

UNDERSTANDING THE CONSEQUENCE OF DUCTILE-TO-BRITTLE TRANSITIONS IN A PLASTIC MATERIALS FAILURE

Jeffrey A. Jansen, Stork Technimet, Inc.

Now with The Madison Group

Abstract

The goal of a failure analysis is to identify the mode and cause of the failure. The assignment of the failure mode is often straightforward through fractographic techniques. Comparatively, the determination of the cause of the failure is often less apparent, but required if proper corrective action is to be carried out. Many times the cause of the failure is related to factors that produce a ductile-to-brittle transition within the material. These factors are associated with material, processing, design, and service issues. This paper addresses the failure modes of thermoplastic resins in regards to a ductile-to-brittle transition as the cause of the failure.

Background

The objective of a failure investigation, regardless of the material, is to identify the mode and cause of the failure. The characterization of the failure mode such as, fatigue, overload, environmental stress cracking, etc... is often straightforward through standard fractographic methods. However, the determination of the cause of the failure is in many cases less apparent. This is particularly true with a plastic component. Thermoplastic resins are utilized in many applications because of their unique property set, including their 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. Experience through conducting over 800 plastic component failure analyses has shown that less than 5% were associated with ductile overload. The remainder represent brittle fractures of normally ductile materials. Thus, within evaluations of plastic component failures, the focus of the investigation frequently turns to identifying the nature of the ductile to brittle transition. This relatively brittle response to stress is evident through the examination and characterization of the fracture surface morphology.

In order to understand the cause of a ductile-to-brittle transition, there must first be a comprehension of the mechanism whereby plastic materials crack. Cracking is simply a response to mechanical stresses, either internal or external. Contrary to popular misconception, cracking of a plastic resin does not represent the scission of the polymer molecules. Although molecular degradation mechanisms, including oxidation and chemical attack, can render the altered material prone to failure, plastic resins do not crack through mechanisms producing gross breakage of individual polymer chains. While mechanical stress will

result in a limited amount of chain scission, the primary response is molecular disentanglement, sometimes referred to as slippage. Cracking within a molded plastic resin represents the disentanglement of the molecular structure, by overcoming the intermolecular forces holding the molecules together, including Van der Waals Forces and hydrogen bonding. In ductile failure, the mechanism resulting in cracking includes several steps including linear elastic deformation, nonlinear elastic deformation, yielding, necking, plastic deformation, and finally, failure. Each of these steps is associated with physical alteration of the molecular structure, as represented graphically in Figure 1.

There are numerous factors that influence a ductile-to-brittle transition within plastic materials, such as:

- Temperature
- Stress Concentration
- Chemical Contact
- Molecular Weight
- Degradation
- Filler Content
- Contamination
- Poor Fusion
- Strain Rate
- Time Under Load
- Crystallinity
- Plasticizer Content

These factors are associated with material, processing, design, and service issues.

Temperature

The most intuitively obvious cause of ductile-to-brittle behavior is temperature. Simply stated, plastic materials exhibit increasingly brittle properties as the temperature is reduced. The apparent behavior and the mechanism, however, are not simplistic. Polymeric materials, including plastics, exhibit a continuum of ductile through brittle behavior across a temperature range. As illustrated in Figure 2, polymeric materials will present properties extending from rubbery through leathery to glassy as the temperature is reduced.

There are several significant points along the temperature scale that 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 of the polymer produced by the structure is the molecular morphology, dictating whether the polymer is semi-crystalline or amorphous.

Semi-crystalline polymers have regular, ordered segments within their structure. This results in a distinct melting point. Melting, a first order transition, occurs when the polymer reaches a temperature sufficient to produce disorder within the polymer chains such that the material becomes a true liquid. However, semi-crystalline polymers have a substantial level of unordered amorphous structure, ranging between 40% and 70% of the polymer chain content, depending on the material. Within semi-crystalline polymers these amorphous regions are known as tie molecules, binding the crystals together. As represented graphically in Figure 1, 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 undergo this motion. It is important to consider that the glass transition and melting transitions that semi-crystalline polymers undergo, affect the respective amorphous and crystalline molecule segments, exclusively. Typical semi-crystalline 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, poly(vinyl chloride), and acrylic resins.

In general, most semi-crystalline polymers are used at temperatures between their glass transition 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 semi-crystalline 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). The DBTT 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 Figure 3. The magnitude of the change in ductility when an amorphous resin is cooled below the DBTT is comparable to that exhibited when a semi-crystalline 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.

Chemical Contact / Environmental Stress Cracking

Environmental stress cracking (ESC) is the single leading cause of plastic component failure. Recent estimates suggest that 25% of plastic part failures occur through ESC. ESC is a phenomenon whereby a plastic resin is apparently embrittled by a chemical agent while under tensile loading. It is a solvent-induced crack mechanism in which the synergistic effects of the chemical agent and the tensile stress result in failure. The contact with the chemical agent does not produce direct chemical attack or molecular degradation. Conversely, the chemical permeates into 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 Figure 4. The speed of ESC craze initiation and crack extension is highly dependent 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, including:

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 prone to ESC and other chemical effects compared with semi-crystalline 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.

Increased 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 is highly dependent on the plastic/chemical combination. For a specific plastic, different chemical agents will produce a varied response in regards to 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

There is a direct correlation between the level of tensile stress, either externally applied or internal, and the rate of crack initiation and extension. Higher levels of stress will 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 will result in more rapid diffusion into the plastic resin. This in turn will shorten the time to crack initiation and increase the rate of crack extension.

Temperature

Higher temperature exposure results in an increased 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

Increased exposure times can result in cracking within plastic/chemical combinations that under 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. 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.

Strain Rate

The strain rate dependence observed within plastics is a unique, distinguishing characteristic relative to the broader scope of traditional materials, including metals and ceramics. It is true that metals do exhibit strain rate dependence at elevated temperatures. However, in the scope of most standard operating conditions, plastics alone display this attribute. Strain rate, the time rate of elongation, is the speed at which a deforming load is applied to a material. The effects of high strain rate stress loading are not insignificant. The application of stress through high strain rate loading results in rapid deformation of the plastic material. At increasingly elevated strain rates, the polymer molecules making up the formed plastic component are precluded from having sufficient time to yield and deform, as normally observed in an overload condition. Conversely, the physical response of the polymer chains under conditions of rapidly applied stress is preemptive disentanglement. 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, catastrophic failure occurs.

The effects of elevated strain rate have a substantial consequence on the mechanical performance of plastic components, as illustrated in Figure 5. In general terms, increased strain rate results in an apparent loss of ductility. Specifically, an increased strain rate will result in a lower yield stress and a reduced elongation at break. Depending on the conditions, an apparent increase in modulus can also occur. As such, under conditions of high strain rate loading, normally ductile plastic materials will exhibit brittle behavior. The application of stress under conditions of high strain rate within plastic materials directly parallels the performance exhibited at reduced ambient temperature. There are many ways in which plastics can be subjected to high strain rate loading. The most common include impact, snap fit assembly, and rapid pressurization.

As is the case regarding the overall performance of plastic components, the impact resistance of a plastic component is determined by four key factors: material, design, processing, and service conditions.

Material

The composition of the material subjected to impact loading is the primary factor in determining the overall performance, because it is the major determinant of the damping properties. The effects of this are presented in Figure 6. Damping is the ability of the material to dissipate the impact energy by converting it into heat. 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, including impact resistance, improve with increasing molecular weight.

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

Modifiers: The presence of formulation ingredients that contribute to damping will improve the impact resistance of the material. Such additives include rubber and plasticizers. Additionally, copolymers often have better impact resistance compared to the corresponding homopolymer, for example polypropylene copolymerized with ethylene is superior to polypropylene homopolymer.

Fillers: The presence of fillers within the plastic resin will alter the impact properties. Chopped glass and most mineral filler will decrease the impact resistance. However, calcium carbonate and talc can help to initiate crazing, which will improve the impact properties.

Contamination: The presence of contamination within a molded plastic part will most often produce localized areas of poor molecular entanglement. This will inherently lead to a reduction in impact resistance.

Design

The design of the component 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 will increase the apparent brittle response of the material. By focusing the stress, the polymer molecules forego yielding, and conversely disentanglement occurs. Such stress concentrators include sharp corners, notches, grooves, recesses, holes, and even variable wall thickness and a textured surface.

Wall thickness: Some plastic materials, polycarbonate for example, 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.

Processing

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

Discontinuities: The presence of included contamination, or voids or porosity within the molded components will

result in points of stress concentration. Such defects will intrinsically reduce the impact resistance of the part.

Fusion: Areas of poor fusion, such as a knit line, correspond to poor molecular entanglement. This regions of the molded part will essentially be more prone to disentangle, rather than yielding, upon impact loading.

Orientation: Orientation of the polymer molecules during molding will alter 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 article, 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 will 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 of the material to damp the impact energy. Thus, higher impact speeds are more severe than slower speeds.

Temperature: A reduction in temperature will correspond to a more brittle response upon impact. This relationship was reviewed in detail in the previous article in this series,

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

Striker geometry: Sharper striker objects will tend to focus the impact energy more tightly, leading to higher levels of localized stress. This will be more severe than the same load applied with a blunt striker, which allows more widespread energy dissipation.

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 will change as the material is loaded over time, as shown graphically in Figure 7. A marked decay in the modulus will be observed for plastics that are loaded statically for an extended period of time. The reduction in modulus is the result of reorganization of the polymer chains, minimizing localized stress. At stresses below the yield point of the material the reorganization takes place 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 will be manifested as brittle fracture, often referred to as creep rupture or static fatigue. This is illustrated in Figure 8. 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 be able to predict the long term loading bearing capabilities of a plastic material. While they are useful in assessing overload conditions, no inference can be made to the effect of time on the component in question. Creep testing, either through the traditional method of hanging weights on a creep stand or dynamic mechanical analysis, is required to predict the effective life of a statically loaded component.

Semi-crystalline polymers, such as polyethylene and polypropylene, are inherently more prone to creep than amorphous resins. This is because semi-crystalline 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. While amorphous resins show a lesser tendency to creep, materials containing rubber constituents, such as acrylonitrile:butadiene:styrene (ABS) resin and high impact modified polystyrene (HIPS), will show a clear creep response. 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 is mechanistically similar to environmental stress cracking (ESC). As described in the previous article, ESC takes place when a susceptible plastic material is subjected to tensile stresses while in contact with a chemical agent. The presence of the chemical agent accelerates the

failure. However, absent the chemical, the cracking would still take place over a longer period of time through creep. In this way, creep is ESC where the chemical agent is air.

Summary

A number of different factors can cause a ductile-to-brittle transition within thermoplastic materials. These factors cover a broad spectrum, but all relate to material, processing, design, and service. While having the appearance of a diverse, seemingly unrelated dynamic, they have in common the same molecular response. All of the factors create a situation in which there becomes less resistance to molecular disentanglement compared to yielding and deformation. When such a transition occurs, the results can be devastating. The unexpected brittle failure of a components expected to produced a ductile response to stress can certainly have severe consequences. Understanding potential ductile-to-brittle situations can help to avoid failures. Absent such prevention, knowledge regarding ductile-to-brittle transitions can greatly aid in the subsequent failure analysis process.

Keywords

failure analysis, ductile, brittle, creep, environmental stress cracking

References

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- 2 Jeffrey Jansen, Environmental Stress Cracking – The Plastic Killer, Advanced Materials & Processes, June, 2004

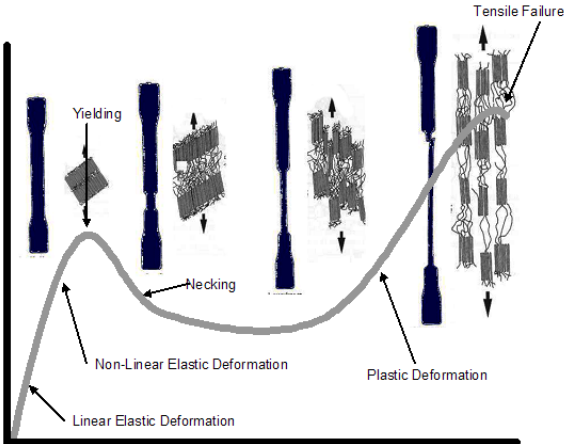


Fig. 1 - Typical tensile response of a ductile plastic resin illustrates the failure mechanism as stress increases.

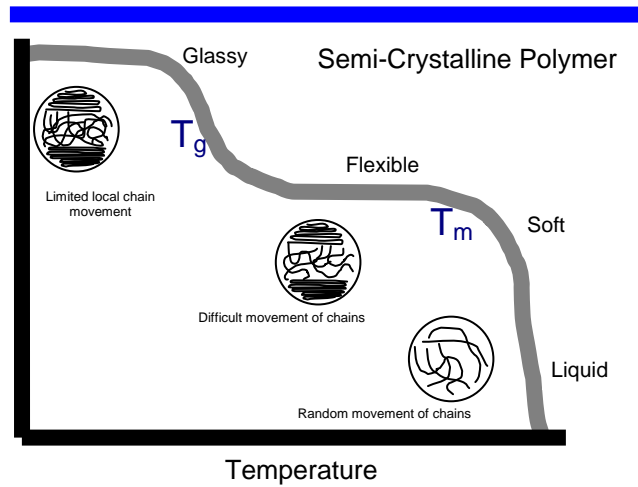
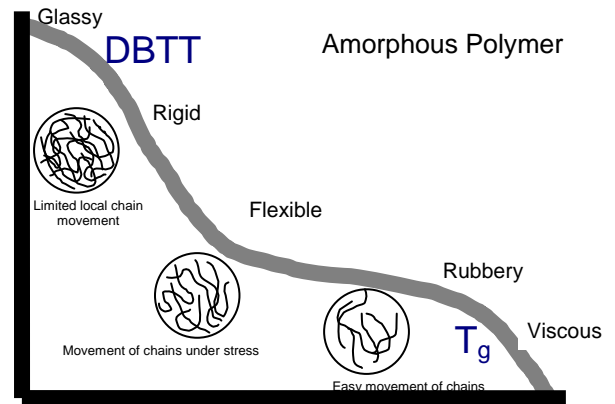


Fig. 3 - The effect of temperature on stiffness / brittleness is illustrated for amorphous and semicrystalline materials.

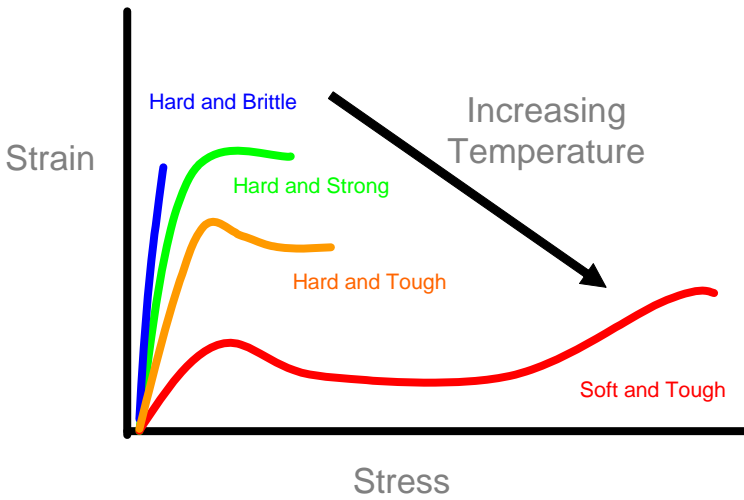


Fig. 2 - The change in tensile response is shown as a function of temperature.

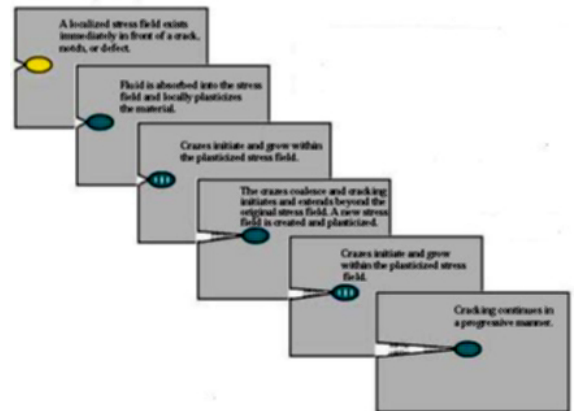


Fig. 4 - The steps involved in environmental stress cracking are shown.

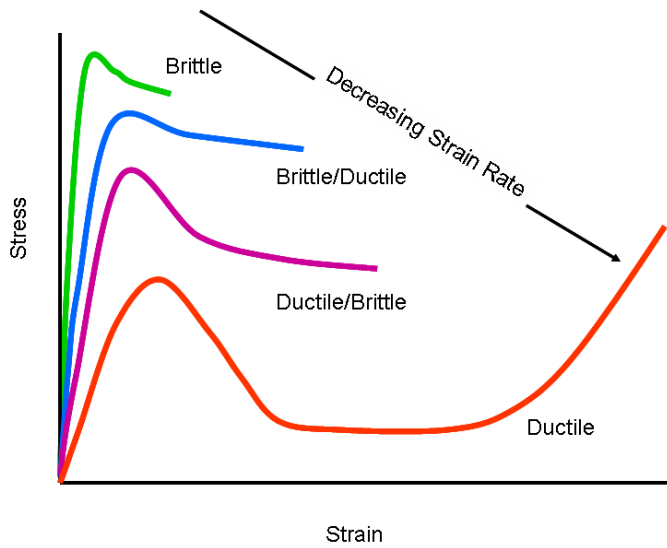


Fig. 5 - The change in tensile response is shown as a function of strain rate.

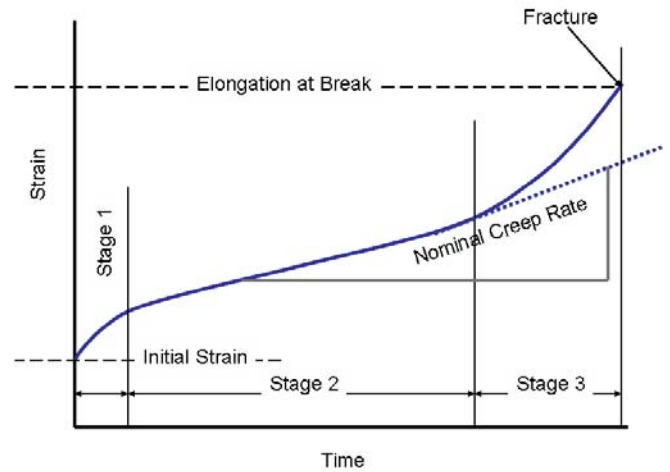


Figure 7 – A creep curve is shown illustrating the effect of time on plastics under load. The viscoelastic nature of plastics leads not only to temperature dependence, but also to reliance on time.

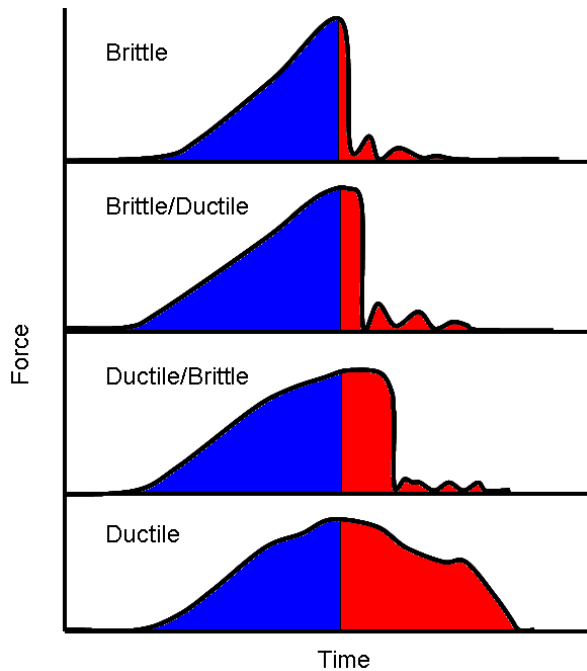


Fig. 6 - Various impact results are shown based on different material compositions and the associated damping properties. The blue portion of the curve represents the energy required to initiate cracking, and the red portion shows the energy absorbed after crack commencement. The bigger the ratio of total energy to crack initiation energy, the higher the level of ductility.

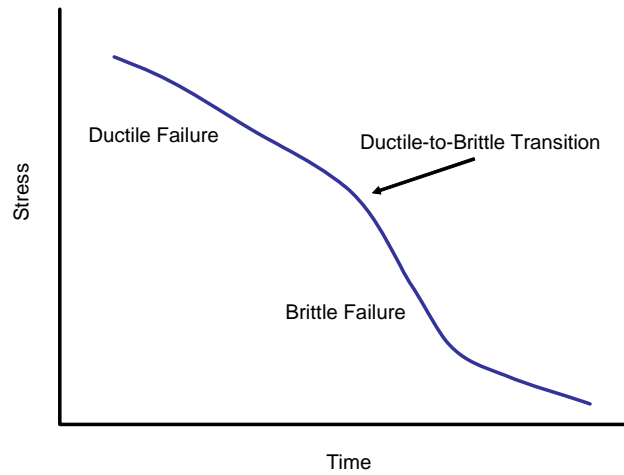


Fig. 8 - The ductile-to-brittle transition as a function of time and stress is illustrated. If the stresses involved are continually below the yield point of the material, the failure is manifested as brittle fracture.