolymer. The results also showed that the part was somewhat undercrystallized. This was evident through a significant increase in the heat of fusion between the initial heating run and the second heating run, after slow cooling. Undercrystallization can reduce the mechanical strength of the molded article and is usually the result of molding in a relatively cold tool. The level of undercrystallization found in the failed parts, however, was moderate in nature and not thought to be a major factor in the failures. Thermogravimetric analysis was also performed on the latch material, and the obtained results were consistent with those expected for an unfilled polyacetal copolymer.

The latch material was also analyzed to determine its MFR. Parts representing the older, failed components and the newer, current design were evaluated. Both sets of molded parts produced results ranging from 10.7 to 11.0 g/10 min. This was in good agreement with the nominal MFR for the molding resin, 9.0 g/10 min. Throughout the analytical testing of the failed latch material, no evidence was found to indicate contamination or degradation of the molded parts.

Mechanical testing was performed in order to assess the effect of the recent design change. Because of the configuration of the parts, standard mechanical testing could not be performed. Instead, a proof load test was devised to directly assess the stress required to produce failure within the tab, at an area consistent with the failure latch assembly. A direct comparison was

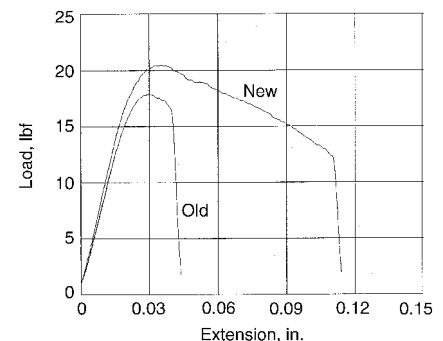


Fig. 33 A comparison of the mechanical test results, showing a significant improvement in the parts produced from the new design

made between the two sets of parts. The parts representing the older design, with the sharp corner at the retaining tab, produced an average value of 78.7 N (17.7 lbf) at failure. More importantly, the parts within this group produced an average tab extension of 0.76 mm (0.03 in.) at failure. The evaluation of the part representing the new design generated significantly different results. Specifically, the failures occurred at a higher load, 92.1 N (20.7 lbf), and a greater tab extension, 2.5 mm (0.10 in.). A comparison of the mechanical test results is shown in Fig. 33. This mechanical evaluation clearly illustrated the advantage afforded by the design change, effectively increasing the tab radius.

Conclusions. It was the conclusion of the evaluation of the failed latch assemblies that the parts failed via brittle fracture associated with stress overload. The stress overload was accompanied by severe apparent embrittlement resulting from a relatively high strain rate event and/or significant stress concentration. The relatively sharp corner formed by the retaining tab was shown to be a primary cause of the failures, with the newer, redesigned parts producing superior mechanical test results.

Example 13: Failure of a Nylon Filtration Unit. A component of a water filtration unit

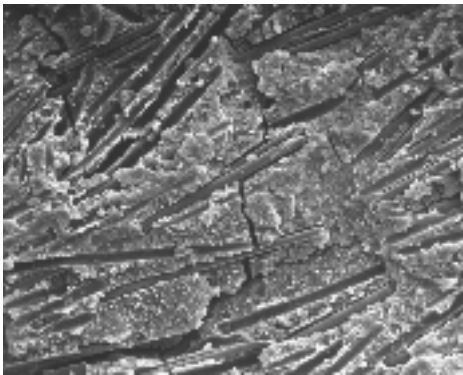


Fig. 34 Scanning electron image showing features characteristic of severe degradation of the filter material. 118×

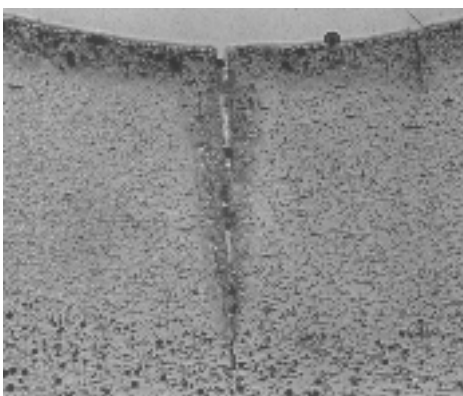


Fig. 35 Micrograph showing the cross section prepared through the filter component. 9×

failed while being used in service for approximately eight months. The filter system had been installed in a commercial laboratory, where it was stated to have been used exclusively in conjunction with deionized water. The failed part had been injection molded from a 30% glass-fiber- and mineral-reinforced nylon 12 resin.

Tests and Results. A visual examination of the filter component revealed significant cracking on the inner surface. The cracking ran along the longitudinal axis of the part and exhibited an irregular pattern. The surfaces of the part presented a flaky texture, without substantial integrity, and displayed significant discoloration. The irregular crack pattern, flaky texture, and discoloration were apparent on all surfaces of the part that had been in contact with the fluid passing through the component. Several of the crack surfaces were further examined using SEM. The fracture surface exhibited a coarse morphology, as illustrated in Fig. 34. The reinforcing glass fibers protruded unbound from the surrounding polymeric matrix. The fracture surface also showed a network of secondary cracking. Overall, the observations made during the visual and SEM inspections were consistent with molecular degradation associated with chemical attack of the filter component material.

To allow further assessment of the failure, a mounted cross section was prepared through one of the cracks. The cross section, as presented in Fig. 35, showed a clear zone of degradation along the surface of the part that had contacted the fluid passing through the filter. The degradation zone extended into the cracks, which indicated massive chemical attack. The prepared

cross section was analyzed using energy-dispersive x-ray spectroscopy, and the results obtained on the base material showed relatively high concentrations of silicon, calcium, and aluminum, with lesser amounts of sulfur and sodium in addition to carbon and oxygen. The results were consistent with a mineral- and glass-filled nylon resin. Analysis of the surface material, which exhibited obvious degradation, showed a generally similar elemental profile. However, significant levels of silver and chlorine were also found. This was important, because aqueous solutions of metallic chlorides are known to cause cracking and degradation within nylon resins.

The filter component material was further analyzed using micro-FTIR in the ATR mode. Analysis of the base material produced results characteristic of a glass- and mineral-filled nylon resin. However, analysis of the surface material showed additional absorption bands characteristic of substantial oxidation and hydrolysis of the nylon. A spectral comparison showing this is presented in Fig. 36. The presence of these bands is consistent with the high level of molecular degradation noted during the visual and SEM examinations.

Comparative TGA of the base material and the surface material also showed a significant difference. In particular, the results obtained on the surface material showed a lower temperature corresponding to the onset of polymer decomposition. This is illustrated in Fig. 37.

Conclusions. It was the conclusion of the evaluation that the filter component failed as a result of molecular degradation caused by the service conditions. Specifically, the part material had un-

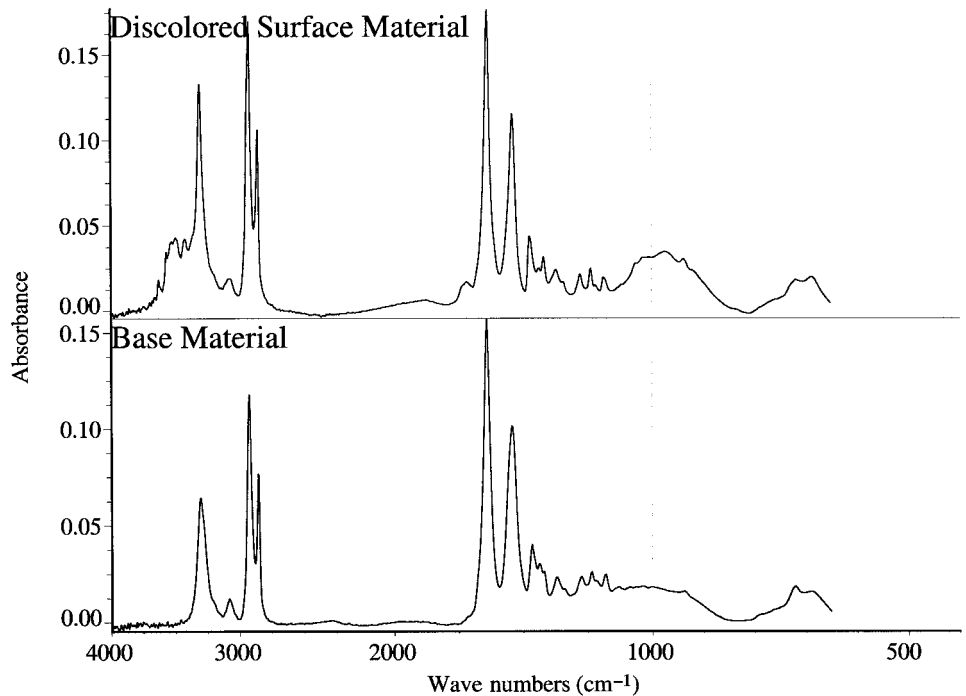


Fig. 36 Fourier transform infrared spectral comparison showing absorption bands associated with hydrolysis at 3350 cm^{-1} and oxidation at 1720 cm^{-1} in the results obtained on the discolored surface

dergone severe chemical attack, including oxidation and hydrolysis, through contact with silver chloride. The source of the silver chloride was not established, but one potential source was photographic silver recovery.

Example 14: Failure of a PC Switch Housing. A housing used in conjunction with an electrical switch failed shortly after being placed into service. A relatively high failure rate had been encountered, corresponding to a recent production lot of the housings, and the failed part was representative of the problem. The housing had been injection molded from a commercially available, medium-viscosity grade of PC, formulated with an ultraviolet stabilizer. In addition to the PC housing, the design of the switch included an external protective zinc component installed with a snap-fit and two retained copper press-fit contact inserts. Control parts representing an earlier production lot were available for reference purposes.

Tests and Results. A visual examination of the submitted housing revealed massive cracking within the base of the part, including the retaining tabs securing the contacts. The fractures were primarily located adjacent to the copper contacts. Gray streaks, commonly referred to as splay, were also apparent on the PC housing, as shown in Fig. 38. Splay is often associated with molecular degradation, caused by insufficient drying or exposure to excessive heat, from the molding process. The visual examination also revealed that the contacts corresponding to the failed housing retaining tabs extended significantly, relative to contacts in nonfailed areas. This suggested a high level of interference stress between the contact and the tab. The fracture surface was

further inspected using an optical stereomicroscope. The fracture surface showed no evidence of ductility, as would be evident in the form of stress whitening or permanent deformation. An oily residue was evident covering the crack surface.

The crack surface was further examined via SEM. The fracture surface exhibited multiple apparent crack origins and classic brittle fracture features, including hackle marks, river markings, and Wallner lines. A representative area on the fracture surface is shown in Fig. 39. No evidence of ductility, which would be apparent as stretched fibrils, was found. Overall, the observed features were indicative of brittle fracture associated with the exertion of stresses below the yield point of the material, over an extended period of time, by a creep mechanism.

The housing base material was analyzed using micro-FTIR in the ATR mode, and the resulting spectrum contained absorption bands characteristic of PC. The results produced an excellent match with a spectrum obtained on a reference part, without evidence of contamination. The oily residue found on the part, including the fracture surface, was also analyzed. The obtained spectrum was characteristic of an aliphatic hydrocarbon-based oil, with no signs of aromatic hydrocarbons or other chemicals known to produce stress cracking in PC resins.

The housing material was also analyzed using DSC. The DSC thermogram showed a single transition at 141 °C (286 °F), associated with the glass transition temperature (T_g) of the material. This temperature was somewhat lower than expected for a PC resin, which usu-

ally undergoes this transition closer to 150 °C (300 °F). This difference was thought to be an indication of potential molecular degradation.

Thermomechanical analysis (TMA) was used to evaluate the failed retaining tab material, using an expansion probe. The TMA results confirmed the relatively low T_g , in particular, with a comparison to a reference part. A comparison showing this is presented in Fig. 40. No evidence was found in the results to indicate molded-in residual stress.

Melt flow testing of the housing samples showed the submitted reference part to have a MFR of 39.7 g/10 min, compared with 78.1 g/10 min for the failed components. The nominal value for the resin used to produce the housing was 9 to 12 g/10 min. This indicated not only severe molecular degradation within the failed housing material but also within the reference parts. The most likely source of the degradation was the molding process. This degradation was consistent with the presence of splay observed on the part as well as the reduced T_g .

Conclusions. It was the conclusion of the evaluation that the switch housings failed via brittle fracture, likely through a creep mechanism. The failure was caused by severe embrittlement of the housing resin associated with massive molecular degradation produced during the molding process. A potential contributing factor was the design of the part, which produced significant interference stresses between the contact and the mating retaining tab.

Example 15: Failure of Nylon Hinges. A production lot of mechanical hinges had failed during incoming quality-control testing. The hinges were used in an automotive application and had cracked during routine actuation testing. Similar parts had been through complete prototype evaluations without failure. However, a change in part supplier had taken place between

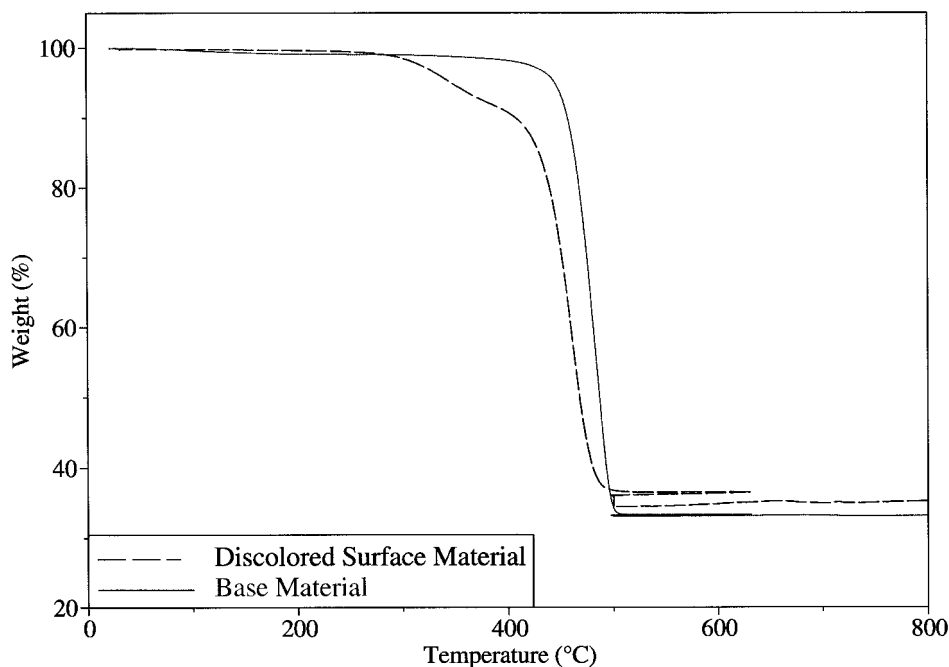


Fig. 37 Thermogravimetric analysis weight-loss profile comparison showing a reduction in the thermal stability of the discolored surface material relative to the base material

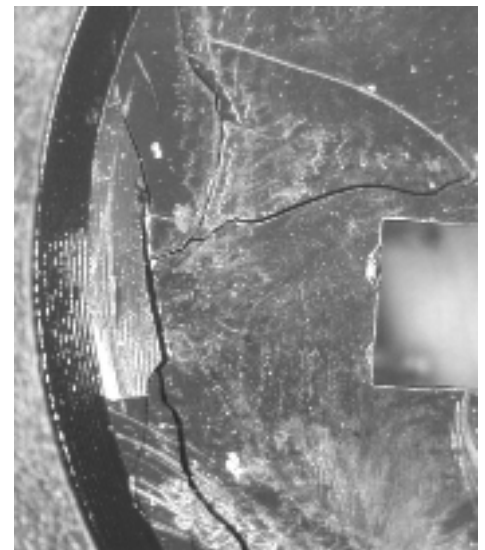


Fig. 38 A view of the housing showing gray streaks characteristic of splay

the approval of the prototype parts and the receipt of the first lot of production parts. The mechanical hinges were specified to be injection molded from an impact-modified, 13% glass-fiber-reinforced nylon 6/6 resin. A resin substitution was suspected, corresponding to the sup-

plier change. Samples representing the failed components and the original prototype parts were available for the failure investigation.

Tests and Results. A visual examination of the failed parts confirmed catastrophic cracking within the mechanical hinge in an area that

would be under the highest level of stress during actuation. The failures did not show signs of macroductility, which would be apparent in the form of stress whitening and permanent deformation. The fracture surfaces of the failed parts were further inspected via SEM. While the presence of glass-reinforcing fibers can render a plastic resin inherently more brittle, a certain level of ductility is still expected at the 13% glass level. This ductility is often only apparent at high magnification and only between the individual glass fibers. However, the failed hinge components did not exhibit any signs of ductility even at high magnification, with the fracture surface showing only brittle features. A laboratory failure was created on one of the prototype parts by overloading the component. Examination of the fracture surface using SEM showed the normally anticipated level of ductility, as indicated by the overlapping, rose-petal morphology. The crack surfaces of both the failed part and the laboratory fracture are shown in Fig. 41.

Analysis of the failed components and the corresponding molding resin via micro-FTIR produced results characteristic of a nylon resin. The molding resin and failed parts generated generally similar results. However, a distinct difference was apparent in that the spectra obtained on the failed parts showed an additional absorption band at approximately 1740 cm^{-1} , indicative of

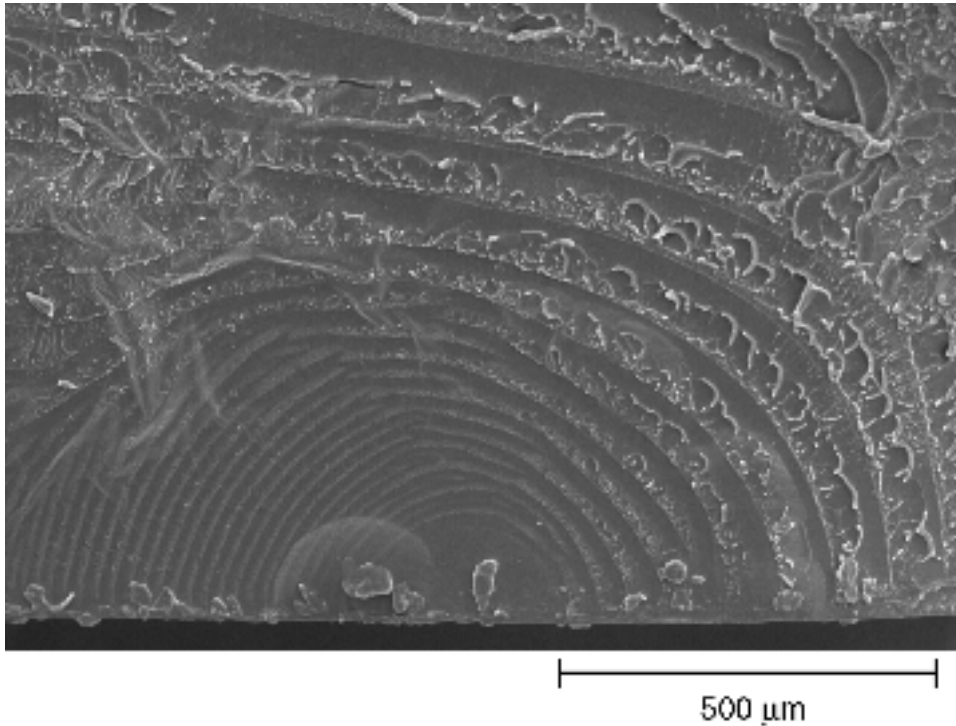


Fig. 39 Scanning electron image showing characteristic brittle fracture features on the housing crack surface. 100×

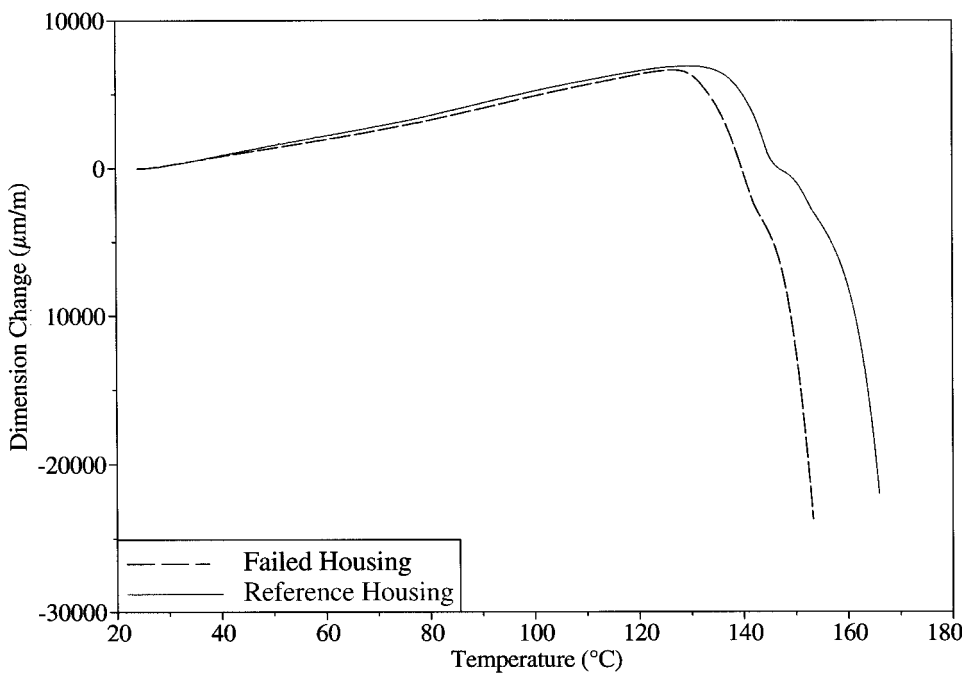


Fig. 40 The TMA results obtained on the failed and reference parts. The results exhibit differences corresponding to a reduction in the glass transition of the failed material.

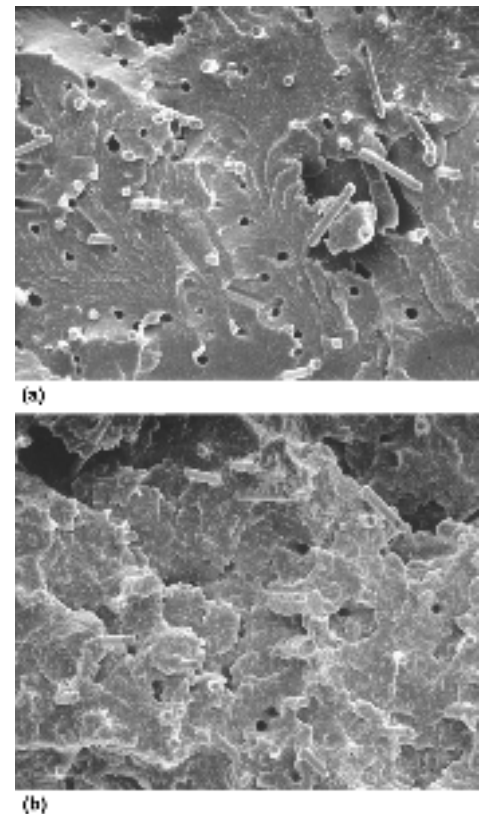


Fig. 41 Scanning electron images showing (a) brittle fracture features on the failed hinge and (b) ductile fracture features on the laboratory fracture. 118×

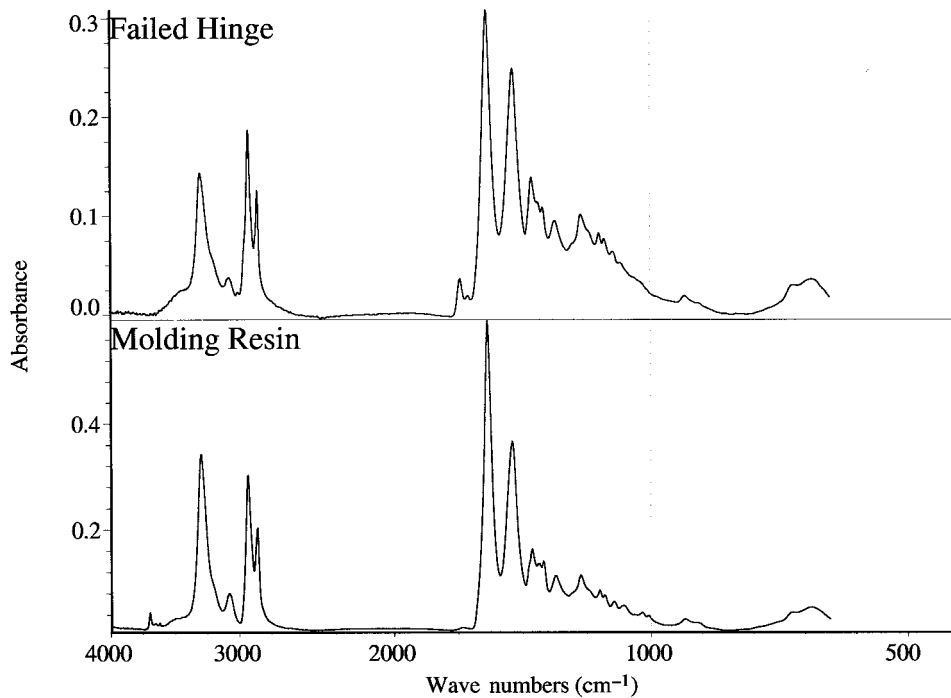


Fig. 42 Fourier transform infrared spectral comparison showing absorption bands at 1740 cm^{-1} , characteristic of oxidation within the results obtained on the failed parts

partial oxidative degradation of the resin. A spectral comparison illustrating this is presented in Fig. 42. Because the parts had not yet been in service, this degradation was thought to have occurred during the molding process.

The failed parts were further tested using DSC. The obtained DSC results showed a melting point of $263\text{ }^{\circ}\text{C}$ ($505\text{ }^{\circ}\text{F}$), consistent with a nylon 6/6 resin. The molding resin was also analyzed via DSC, and a comparison of the results further indicated degradation of the molded nylon resin. This was apparent by a noted reduction in the heat of fusion in the results representing the failed parts.

The failed parts and the prototype parts were also analyzed using conventional thermogravimetric analysis (TGA), and both analyses produced results indicative of a nylon resin containing approximately 13% glass-fiber reinforcement. Further testing was performed using TGA in the high-resolution mode. This analysis was conducted in order to assess the level of impact-modifying rubber resin. The weight loss associated with the rubber was observed as a shoulder on the high-temperature side of the weight loss representing the nylon resin. This weight loss was particularly evident in the derivative curve. Because the weight losses could not be totally resolved, an absolute level of rubber could not be determined. However, a comparison of the results allowed a determination of the relative level of the impact modifiers in the two materi-

als. This comparison showed a distinctly higher level of impact modifier in the prototype part material, relative to the failed part material.

Conclusions. It was the conclusion of this evaluation that the hinge assemblies failed through brittle fracture associated with stress overload during the actuation of the parts. The failed part material was found to be degraded, as indicated by both the FTIR and DSC analysis results. This degradation likely occurred either during the compounding of the resin or during the actual molding of the parts. A significant factor in the hinge failures is the conversion to a different grade of resin to produce the failed production parts as compared to the prototype parts. While both resins produced results characteristic of a 13% glass-fiber-reinforced, impact-modified nylon 6/6, the failed part material contained a significantly lower level of rubber. This decrease in rubber content rendered the parts less impact resistant and subsequently lowered the ductility of the molded hinge assemblies.

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