DUCTILE-TO-BRITTLE TRANSITION OF PLASTIC MATERIALS

Failure analysis of polymers often shows that the part failed after the material changed from a ductile to a brittle microstructure.

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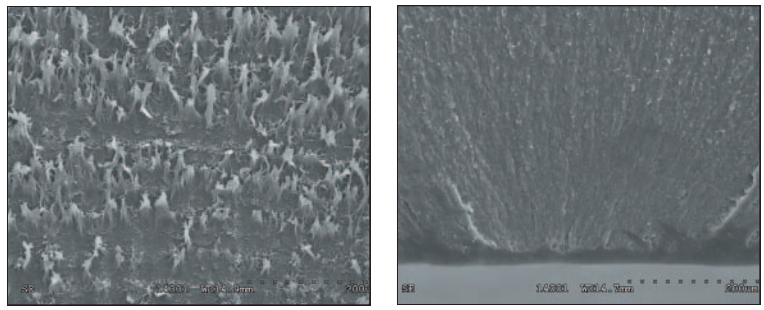

Fig. 1 — Comparison of polyethylene crack surfaces exhibiting ductile (left) and brittle fracture features.

The goal of a failure analysis, regardless of the material, is to identify the mode and cause of the failure. The assignment of the failure mode, such as fatigue, overload, or environmental stress cracking, is often straightforward through standard fractographic methods. However, the determination of the cause of the failure is often less apparent, particularly with a plastic component.

This article discusses the failure modes of thermoplastic resins. Many factors influence a ductile-to-brittle transition within plastic materials, as shown in the table.

Factors that influence the ductile-to-brittle transition

Temperature	Contamination
Stress concentration	Poor fusion
Chemical contact	Strain rate
Molecular weight	Time under load
Degradation	Crystallinity
Filler content	Plasticizer content

These factors are associated with material, processing, design, and service issues. Over the course of this article and the subsequent two installments, several key factors will be reviewed, including temperature, chemicals, and environment.

Resin cracking mechanisms

Thermoplastic resins are utilized in many applications because of their unique property set, including ductile response to applied stress. This ductility is associated with the viscoelastic nature of polymers, and is attributed to their unique molecular structure. In spite of that inherent ductility, most plastic components fail through one of the many brittle fracture modes.

In my experience, having conducted over 800 plastic component failure analyses, less than 5% were associated with ductile overload. The remainder represent brittle fractures of normally ductile materials. Therefore, within evaluations of plastic component failures, the focus of the investigation frequently turns to identifying the nature of the ductile-to-brittle transition. The objective of the successful evaluation becomes to identify the source of the brittle behavior. This relatively brittle response to stress is evident through the examination and characterization of the fracture surface morphology, as illustrated in Fig. 1.

To understand the cause of a ductile-to-brittle transition, the analyst must first understand the mechanism that causes plastic materials to crack. Cracking is simply a response to mechanical stresses, either internal or external. Contrary to widespread opinion, cracking of a resin does not represent the scission of the polymer molecules.

Molecular degradation mechanisms such as oxidation and chemical attack can render the altered material susceptible to failure. However, plastic resins do not crack through mechanisms that produce gross breakage of individual polymer chains. Although mechanical stress does result in a limited amount of chain scission, the primary response is molecular disentanglement, sometimes referred to as slippage. In fact, cracking within a molded plastic resin represents the disentangle-

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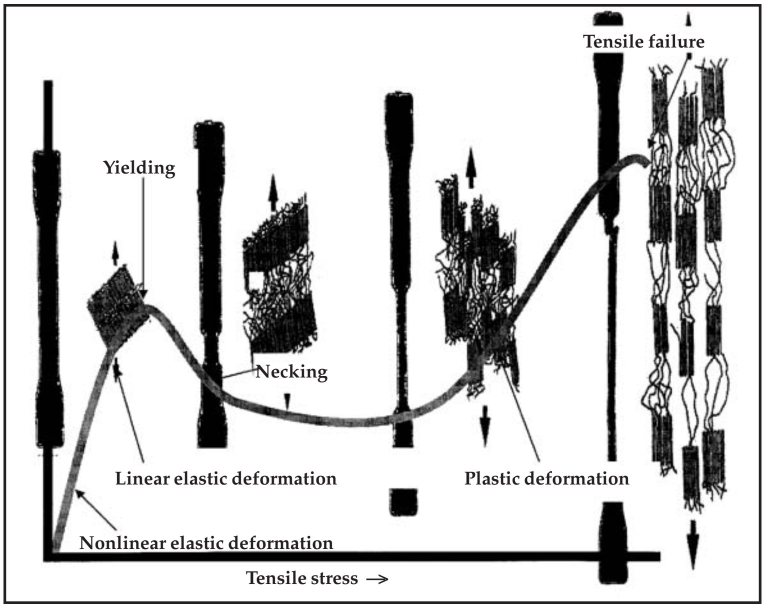

Fig. 2 — Typical tensile response of a ductile plastic resin specimen illustrates the failure mechanism as stress increases.

ment of the molecular structure by overcoming the intermolecular forces holding the molecules together. These forces include Van der Waals forces and hydrogen bonding.

In ductile failure, the mechanism that ultimately results in cracking includes several steps: linear elastic deformation, nonlinear elastic deformation, yielding, necking, plastic deformation, and failure. Each of these steps is associated with physical alteration of the molecular structure, as represented graphically in Fig. 2.

Amorphous and ordered segments

Perhaps the most readily obvious cause of ductile-to-brittle behavior is temperature. Plastic materials exhibit increasingly brittle properties as the temperature is reduced. However, the visible indications and the mechanism are not simplistic. Polymeric materials exhibit a continuum of ductile through brittle behavior across a temperature range. As illustrated in Fig. 3 and 4, polymeric materials present properties extending from rubbery through leathery to glassy as the temperature is reduced.

Several significant points along the temperature scale correlate to important physical transitions within the plastic resin. These transitions are a direct result of the structure of the polymer, although some minor modifications can be produced by additives within the formulated resin, particularly plasticizers. The most basic characteristic produced by the structure is the molecular morphology, dictating whether the polymer is semicrystalline or amorphous.

• **Ordered segments:** Semicrystalline polymers have regular, ordered segments within their structure. This results in a distinct melting point. A polymer melts when it reaches a temperature sufficient to produce disorder within the polymer chains such that the material becomes a true liquid. Melting is defined as a first-order transition.

• **Amorphous structures:** Semicrystalline polymers have a substantial level of disordered amorphous structure, ranging between 40% and 70% of the polymer chain content, depending on the material. Within semicrystalline polymers, these amorphous regions are known as tie molecules, and they bind the crystals together. As represented graphically in Fig. 4, it is the amorphous region of the polymer that undergoes elastic deformation and yielding.

The principal thermal transition associated with the amorphous structure of the polymer is the glass transition, a second-order transition. At temperatures above the glass transition, the polymer molecules have sufficient kinetic energy to allow considerable motion. Below the glass transition, the molecules lack the ability to move any distance.

It is important to note that only the amorphous segments go through the glass transition, and only the ordered segments go through the melting transition. Typical semicrystalline polymers include polyethylene, nylon, polyacetal, and thermoplastic polyesters.

Amorphous polymers lack ordered structure, with the entirety of the molecules having a disordered morphology. The primary thermal transition that these materials go through is the glass transition. Amorphous polymers include polystyrene, polycarbonate, polyvinyl chloride, and acrylic resins.

Transition temperatures

Most semicrystalline polymers are chosen for service at temperatures between the glass transi-

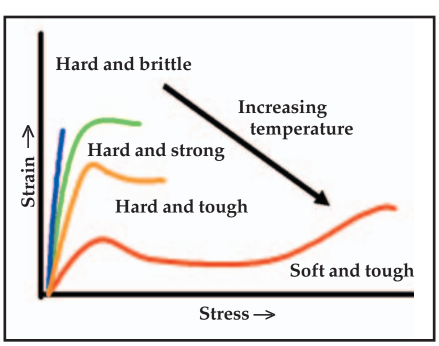

Fig. 3 — The change in tensile response is shown as a function of temperature.

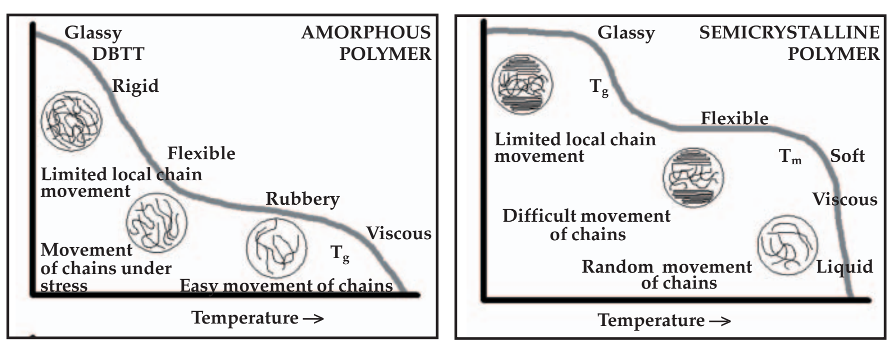

Fig. 4 — The effect of temperature on brittleness and structure is illustrated for amorphous and semicrystalline polymers. DBTT is the ductile-to-brittle transition temperature. Tg is the glass transition temperature.

tion temperature and melting point. Above the melting point, the resin becomes liquid. Below the glass transition, the resin loses the kinetic energy required for the amorphous tie molecules to move in response to applied stress. Thus, the polymer lacks the capacity to undergo substantial elastic deformation and yielding. Without the ability to elastically deform and yield, the polymer undergoes molecular disentanglement, and exhibits brittle properties.

Thus, the glass transition temperature of a semicrystalline polymer represents a ductile-to-brittle transition.

In contrast, amorphous polymers are typically utilized at temperatures below their glass transition. At temperatures approaching the glass transition, amorphous polymers attain sufficient kinetic energy to facilitate viscous flow within the material. **This represents a total loss of load bearing capability.**

However, as an amorphous polymer is exposed to progressively lower temperatures, the material undergoes another transition, known as the ductile-to-brittle transition temperature (DBTT). This represents passage through a lower-order transition. During this transition, the polymer loses a substantial level of kinetic energy, which results in restricted motion of the chains. This transition results in a sudden, sharp loss in ductility, as illustrated in Fig. 5. The magnitude of the change in ductility when an amorphous resin is cooled below the DBTT is comparable to that exhibited when a semicrystalline polymer is cooled below the glass transition.

The DBTT is not a fundamental property of the polymer type, but can be altered by composition factors, most notably molecular weight. The effect of molecular weight on the DBTT will be reviewed further during a future installment of this article series.

Environmental stress cracking

Environmental stress cracking (ESC) is the leading cause of plastic component failure. Recent estimates suggest that 25% of plastic part failures are caused by ESC, in which a plastic resin is apparently embrittled by a chemical agent while under tensile load. ESC is a solvent-induced crack mechanism in which the synergistic effects of the chemical agent and the tensile stress result in failure.

Contact with the chemical agent does not produce direct chemical attack or molecular degradation. However, the chemical permeates the molecular network and interferes with the intermolecular forces binding the polymer chains. This leads to accelerated brittle behavior and premature failure through molecular disentanglement.

The mechanism of ESC involves several individual steps, beginning with fluid absorption, and followed in succession by plasticization, craze initiation, crack growth, and ultimately fracture. This is shown graphically in Fig. 6. The speed of ESC craze initiation and crack extension is depends greatly on the rate of diffusion of the chemical agent into the plastic resin. As such, different plastic/chemical combinations produce varied responses. The rate of diffusion of the chemical agent, and ultimately the speed of crack initiation and propagation, are influenced by several factors. These include the chemistry of the polymer, the nature of the chemical agent, the stress level, the concentration of the chemical, the temperature, the length of time of exposure, and surface irregularities.

- **Plastic material:** Different polymers are affected by chemical agents in varying degrees. The composition of the plastic resin and in particular the molecular structure determines the general sensitivity of the resin to chemical interaction and which chemicals will act as ESC agents. In general, increased crystallinity within the polymer structure results in improved ESC resistance. This correlates to the amount of free volume within the resin. For this reason, amorphous plastic resins are significantly more susceptioble to ESC and other chemical effects than semicrystalline materials. Molecular weight is also an important material characteristic. The higher the molecular weight of the polymer, the more resistant the resin will be to ESC. Higher molecular weight resins tend to have a greater level of molecular entanglement, and this will be detailed in an upcoming article.
- **Chemical agent**: The rate of ESC depends

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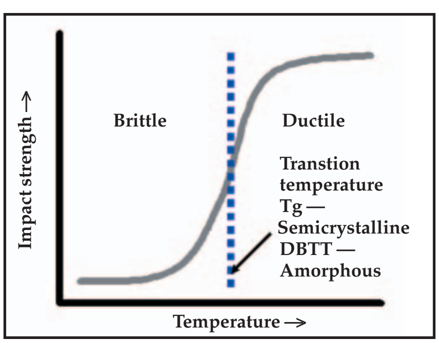
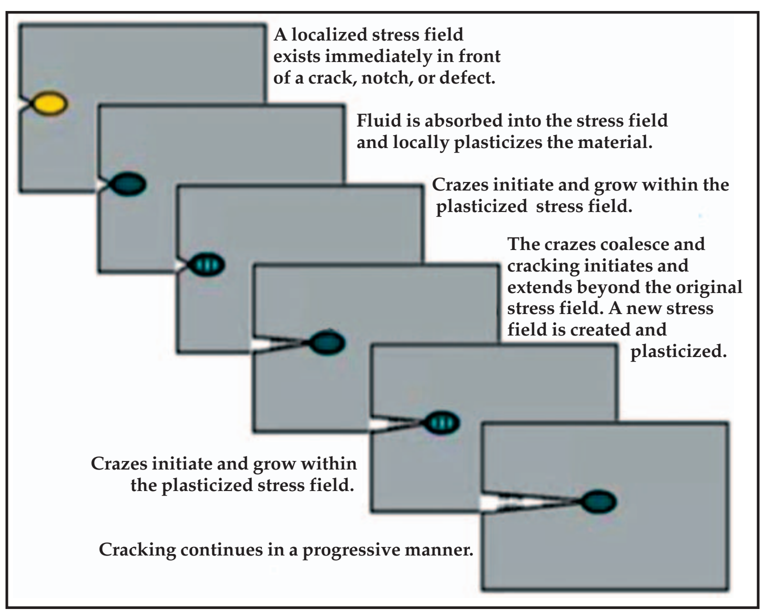


Fig. 5 — The ductile-to-brittle transition is shown as a function of temperature.

Fig. 6 — Six steps are involved with environmental stress cracking.



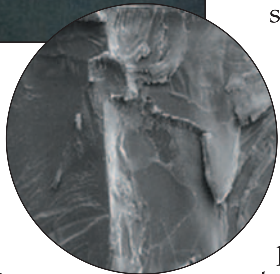



Fig. 7 — Environmental stress cracking is shown with a polycarbonate resin.

highly on the plastic/chemical combination. For a specific plastic, different chemical agents produce a varied response in crack initiation and extension. Because diffusion rate is the driving factor in the time to failure, combinations producing absorption of the chemical are the most severe. In general, chemicals with moderate levels of hydrogen bonding are the most active ESC agents. Additionally, low molecular-weight chemicals are the most aggressive. This is directly associated with the ability of the small molecules to permeate into the molecular structure of the plastic resin.

• **Stress level**: The level of tensile stress, applied either externally or internally, correlates directly with the rate of crack initiation and extension. Higher levels of stress result in a shorter time to failure. Design features such as sharp corners, molded-in defects, and mechanical damage can significantly concentrate the applied stress.

• **Chemical agent concentration**: Higher concentrations of the chemical agent result in more rapid diffusion into the plastic resin. This in turn shortens the time to crack initiation and increases the rate of crack extension.

• **Temperature**: Higher temperature exposure speeds the rate of diffusion of the chemical agent into the plastic resin. Thus, increases in temperature produce more rapid crack initiation and accelerated crack propagation.

• **Exposure time**: Longer exposure times can result in cracking within plastic/chemical combinations that over shorter time periods may appear innocuous. The extended time allows for permeation of the chemical into the resin.

• **Surface irregularities:** Surface irregularities and defects act as points of stress concentration. This serves to intensify the level of stress and facilitate localized cracking.

ESC is a brittle fracture mechanism and produces a fracture surface lacking substantial ductility because the stress responsible for the failure is insufficient to cause yielding within the material. A typical ESC fracture surface is presented in Figure 7. In spite of the relatively low stresses, the material cracks as a direct result of the disruption of the cohesive intermolecular forces generated by the presence of the chemical agent.

The ductile-to-brittle factors that will be reviewed as part of the next installment in this series include strain rate and the effect of time under load.

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This article reviews the factors that result in brittle performance of normally ductile plastic materials.

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Plastic materials exhibit viscoelastic properties, meaning that they display both elastic and plastic (viscous) response to stress. The viscoelastic nature of polymers makes strain rate and time important factors in the performance of plastics. This article describes the effects of strain rate and discusses how materials, design, processing, and service conditions influence impact resistance. The article further reviews the effects of time on plastic materials and their susceptibility to creep failure.

Strain rate

Strain rate, the time rate of elongation, is the speed at which a deforming load is applied to a material. The strain rate dependence of plastics is a unique, distinguishing characteristic relative to the broader scope of traditional materials, including metals and ceramics. Although metals do exhibit strain rate dependence at elevated temperatures, plastics alone display this attribute in the scope of most standard operating conditions.

The application of stress through high strain rate loading results in rapid deformation of the plastic material. At faster strain rates, the polymer molecules making up the plastic component do not have time to yield and deform as they normally do in an overload condition.

Conversely, the physical response of the polymer chains under conditions of rapidly applied stress is pre-emptive disentanglement. This means that cracking initiates and continues to extend when the applied stress exceeds a minimum energy. When the energy is in excess of the total level required for initiation and complete propagation, the result is catastrophic failure.

Effects of strain rate

The effects of elevated strain rate have substantial consequences on the mechanical performance of plastic components. In general terms, a higher strain rate results in an apparent loss of ductility. Specifically, a faster strain rate will result in a lower yield stress and a reduced elongation at break, as illustrated in Fig. 1. Depending on the conditions, a high strain rate can even produce an apparent increase in modulus. This means that normally ductile plastic materials exhibit brittle behavior under conditions of high strain rate loading. In fact, the application of stress under conditions of high strain rate within plastic materials directly parallels the performance exhibited at reduced ambient temperature.

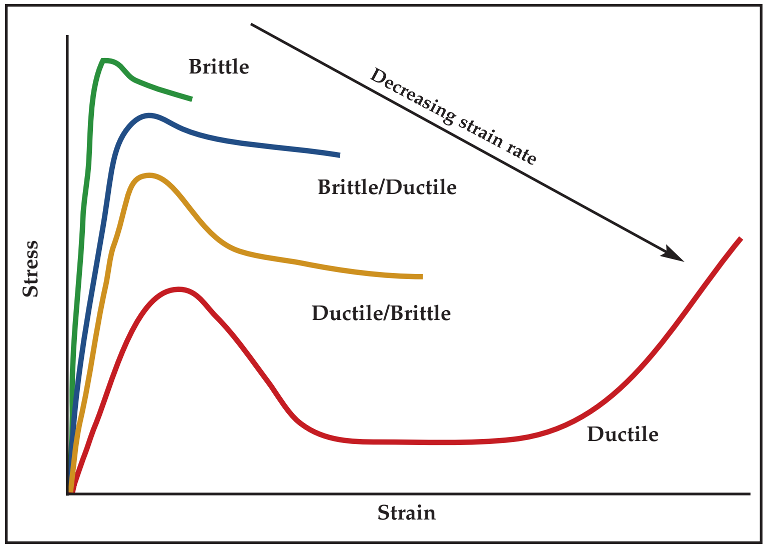

Fig. 1 — The change in tensile response is shown as a function of strain rate.

Plastics can be subjected to high strain rate loading in many ways, including rapid pressurization, snap fit installation, and impact, which is the most significant mechanism. The impact resistance of a plastic component is determined by four key factors: material composition, design, processing, and service conditions.

Material composition

Damping is the ability of a material to dissipate impact energy by converting it into heat. The composition of the material subjected to impact loading is the primary factor in determining overall performance, because it is the major determinant of damping properties. Various impact responses resulting from different material types are presented in Fig. 2. Important aspects of material composition include:

• **Polymer type**: The molecular structure of the polymer determines the chain mobility, which is a key factor in the ability of the material to yield. For this reason polystyrene, with a large pendant phenyl ring, is less impact resistant than polyethylene.

• **Molecular weight**: All material properties,

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The conditions under which a plastic component is subjected to a high strain rate event alter the ability of the material to respond.

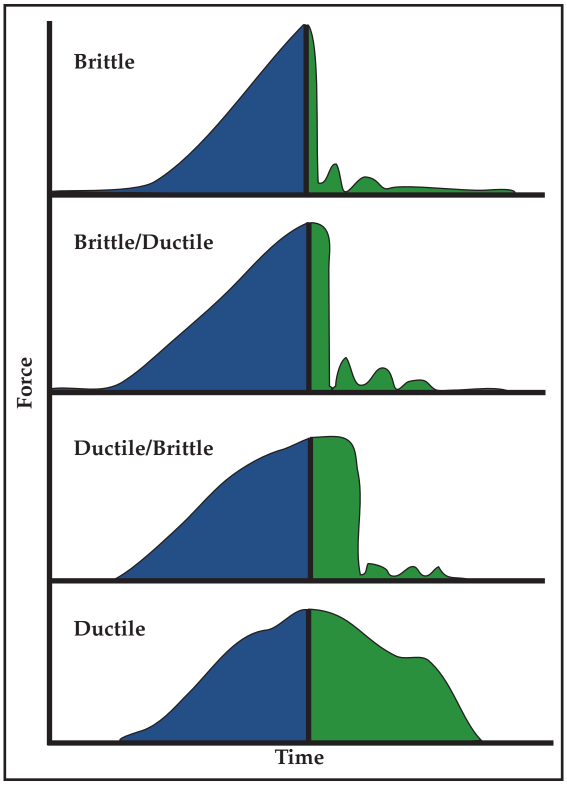

Fig. 2 — Various impact results are shown based on different material compositions and the associated damping properties. The blue portion of the curve illustrates the energy required to initiate cracking, and the green portion shows the energy absorbed after crack commencement. The bigger the ratio of total energy to crack initiation energy, the higher the level of ductility.

including impact resistance, improve with increasing molecular weight.

• **Crystallinity**: Within a family of materials, greater crystallinity is accompanied by a reduction in impact resistance. For example, low-density polyethylene is more impact-resistant than high-density polyethylene.

• **Modifiers**: Formulation ingredients that contribute to damping also improve impact resistance. Such additives include rubber and plasticizers. Additionally, copolymers often have better impact resistance than the corresponding homopolymer. For example, polypropylene copolymerized with ethylene is superior to polypropylene homopolymer.

• **Fillers**: Fillers within the plastic resin alter the impact properties. Chopped glass and most mineral fillers reduce impact resistance. However, calcium carbonate and talc can help to initiate crazing, which improves impact properties.

• **Contamination:** Contamination within a molded plastic part most often produces localized areas of poor molecular entanglement. This leads to an inherent reduction in impact resistance.

Component design

The design of the part can have a great influence on the ability of the material to accept impact loading. Important factors include:

• **Stress concentration**: Design aspects that serve as points of stress concentration increase the apparent brittle response of the material. By focusing the stress, the polymer molecules forego yielding, and conversely disentanglement results. Such stress concentrators include sharp corners, notches, grooves, recesses, holes, and even variable wall thickness and a textured surface.

• **Wall thickness**: Some plastic materials, such as polycarbonate, are sensitive to the wall thickness of the impacted area. Thicker walls lead to a reduction in the ability of the material to adequately dissipate the energy in a ductile manner, leading to brittle fracture.

Material processing

The processing of a plastic material can alter the capacity of the molecular structure to damp energy resulting from impact loading. Essential aspects of processing include:

• **Discontinuities:** Contamination, voids, or porosity within molded components provide points of stress concentration. Such defects intrinsically reduce the impact resistance of the part.

• **Fusion**: Areas of poor fusion, such as a knit line, correspond to poor molecular entanglement. These regions of the molded part are essentially more likely to disentangle rather than yield upon impact loading.

• **Orientation**: Orientation of the polymer molecules during molding alters the impact response of the material. Depending on the direction of orientation relative to the impact load, the results may be an increase or decrease in the impact resistance.

• **Molded-in stress**: Internal and external stresses are additive within a formed part; thus the presence of molded-in stress can severely reduce the level of impact stress a material can accommodate.

Service conditions

The conditions under which a plastic component is subjected to a high strain rate event alter the ability of the material to respond. These external factors include:

• **Impact speed**: Higher impact speeds translate into more rapid deformation, leading to a reduction in the ability to damp the impact energy. Thus, higher impact speeds are more severe than slower speeds.

• **Temperature**: A reduction in temperature corresponds to a more brittle response upon impact.

• **Impact fatigue**: Repeated impacts produce fatigue-like response in a plastic component. This generally results in brittle failure through premature disentanglement.

• **Striker geometry**: Sharper striker objects tend to focus impact energy more tightly, leading to higher levels of localized stress. This is more severe than the same load applied with a blunt striker, which allows energy dissipation over a wider surface.

Time under load

The viscoelastic nature of plastic materials leads not only to temperature dependence, but also to reliance on time. Specifically, the mechanical properties of a plastic material change as the material is loaded over time, as shown graphically in Fig. 3. A marked decay in the modulus is observed for plastics that are loaded statically for an extended period. The re-

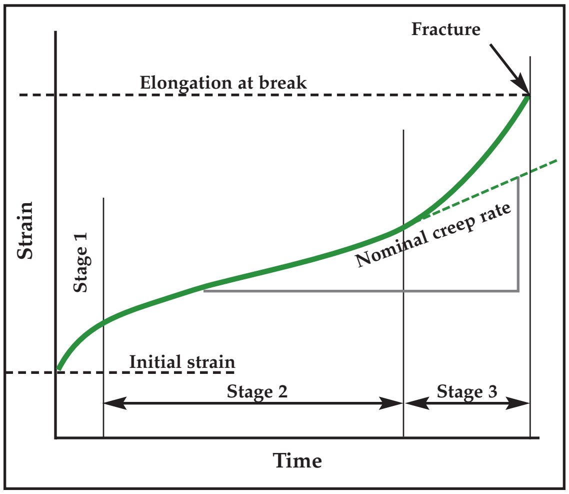

Fig. 3 — A creep curve is shown illustrating the effect of time on plastics under load. The viscoelastic nature of plastic materials leads not only to temperature dependence, but also to reliance on time.

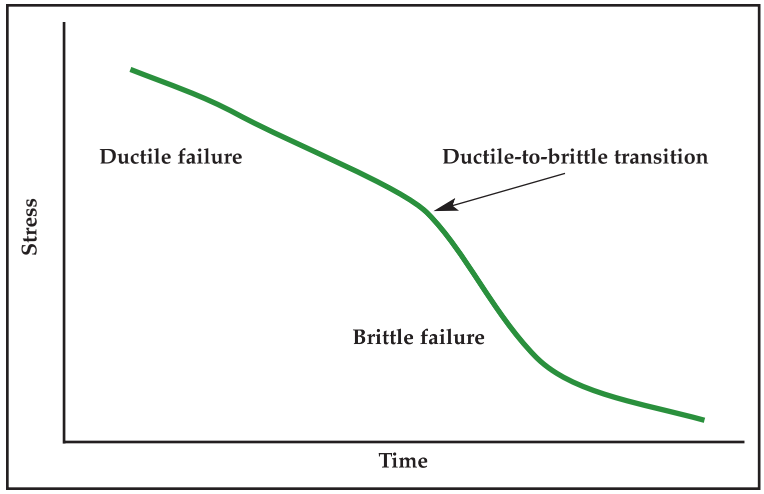

Fig. 4 — The ductile-to-brittle transition within the applied stress level is illustrated. If the stresses involved are continually below the yield point of the material, the failure is manifested as brittle fracture.

duction in modulus is the result of reorganization of the polymer chains, minimizing localized stress. At stresses below the yield point of the material, the chains reorganize through disentanglement. This subsequently leads to crack initiation, when a sufficient time/load condition has been met, and ultimately to failure through continued exposure.

If the stresses involved are continually below the yield point of the material, the failure is manifested as brittle fracture, often called creep rupture or static fatigue. This is shown in Fig. 4. The susceptibility of plastics to creep is uniquely different than the properties exhibited by most metals.

Short-term mechanical properties, such as tensile or flexural strength, are inadequate to predict the long-term load-bearing capabilities of a plastic material. While they are useful in assessing overload conditions, no inference can be made regarding the effect of time on a component. Creep testing is required to predict the effective life of a statically loaded component, either through the traditional method of hanging weights on a creep stand, or by dynamic mechanical analysis.

Semicrystalline polymers such as polyethylene and polypropylene are inherently more susceptible to creep than amorphous resins, because semicrystalline resins generally have glass transition temperatures (T_g) below ambient. At temperatures above T_g, the molecular structure comprising the material has sufficient energy to allow the mobility required for creep.

Although amorphous resins show a lesser tendency to creep, materials containing rubber constituents show a clear creep response, such as acrylonitrile:butadiene:styrene (ABS) resin and high impact modified polystyrene (HIPS). In general, the aspects of material structure and composition that give materials good impact resistance impart a proclivity to creep. The exception to this is molecular weight. As with any mechanical property, creep resistance improves with increasing molecular weight.

Creep failure

Creep failure is mechanistically similar to environmental stress cracking (ESC). ESC takes place when a susceptible plastic material is subjected to tensile stresses while in contact with a chemical agent that accelerates the failure. However, absent the chemical, the cracking would still take place over a longer period of time through creep. In other words, creep is an example of environmental stress cracking in which the chemical agent is air.

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