

PDHonline Course M399 (4 PDH)

Plastics Fundamentals: Properties and Causes of Failures

Instructor: Semih Genculu, P.E.

2020

PDH Online | PDH Center

5272 Meadow Estates Drive
Fairfax, VA 22030-6658
Phone: 703-988-0088
www.PDHonline.com

An Approved Continuing Education Provider

COURSE CONTENT

As the demand for plastics has grown exponentially over the years, mainly driven by the appliance, automotive, construction, electronics, medical device, and packaging industries, the importance of successful design and application has become more critical. The sensitivity of polymeric materials to processing and environmental conditions is much greater than for traditional engineering materials. Despite these limitations, significant benefits that include a weight-to-strength ratio advance the use of plastics for high technology applications. Furthermore, relative ease of processing and component integration makes plastics an attractive alternative for use in various applications in the consumer goods industry. The successful application relies on the basic understanding of their fundamental behavior.

BASIC DEFINITIONS

Nowadays, much of what you see on store shelves is made of or packaged in plastic. There are many examples-cooking trays for frozen meals, beverage bottles, the bags you use to carry your purchases home, vinyl siding, plastic pipes, insulation on electrical wires, floor mats, your car's dashboard-are all made of polymers. Although it does not seem terribly exciting to think about what makes up the casing on a cellular phone, the chemical structure of the plastic makes the casing strong, heat resistant, scratch resistant, and shiny. These attributes make the cell phone case what it is. A polymer is a chain of linked repetitive units: "poly," many, and "mer," units. The organization and the components of the units are what create the many different types of polymers in the world.

Polymeric materials can be arranged into the following main groups:

Polymer: A substance consisting of molecules (often large ones characterized by the repetition of one (homopolymer) or more (copolymer, terpolymer, etc.) types of monomeric units. In the simplest form monomers are ordered into a thread or chainlike structure. The concept of the chain is based on the macromolecular structure. The structure is such that the movement of an individual element within the chain is transferred to neighboring elements. On the backbone of a linear macromolecule, which is a more or less regular structure, substitution of individual atoms by substituents can occur. The substituents are commonly chemically different from the monomer. If the structure of the substituents is identical to that of the backbone, they are called branches. Substituents can either make the main chain and the network of macromolecules stronger and stiffer or looser and more flexible. Macromolecules can be linked to one another via either chemical or physical bonds. Chemically linked macromolecules are known as cross-linked (thermosets). One significant difference between the two bond types is that the physical bonds are reversible when subjected to heat, solvents or mechanical forces whereas chemical bonds are irreversible. Physically bound linear or branched macromolecules are called thermoplastics and they are solid at ambient temperatures but become deformable at elevated temperatures.

Plastic: A material that contains as an essential ingredient one or more organic polymeric substances of large molecular weight, is solid in its finished state, and at some stage in its manufacture or processing into finished articles, can be shaped by flow. Used strictly as a synthetic engineering material for the replacement of conventional materials such as metal, wood, stone, glass and ceramic. Modern plastics are lightweight, tough, corrosion resistant and can be easily molded into complex components with various functions and features.

Rubber (elastomers): Even though it possesses a chemically and technically similar structure to that of plastics, differences in processing techniques and viscoeleastic deformation behavior distinguish this group from plastics. It is a material that is capable of recovering from

large deformations quickly and forcibly, and can be, or already is, modified to a state in which it is essentially insoluble (but can swell) in boiling solvent, such as benzene, methylethylketone, and ethanol-toluene azeotrope. In general, a rubber is flexible at room temperature (glass transition temperature less than 25°C), while most plastics are tough and rigid at room temperature (glass transition temperature greater than 25°C).

Thermoplastic Polymer: A plastic that can repeatedly be softened by heating and hardened by cooling through a temperature range characteristics of the material, and that in the softened state can be shaped by flow into articles by molding or extrusion. It can be processed many times without a chemical change in or bonding between the chains of the polymer. Because there is no chemical change, these materials can be melted again and again and reformed as many times as desired. There is one exception to this statement, in that many polymers degrade during processing because of the high temperatures used in the process. This degradation is a chemical process that cannot be reversed and is guarded against by the use of stabilizers. Because they can be processed many times, these materials are the backbone of the plastics recycling industry. Common examples of thermoplastics are polyethylene, polyvinylchloride, and polypropylene, and some common uses are vinyl siding, plastic grocery bags, and milk bottles.

Thermoset Polymer: A thermoset is a type of plastic that undergoes a chemical change during production that cannot be repeated or reversed. The way that this happens is called cross-linking. This process results in permanent chemical bonding of the individual polymer chains to one another. These materials can never be reshaped into a new form with the same chemical composition by heating and mixing as the other type of polymers can. Some examples of materials made of thermosets are fiberglass boats or bathtubs, foam insulation, and epoxy glues.

Homopolymer: Earlier a polymer was described as a long chain of repeating units-many "mers" lined up. Many polymers are made from the same units repeated again and again; these are called homopolymers. In other words, every repeat unit is the same within the material. Another type of polymer, a copolymer, is different because there are at least two different repeat units in the polymer chain. In this type of polymer, the different units are bonded to one another. Some simplistic way of illustrating copolymers are listed below:

A-B-A-B-A-B . . . . . .alternating copolymer
A-A-A-A-B-B-B-B . . . . . block copolymer
A-B-B-B-B-A-A-B-A-A-A . . ..random copolymer

In these examples A is one type of "mer" and B is another. Another way to have different "mers" combined in the same polymer material is in a blend. The difference between a blend and a copolymer is that the blend is a mixture of two or more homopolymers or copolymers into a thoroughly mixed material whereas in a copolymer the different types of "mers" are bonded to one another. These polymers are often made to improve specific characteristics for an end use.

Random Copolymer: A copolymer in which the monomer units are distributed at random along the polymer chains (-A-A-B-A-B-B-A-A-A-B-A-A-B-B-B-).

Block Copolymer: An essentially linear copolymer in which there are repeated sequences of polymeric segments of different chemical structure (-A-A-A-A-A-A-B-B-B-B-B-).

Graft Copolymer: A copolymer in which polymeric side chains have been attached to the main chain of a polymer of different structure. An important technical application of graft copolymerization is the manufacture of impact-resistant polystyrene (PS-HI) and of acrylonitrile-butadiene-styrene copolymer (ABS). In both cases a hard polymer component

and a highly tough, elastomeric component are combined by means of graft copolymerization to produce a high-impact polymeric material.

INFLUENCE OF VARIOUS FACTORS ON PROPERTIES

The molecular weight of a molecule is the sum of the atomic weights of its atoms. Polymeric materials do not have a uniform molecular weight. This is because the polymerization process gives rise to macromolecules of different length. Therefore, polymers are characterized by having a molecular weight distribution. In general, a narrow molecular weight distribution can be expected to lead to a polymeric material with more uniform property values, a narrower softening/melting temperature range, a lower stress cracking sensitivity, and better chemical resistance. A broad molecular weight distribution has advantages for processing of the polymer because the low molecular weight fractions present behave like lubricants. The polymer is less brittle since these fractions act as plasticizers.

With increasing molecular weight, in other words with increasing chain length, the macromolecules become increasingly entangled. This hinders their ability to move freely in the melt and slide past each other. Unfortunately, with increasing molecular weight, the viscosity increases and injection molding of the polymer becomes more difficult. On the other hand, extrusion and blow molding of the polymer now becomes possible due to the greater cohesion between the molecules. The increasing entanglement of the macromolecules and their increasing length reduces their mobility and makes it more difficult for crystallites to form. Thus, the ratio of crystalline to amorphous material in the polymer decreases with increasing molecular weight. This results in reduced density, because a crystalline arrangement of the molecules represents the state of greatest packing density. Furthermore, because secondary valence forces acting between macromolecules are most effective in the crystalline state, a decrease in the amount of crystalline material in the polymer, as a result of increasing molecular weight, leads to a decrease in the elastic modulus and a decrease of abrasion resistance.

Polymers can be described by a degree of crystallinity; this tells you how much of the polymer is made of crystalline areas. The degree of crystallinity can tell you a lot about how a polymer will behave. Materials that have low crystallinity are flexible and will bend easily; those that have high crystallinity are brittle and hard. Another property that is affected by crystallinity is the opacity of the plastic. A plastic sheet that is transparent most likely has a low level of crystallinity whereas one that is opaque has a very high level of crystallinity. This is clearly illustrated by two types of plastic cups. Isotactic polypropylene cups are made of a resin that has a high degree of crystallinity, making the cups translucent due to the light scattering between the amorphous and crystalline regions. Polystyrene cups, however, are perfectly transparent and clear because the polymer itself is amorphous. Yet another property that is influenced by crystallinity is chemical resistance. The higher crystallinity makes the polymer more difficult to penetrate by an attacking species, thereby making it more resistant.

The number of repeat units in a polymer molecule is described as its chain length. Increasing the chain length results in a longer distance in which the chains can slide past each other when subjected to tension and, therefore, an increase in the strain at failure. With high molecular weight polymers fewer and fewer chains are able to slide past each other because there are fewer short chains present. As the applied tension increases, it approaches the strength of the covalent bonds in the chain resulting in their rupture and thus a reduction in the strain at failure.

In the production of plastics it is common to select a certain average molecular weight taking into account that compromises have to be made in achieving the desired properties. For example, on the one hand the polymer melt has to be easily processable, but on the other hand, it is desirable to reach high values for elastic modulus, strength, and toughness.

Permitting a variation of these properties with molecular weight for polymers of the same chemical composition is only possible with thermoplastics. With thermosets and cross-linked elastomers, if it is assumed that in the ideal case the polymer consists of only a single macromolecule, then its molecular weight has no significance because it is infinitely large. The degree of cure is one of the most important characteristics of a thermoset. Theoretically, a 100% degree of cure indicates that all reactive groups of the resin and of the curing agent have reacted. In practice, this situation is almost never reached because not all the reactive groups find their way to each other. However, the highest possible degree of cure should be sought in order to obtain a product with optimal properties, such as high stiffness, strength, and dimensional stability at elevated temperatures. Of greater influence on the properties of cross-linked polymers is the so-called net chain length, i.e. the chain length or number of monomer units between cross-links. If many unsaturated, i.e. cross-linkable, double bonds per polyester chain length exist within the resin, the resulting resin will be tightly cross-linked and will be very stiff, brittle and resistant to chemical attack.

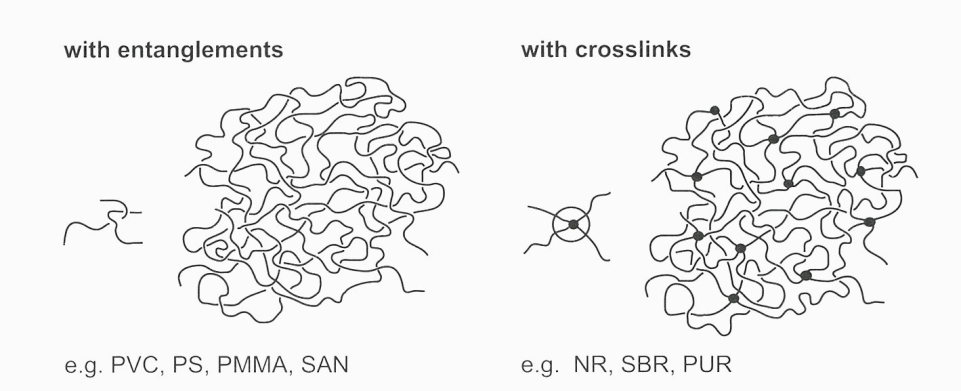
STRUCTURE OF POLYMERIC MATERIALS

The structure of polymeric material is rather complex. The position of the various structural elements that make up the morphology of the bulk material depends on chemical composition, thermal and mechanical history, and the “length scale” being considered. What looks homogeneous at one magnification may appear quite heterogeneous at another.

A polymer is an organic material and the backbone of every organic material is a chain of carbon atoms. The carbon atom has four electrons in the outer shell. Each of these valence electrons can form a covalent bond to another carbon atom or to a foreign atom. The key to the polymer structure is that two carbon atoms can have up to three common bonds and still bond with other atoms. The elements found most frequently in polymers and their valence numbers are: H, F, Cl, Bf, and I with 1 valence electron; O and S with 2 valence electrons; N with 3 valence electrons and C and Si with 4 valence electrons.

The ability for molecules to form long chains is vital to producing polymers. Consider the material polyethylene, which is made from ethane gas, C_2H_6. Ethane gas has two carbon atoms in the chain and each of the two carbon atoms share two valence electrons with the other. If two molecules of ethane are brought together, one of the carbon bonds in each molecule can be broken and the two molecules can be joined with a carbon-to-carbon bond. After the two mers (repeating units in a polymer chain) are joined, there are still two free valence electrons at each end of the chain for joining other mers or polymer chains. The process can continue linking more mers and polymers together until it is stopped by the addition of another chemical (a terminator) that fills the available bond at each end of the molecule. This is called a linear polymer and is the building block for thermoplastic polymers. To give an idea of what this means-a typical chain length of a polyethylene polymer that is used to make trash bags is 30,000 “mers,” which means that the average molecular weight would be 420,000 g/mole. Because the material has many different chain lengths (as described by the molecular weight distribution), it is necessary to describe an average molecular weight. The polymer chain is often shown in two dimensions, but it should be noted that they have a three dimensional structure. Each bond is at 109° to the next and, therefore, the carbon backbone extends through space like a twisted chain of Tinker Toys. When stress is applied, these chains stretch and the elongation of polymers can be thousands of times greater than it is in crystalline structures. The length of the polymer chain is very important. As the number of carbon atoms in the chain is increased to beyond several hundred, the material will pass through the liquid state and become a waxy solid. When the number of carbon atoms in the chain is over 1,000, the solid material polyethylene, with its characteristics of strength, flexibility and toughness, is obtained. The change in state occurs because as the length of the molecules increases, the total binding forces between molecules also increases. It should also be noted that the molecules are not generally straight but are a tangled mass. Thermoplastic

materials, such as polyethylene, can be pictured as a mass of intertwined worms randomly thrown into a pail. The binding forces are the result of Van der Waals forces between molecules and mechanical entanglement between the chains. When thermoplastics are heated, there is more molecular movement and the bonds between molecules can be easily broken. This is why thermoplastic materials can be remelted.



Left: Amorphous thermoplastic, Right: Lightly cross-linked elastomer

There is another group of polymers in which a single large network, instead of many molecules is formed during polymerization. Since polymerization is initially accomplished by heating the raw materials and bringing them together, this group is called thermosetting polymers or plastics. For this type of network structure to form, the mers must have more than two places for bonding to occur; otherwise, only a linear structure is possible. These chains form jointed structures and rings, and may fold back and forth to take on a partially crystalline structure. Since these materials are essentially comprised of one giant molecule, there is no movement between molecules once the mass has set. Thermosetting polymers are more rigid and generally have higher strength than thermoplastic polymers. Also, since there is no opportunity for motion between molecules in a thermosetting polymer, they will not become plastic when heated.

The morphology of a piece of polymeric material is a description of the spatial arrangement of the various microstructural domains in the bulk sample. The crystalline domains are characterized by an ordered arrangement of the polymer chains from which they are composed. The crystalline domains will become disordered when the material is heated above its melt temperature, Tm. The melt transition is associated with an abrupt decrease in bonding (increase in enthalpy) and increase in disorder (increase in entropy).

The amorphous domains contain disordered chains. These chains begin to move in a coordinated fashion at the glass transition temperature, Tg. The glass transition temperature of amorphous thermoplastics, elastomers, and thermosets as well as the melting temperature of semi-crystalline thermoplastics are determined by their polymeric structure. Even for polymers consisting of the same chemical elements, different softening and melting temperatures are possible. If the amorphous polymer is held at temperatures below Tg there is insufficient thermal energy to overcome the activation energy for chain motion. This glassy state can be described as a structural liquid, yet a dynamic solid. In general, the higher the chain length in a polymer material, the higher the melting point and glass transition point. It is important to differentiate between melting point and the glass transition point. The melting point describes a physical change of the polymer from a solid to a liquid. This point can be easily measured because, at this temperature, the heat that is added to the polymer just makes it molten rather than increasing the temperature of the material.

The morphology of a polymer, to a great extent, determines its properties and, in turn, its potential uses. The development of morphology is governed by the thermodynamics and kinetics inherent to the processing technology being employed. It can be said that these processes are thermodynamically driven and kinetically controlled.

Although there is an enormous variety in types and grades of commercial polymers, only a few are mass-produced. A listing on the most commonly used monomers is given below. These are reacted to make polymers by either:

1. Addition or Chain-Growth Polymerization, or

2. Condensation of Step-Growth Polymerization

In addition polymerization monomers are added one at a time to the end of a growing chain, sometimes completing a 10,000-bond chain in a matter of seconds. In step-growth polymerization polymers grow by adding successively larger pieces together throughout the overall polymerization.

Common polymers can be divided into the following categories:

Commodity plastics
- PE = Polyethylene
- PS = Polystyrene
- PP = Polypropylene
- PVC = Poly(vinyl chloride)
- PET = Poly(ethylene terephthalate)

Specialty or Engineering Plastics
- Teflon (PTFE) = Poly(tetrafluoroethylene)
- PC = Polycarbonate (Lexan)
- Polyesters and Polyamides (Nylon)

Table listing most common polymers, properties and typical applications

Material name	Abbreviation	Trade names	Properties	Applications
Acetal (Polyoxy-methylene)	POM	Celcon, Delrin, Hostaform, Lucel	Strong, rigid, excellent fatigue, creep, chemical and moisture resistance, naturally opaque white, low/medium cost	Bearings, cams, gears, handles, plumbing components, rollers, rotors, slide guides, valves
Acrylic (Polymethyl-methacrylate)	PMMA	Diakon, Oroglas, Lucite, Plexiglas	Rigid, brittle, scratch resistant, transparent, optical clarity, low/medium cost	Display stands, knobs, lenses, light housings, panels, reflectors, signs, shelves, trays
Acrylonitrile Butadiene Styrene	ABS	Cycolac, Magnum, Novodur, Terluran	Strong, flexible, low mold shrinkage (tight tolerances), chemical resistance, electroplating capability, naturally opaque, low/medium cost	Automotive (consoles, panels, trim, vents), boxes, gauges, housings, inhalers, toys
Cellulose Acetate	CA	Dexel, Cellidor, Setilithe	Tough, transparent, high cost	Handles, eyeglass frames
Polyamide 6 (Nylon)	PA6	Akulon, Ultramid, Grilon	High strength, fatigue and chemical resistance, low creep and friction, almost opaque/white, medium/high cost	Bearings, bushings, gears, rollers, wheels

Material name	Abbreviation	Trade names	Description	Applications
Polyamide 6/6 (Nylon)	PA6/6	Kopa, Zytel, Radilon	High strength, fatigue and chemical resistance, low creep and friction, almost opaque/white, medium/high cost	Handles, levers, small housings, zip ties
Polyamide 11+12 (Nylon)	PA11+12	Rilsan, Grilamid	High strength, fatigue resistance and chemical resistance, low creep and friction, almost opaque to clear, very high cost	Air filters, eyeglass frames, safety masks
Polycarbonate	PC	Calibre, Lexan, Makrolon	Very tough, temperature resistance, dimensional stability, transparent, high cost	Automotive (panels, lenses, consoles), bottles, containers, housings, light covers, reflectors, safety helmets and shields
Polyester - Thermoplastic	PBT, PET	Celanex, Crastin, Lupox, Rynite, Valox	Rigid, heat and chemical resistance, medium/high cost	Automotive (filters, handles, pumps), bearings, cams, electrical components (connectors, sensors), gears, housings, rollers, switches, valves
Polyether Sulphone	PES	Victrex, Udel	Tough, very high chemical resistance, clear, very high cost	Valves
Polyether-etherketone	PEEKEEK		Strong, thermal stability, chemical resistance, abrasion resistance, low moisture absorption	Aircraft components, electrical connectors, pump impellers, seals
Ethylene vinyl acetate	EVA		Improved clarity, flexibility at low temp over PE, good adhesion and heat seal	Films, flexible hosing, gaskets
Polyetherimide	PEI	Ultem	Heat and flame resistance, transparent (amber color)	Electrical components (connectors, boards, switches), covers, shields, surgical tools
Polyethylene - Low Density	LDPE	Alkathene, Escorene, Novex	Lightweight, tough and flexible, excellent chemical resistance, natural waxy appearance, low cost	Kitchenware, housings, covers, and containers
Polyethylene - High Density	HDPE	Eraclene, Hostalen, Stamylan	Tough and stiff, excellent chemical resistance, natural waxy appearance, low cost	Chair seats, housings, covers, and containers
Polyphenylene Oxide	PPO	Noryl, Thermocomp, Vamporan	Tough, heat and flame resistance, dimensional stability, low water absorption, electroplating capability, high cost	Automotive (housings, panels), electrical components, housings, plumbing components
Polyphenylene Sulphide	PPS	Ryton, Fortron	Very high strength, heat resistance, brown, very high cost	Bearings, covers, fuel system components, guides, switches, and shields
Polypropylene	PP	Novolen, Appryl, Escorene	Lightweight, heat, chemical and scratch resistance, natural waxy appearance, tough and stiff, low cost.	Automotive (bumpers, covers, trim), bottles, caps, crates, handles, housings

Material name	Abbreviation	Trade names	Description	Applications
Polystyrene (general purpose)	GPPS	Lacqrene, Styron, Solarene	Brittle, transparent, low cost	Cosmetics packaging, pens
Polystyrene - High impact	HIPS	Polystyrol, Kostil, Polystar	Impact strength, rigidity, toughness, dimensional stability, naturally translucent, low cost	Electronic housings, food containers, toys
Polyvinyl Chloride - Plasticized	PVC	Welvic, Varlan	Tough, flexible, flame resistance, transparent or opaque, low cost	Electrical insulation, house wares, medical tubing, shoe soles, toys
Polyvinyl Chloride - Rigid	UPVC	Polycol, Trosiplast	Tough, flexible, flame resistance, transparent or opaque, low cost	Outdoor applications (drains, fittings, gutters)
Styrene Acrylonitrile	SAN	Luran, Arpylene, Starex	Stiff, brittle, chemical and heat resistance, hydrolytically stable, transparent, low cost	House wares, knobs, syringes
Thermoplastic Elastomer/ Rubber	TPE/R	Hytrel, Santoprene, Sarlink	Tough, flexible, high cost	Bushings, electrical components, seals, washers
Polytetrafluoro ethylene	PTFE		Very low heat resistance during processing Rigid—tough, resistant to weathering, good chemical and moisture resistance Flexible—ease of processing, excellent electrical properties	Rigid—pipe, pipe fittings, vinyl siding, lawn furniture, window frames, guttering Flexible—wire insulation, floor tile, packaging films, garden hose, raincoats

PLASTICS ADDITIVES

Additives are often added to polymers to improve processability, improve properties, or reduce cost. The presence of additives often has negative consequences however, so they must be used carefully. There are a number of different categories of additives: antioxidants, blowing agents, flame retardants, fillers, impact modifiers, lubricants, pigments, plasticizers, thermal stabilizers, and UV absorbers, to name a few. When designing a new product, a combination of polymer optimization and additive optimization is used to determine the formulation, or recipe, that will be used. If the polymer is equivalent to the flour in a bread recipe, the additives are the salt, sugar, and yeast. A brief explanation of each of the additives is given below.

Antioxidants: An antioxidant is added to polymers that can be attacked by oxidizing agents to change their chemistry. An example of oxidation that we see every day is rusting of metals. The metal is attacked by oxygen and changes chemically into rust. Polymers can be affected in a similar way if an additive is not present in the system.

Blowing agents: Blowing agents are incorporated into polymers to make a foamed product. These materials, when heated during processing, break down into a gas that makes a bubble in the plastic while the polymer is still molten. A great example of a material made with a blowing agent is foamed hot drink cups.

Flame retardants: Many polymers are highly flammable (meaning that they will burn in air without any other fuel), so it is necessary to add something that reduces their flammability. These materials are most often added to plastics that are used as building materials, automotive interiors or in electrical applications where the tendency to ignite in the presence of an open flame is very detrimental.

Fillers: Fillers, as a category, is very broad. It includes a variety of materials that are added to a polymer to reduce the cost of the final part. Sometimes they also improve properties such as impact strength and hardness. Some standard fillers in use today are calcium carbonate, glass spheres, wood flour, and silica.

Impact modifiers: Impact modifiers are added to polymers to improve the impact strength of a product. They are usually a type of elastomer that can absorb the shock the same way that the rubber soles of tennis shoes do. A good way to see this is to imagine that the plastic is filled with lots of little balls that are spread throughout the plastic.

Lubricants: A number of polymers are very difficult to process because of high viscosity or a tendency to stick to the metal equipment and burn. To prevent a polymer from sticking, lubricants are added. Lubricants are often waxes, like candle wax, that help the polymer flow through the processing equipment. Also, some lubricants stick to the metal of the equipment and prevent the polymer from sticking-like Teflon® coating a frying pan.

Pigments and dyes: Both pigments and dyes are added to plastics to color them. The pigments are small particles that are mixed into the polymer but do not dissolve in the plastic; instead, they remain as small particles that can be found throughout the plastic. Dyes, on the other hand, are colored materials that dissolve in the plastic and become part of the polymer solution. It is common to think of dyes as behaving like food color in water, whereas a pigment is like chocolate chips in a chocolate chip cookie.

Plasticizers: Some applications require a plastic to be flexible or rubbery. It is possible to create this property in some polymers by adding a plasticizer. When a plasticizer is added, a plastic can go from being rigid and hard to flexible and soft. The plasticizer works the same way as grease does in a machine. It gets between two polymer chains and helps them slip past one another just as grease gets between two metal parts and helps them slip past one another.

Thermal stabilizers: Because thermoplastics are processed with a lot of heat and shearing energy, it is often necessary to add thermal stabilizers to the formulation. A thermal stabilizer protects the polymer from burning during processing.

UV stabilizers: Often final products are exposed to sunlight or other sources of UV radiation. Ultraviolet light has a very high energy and can cause the polymer to break down unless a UV stabilizer is added to protect it. Commonly, UV stabilizers are added to anything that will be used outdoors such as vinyl siding, plastic furniture, and agricultural films, to prevent this breakdown.

WHY DO PLASTICS FAIL?

There are four key areas to examine when considering the causes of plastic failures. These factors include:

- Material selection
- Design
- Process
- Service Conditions

It seems logical that ***material selection*** is an essential part of creating a strong product. However, it is understandable that when pushed to meet time constraints and high consumer demands, proper plastic material selection may not receive all the attention it warrants. Manufacturers may consider a range of factors when selecting materials, but perhaps most important is the intended use of the product. High-impact applications require materials that can withstand extreme amounts of force, just as outdoor applications must be constructed from a material that can handle prolonged exposure to the elements. Through carefully considering a material's thermal, environmental, electrical, and chemical aspects, manufacturers can select a material that will serve its appropriate function.

After selecting a material, the focus shifts to ***design***. Not only does a product need to be designed with its function in mind, but with attention to the material and its work-properties. Since different materials respond differently, the way a manufacturer approaches design is heavily contingent upon the product's composition. Poor design is the leading cause of plastic product failure.

The ***manufacturing process*** itself is crucial when it comes to preventing plastic failure. Often moisture in the material, weak welding, or molded-in stress can result in a dramatically weakened product, shortening the projected lifespan of the work piece. New innovations enable manufacturers to carefully monitor the process, helping protect the product against process-induced flaws that could lead to various kinds of failure, such as stress cracking. Successful manufacture of plastic parts is a far more complicated matter than may be realized. The technology involved cannot be used most effectively without knowledge of the basic organic chemistry and physical chemistry that underlie the materials, including polymers and additives, and the rheology that is involved in melt flow processing. Failure to understand the ways in which design and material affect processing and, in turn, how all three affect product performance is the underlying cause of many plastic problems. In many cases, the cause is at least partly due to failure to understand the potential consequences of seemingly safe practices or decisions. Also, in majority of the cases the failure occurs at the manufacturing stage, either in primary processing, such as injection molding, or in secondary operations.

Assuming that service conditions are not unusually severe, all failures can be traced to design, material, or processing. The interdependence of the three main causes of failure is such that often all are contributors. Material and processing are particularly strongly linked. The material contribution to failure may be in the polymer itself or in an additive. Processing imposes thermal and mechanical stresses on plastics that frequently are the most severe a part will experience in its lifetime. Failure is often the result of lack of realization of how severe the stresses in processing are and of their effect on the material. Orientation and frozen-in stress play a major role in environmental stress cracking and warpage. Orientation is affected very strongly by polymer molecular weight and composition, as well as processing; design also plays a role.

Aside from problems with material selection, design, and manufacturing, issues also can arise concerning ***service conditions***. Even though there are manuals and specific directions regarding a product's use, failure can still occur as a result of inappropriate use or

unintentional overextension of a component. Undue stress, such as two opposing forces acting on a product simultaneously, or exposure to incompatible solvents, can also cause failure. The most common types of failures and contributing factors are discussed below.

TYPES OF FAILURES

Mechanical Failure

Mechanical failure arises from the applied external forces which when exceed the yield strength of the material, cause the product to deform, crack, or break into pieces. The force may have been applied in tension, compression, and impact for a short or a long period of time at varying temperatures and humidity conditions. The failure isn't always sudden-often a part is exposed to the same inappropriate force or condition repeatedly over a long period of time, thereby weakening the part gradually until it finally gives in. Majority of the plastic parts, although inherently ductile, fail in a brittle manner. The objective of a successful failure evaluation therefore becomes the identification of the embrittling mechanism. Even though mechanical stress results in a limited amount of chain scission, the primary response is molecular disentanglement (slippage). Cracking within a molded plastic represents the disentanglement of the molecular structure by overcoming the intermolecular forces holding the molecules together (Van der Waals forces and hydrogen bonding).

Thermal Failure

Thermal failures occur from exposing products to an extremely hot or extremely cold environment. At abnormally high temperatures the product may warp, twist, melt, or even burn. Plastics tend to get brittle at low temperatures. Even the slightest amount of load may cause the product to crack or even shatter.

Chemical Failure

Plastics resemble a lot of similarities to metals with regards to environmental degradation. While metals corrode by an electrochemical process, plastics are susceptible to chemical changes from heat aging or weathering. Stress corrosion cracking, a form of corrosive attack in metals, is similar in many ways to stress cracking of plastics. Both result in brittle fractures due to the combined effects of stress and a material specific aggressive environment. Also, dealloying or selective leaching in metals, the preferential removal of the more active element from an alloy by corrosion, is somewhat similar to scission of polymers, a form of aging which can lead to structural changes by selectively cutting molecular bonds.

Very few plastics are totally impervious to all chemicals. Failure occurring from exposing the products to certain chemicals is quite common. Residual or molded-in stress, high temperatures, and external loading tend to aggravate the problem. The nature and strength of the chemical will affect the amount of damage. While some dilute chemicals will not attack a polymer, more concentrated solutions can do considerable harm. The extent of chemical attack on a certain polymer is mainly dependent on the chemical structure of the polymer. In addition, the severity of attack generally reduces with increase in polymer molecular weight, crystallinity, and level of chain branching. Amorphous polymers are more prone to stress cracking than crystalline polymers. The effects of chemical exposure are increased at higher temperatures and with longer periods of exposure. Chemical attack can cause polymers to partially dissolve, plasticize, react chemically and absorb these chemicals. These events will not always lead to product failure, but the mechanical properties may be reduced and the weight of the products may change. For non-loaded parts this will often not influence the parts functionality. Most important, however, is that chemical attack can cause stress cracks, which can be defined as fine cracks on or under the surface of the plastic. These cracks may range

from those of relatively large size, individually visible to the unaided eye, down to those of almost microscopic size, visible only by the appearance of 'blooming' or haziness (a dull surface). Stress cracks or crazes will usually lead to failure or rejection of the affected part. Attack will usually lead to preferential softening/plasticizing of the polymer, which in turn will lower the stress level for crack generation. The amount and severity of cracking/crazing depends largely on the chemical similarity of the solute and the solvent. Even though the stress cracking phenomenon has been extensively studied for many years, there is no reliable predictive scheme available that can determine if a certain chemical will produce cracking in a given polymer. Such determination usually has to be conducted by actual testing, during which a stress crack agent is applied to a stressed specimen. The table below lists some of the potential stress cracking agents of common polymers.

Polymer	Potential Stress Crack Agents
PE	Detergents
POM	Sulfuric Acid, Zinc Chloride
PC	Chlorinated solvents
PS, HIPS	Hydrocarbons
PMMA	Alcohols
ABS	Plasticizers, Acetic Acid
PVC	Plasticizers
PSu	Hydrocarbons

Environmental Failure

Plastics exposed to outdoor environments are susceptible to many types of detrimental factors. Ultraviolet rays, humidity, microorganisms, ozone, heat, and pollution are major environmental factors that seriously affect plastics. The effect can be anywhere from a mere loss of color, slight crazing and cracking, to a complete breakdown of the polymer structure. This process is commonly referred to as aging and leads to brittleness.

Ultraviolet light can initiate chemical reactions in polymers that cause breakdowns thus degrading the chemical and physical properties. This process of photo degradation ultimately causes cracking, chalking, color changes and loss of other physical and chemical properties. Therefore, polymer products that are frequently used outdoors require UV protection. Light stabilizers can be classified as either ultraviolet light absorbers (UVAs) or hindered amine light stabilizers (HALS). In many cases light absorbers and hindered amines are used together to provide a level of light stability that is higher than using either type of stabilizer by itself. These combinations are effectively used in many plastics today. For rubber-modified polymers such as ABS and high impact Polystyrene (HIPS), long term exposure to the outdoor environment inevitably leads to the formation of a degraded surface layer containing cross-linked rubber particles in a matrix of reduced molecular eight. Since cross-linked rubber is ineffective as a toughening agent, the embrittled surface may serve as a site for brittle crack initiation, which may ultimately lead to catastrophic failures.

Testing of the effectiveness of light stabilizers in plastics is now routine, and is commonly carried out under artificial irradiation in a Xenon arc or QUV weatherometer. This is also commonly referred to as laboratory accelerated weathering. Data analysis involves taking samples from the weatherometer after prescribed intervals and testing them. It is important to note that no artificial test can ever precisely duplicate outdoor exposure conditions and the main objective for doing accelerated weathering is to provide a uniform basis for material comparison to test effectiveness of different UV stabilizers and influence of other additives such as pigments, fillers, etc. Destructive tests may involve tensile, impact or other physical property measurements. Nondestructive testing may involve color, gloss or other surface

appearance measures.



Photograph showing an oxidized/degraded surface due to natural weathering

Ozone is a powerful oxidizer that causes the physical properties of many thermoplastics, thermosets, and rubber materials to degrade over time, and can also affect the physical properties of some metals. Mechanical devices such as check valves, which contain ozone sensitive plastics, rubber materials, and ozone sensitive metals, eventually fail or do not perform as designed in the prolonged presence of ozone. Natural rubber and synthetic elastomers containing active ethylenic unsaturation are rapidly degraded by ozone when they are under stress. Degradation is evidenced by cracks on the surface that are perpendicular to the direction of stress. Ozone cracking occurs only in rubbers subjected to tensile stresses. The severity of cracking increases rapidly if the applied strain is above a small threshold level on the order of 10%. Rubber components used in compression crack only in the regions of the surface where tensile stresses are induced. Unsaturated rubber exposed to ozone in a strained state quickly develops surface cracks. The rate of crack growth depends on the type of rubber and the ozone concentration. The ozone crack grows at a right angle to the direction of principal strain, and the micro cracks generated at the surface may extend, depending on the stress level and ozone concentration. Thus, it is relatively easy to differentiate between cracking caused by ozone and that resulting from thermal oxidation.

CONTRIBUTING FACTORS

Material Selection

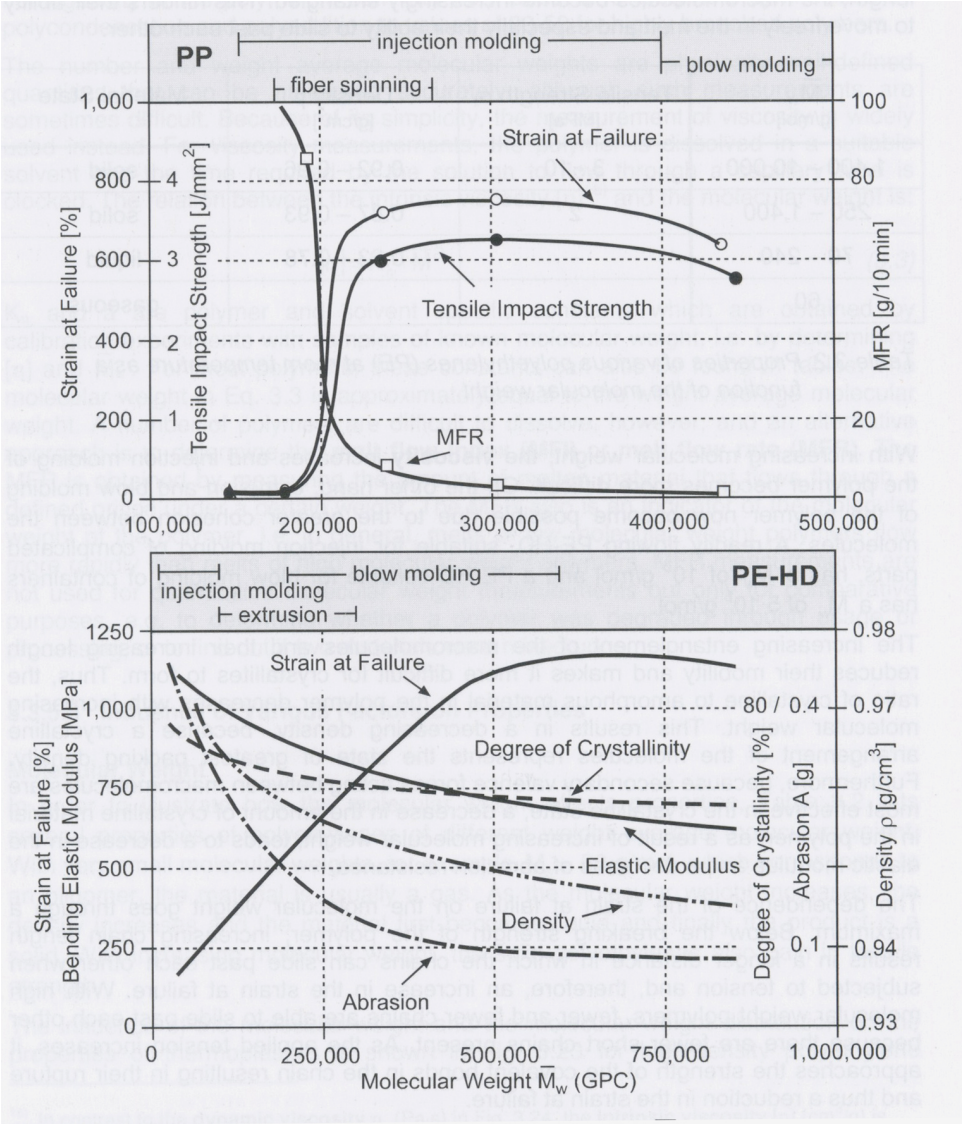
Failures arising from hasty material selection are not uncommon in plastics or any other industry. In an application that demands high-impact resistance, a high-impact material must be specified. If the material is to be used outdoors for a long period, a UV-resistant material must be specified. For proper material selection, careful planning, a thorough understanding of plastic materials, and reasonable prototype testing are required. The material selection should not be merely based on cost. A systematic approach to material selection process is necessary in order to select the best material for any application. The proper material selection technique involves carefully defining the application requirement in terms of mechanical, thermal, environmental, electrical and chemical properties. In many instances, it

makes sense to design a thinner wall part taking advantage of the stiffness-to-weight ratio offered by higher-priced, fast cycling engineering materials. Many companies, including material suppliers, have developed software to assist in material selection simply by selecting application requirement in the order of importance. The choices of polymers and additives are very broad, and each must be chosen carefully to avoid failure due to improper combinations. An incompatible plasticizer or other additive, for example, could exude to the surface and cause adhesive failure or environmental stress cracking. One similar example is where plastic clothes hangers caused colorant in the plastic to migrate into jacket linings, making the jackets unusable. It was discovered that the supplier had changed from impact polystyrene (IPS) to polypropylene (PP). A dye had been used as colorant. It was compatible in amorphous IPS, so that there was no driving force for it to migrate. In PP, however, the highly crystalline polymer could not accommodate the dye so it migrated to the surface and into the jacket lining. A pigment colorant would not have caused this type of problem.

An antioxidant (AO) or stabilizer may not be present at an adequate level to protect the polymer from degrading during processing and to leave enough to be protective in service. Such additives have to be chosen well to provide protection for various types of polymers. In cases where fracture occurs after a short service time, oxidative induction time (OIT) tests by differential scanning calorimetry (DSC) can be utilized to determine the amount of antioxidants in the polymer. DSC results for PP before molding, molded into a rotor for steam service, and a rotor degraded in service can illustrate whether most of the depletion of AO took place in processing or during service.

Some additives are not introduced intentionally, but are present nevertheless. Water is a common example. Even at levels as low as 0.01-0.02%, it can cause hydrolytic degradation in processing of condensation polymers like polyamide (PA) and polycarbonate (PC) to lower molecular weight (MW), with possible failure due to lower MW. Contaminants are another unintentional additive. It was discovered that delamination of PE sheet on punching to size and shape was due to a thin plastic film which interfered with fusion of the PE, so that separation occurred on punching. Residual monomer or solvents are other unintentional additives that can contribute to failure.

The long chain nature of polymers is what makes polymers unique. MW is a controllable variable, as polymerized. High MW is the most important feature of polymers. The long chains exist entangled with themselves and with other chains. Polymer strength, toughness, and chemical resistance depend on chain length and chain entanglements. MW is the number of monomer units in a chain times the MW of each unit. The figure below shows the typical effect of MW on properties such as strength, toughness and chemical resistance. Properties change rapidly with increasing MW at low MW, and tend to level off at high MW. In most applications, only a small reduction in MW is allowable without affecting properties.



Representative figures showing influence of average molecular weight on the properties of polymeric materials
(polypropylene-PP: top, high density polyethylene-HDPE: bottom)

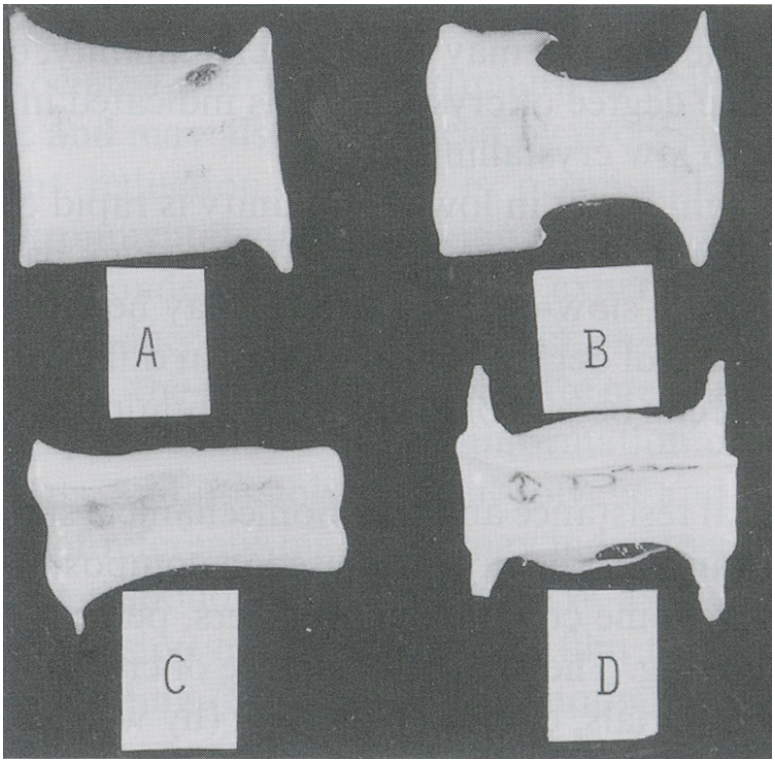
The difficulty with MW is that it can be lowered in processing, due to mechanical shear, oxidative degradation or hydrolysis of groups like amide (-CONH-) or polycarbonate (-O-CO-O). The effect is greater at lower MW affecting polymers such as PC and PA severely. As little as 5% lowering of MW can cause a high failure rate. Polyolefins (PE, PP) are particularly susceptible to formation of free radicals, which may react with oxygen to form peroxy radicals and ultimately chain scission to lower MW. A practical test for antioxidant has been referred to above. Ideally, OIT should be at least about 10-20 minutes after processing. If it is known that the polymer will degrade in processing, even if properly processed and stabilized, a higher MW may be a way of ensuring that MW will be adequate for service life.

Crystallinity is the ability of molecules to assemble into highly ordered arrays, which confer properties such as thermomechanical resistance, chemical resistance, as well as strength and toughness. If a crystalline polymer does not crystallize to the degree required, failure may occur. Processing conditions have to allow time for the crystallization to progress adequately. A nucleating agent may be needed to accelerate the rate of crystallization. If a pigment

unintentionally acts as a nucleating agent, a high degree of undesired crystallinity may result and cause failure. One such example is where PP caps of various colors included copper phthalocyanine blue. Blue caps broke when tightened on the tube thread. The pigment had brought the degree of crystallinity to a much higher level than in other caps of different color. At higher crystallinity, cap dimensions were smaller, causing fracture when screwed onto the tube. A property like crystallinity can be desirable or undesirable, contributing to failure. DSC showed the failed cap to have high crystallinity.

Another example of how crystallinity may contribute to failure is environmental stress cracking of high-density polyethylene (HDPE). Comonomers such as hexene reduce crystallinity and improve stress crack resistance.

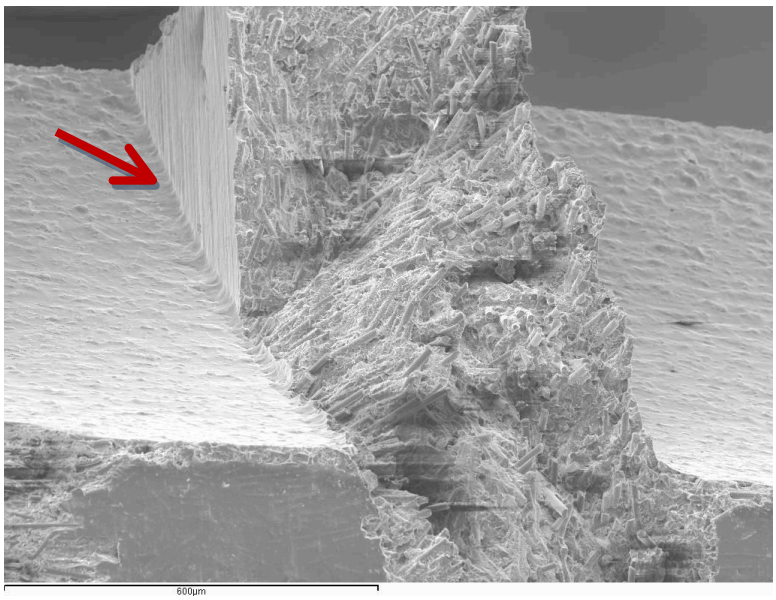
Orientation and resultant frozen-in stress are present in crystalline and non-crystalline (amorphous) plastics. Molded parts and extruded shapes generally are cooled on exiting the machines so that the plastic does not have time to relax completely to an unoriented condition. This is a problem especially for injection-molded parts, which have high frozen-in stress, resulting in a lower level of environmental stress crack resistance. Figure below shows PE samples after heat reversion by heating above Tg (glass transition temperature). The high level of shrinkage and distortion upon heating are indicative of the internal stress of the as molded part.



Heat-shrunk PE samples (originally 1"x1") showing various degrees of frozen-in stress (the higher the shrinkage the higher the frozen-in stress, making them susceptible to failure in service)

Design

Proper material selection alone will not prevent a product from failing. While designing a plastic product, the designer must use the basic rules and guidelines provided by the material supplier for designing a particular part with that material. One must remember that with the exception of a few basic rules in designing plastic parts, the design criteria changes from material to material as well as from application to application. Design-related failures are by far the most common type of failure. The importance of adequate fillet radius to reduce stress concentration points cannot be overemphasized. The following figure shows the dramatic stress concentration factor introduced by the sharp fillet radius.



A gear tooth fractured at its root where the sharp transition acted as a stress concentrator

Processing

After proper material selection and design, the responsibility shifts from the designer to the plastic processor. The most innovative design and a very careful material selection cannot make up for poor processing practices. Molded-in stresses, voids, weak weld lines, and moisture in the material are some of the most common causes for premature product failures. For example, PC and its blends absorb water from direct immersion and humid air and the moisture content in the resin can reach 0.35%. This must be reduced to less than 0.02% prior to processing to avoid molecular weight degradation and loss of toughness. Drying is required just prior to processing.

The latest advancements in process control technology allow the processors to control the process with a high degree of reliability and also help in record keeping should a product fail at a later date. Such records of processing parameters are invaluable to a person conducting failure analysis. Any assembly or secondary operation on processed part must be evaluated carefully to avoid premature failures. Failures arising from stress cracking around metal inserts, drilled holes and welded joints are quite common.

The thermal, mechanical, oxidative and hydrolytic stresses on material during processing is as or more severe than the plastic will experience in its total history, including service.

Temperatures well above the Tg or Tm (melt temperature) are required to convert the solid polymer to a liquid viscosity that the processing equipment can handle. Some polymers such as PVC may decompose during processing in the absence of oxygen, requiring stabilization and/or use of lowest possible heat. But lower temperature means higher melt viscosity, possibly incomplete fusion or incomplete filling of the mold. Due to the high temperature required in processing, all chemical reactions causing degradation to lower MW are accelerated. Processing means walking a virtual "tightrope" to achieve a well-fused part without excessive frozen-in stress, without degrading the polymer. Very little drop in MW can be tolerated in many cases without significant failures. Design must take into account the difficulty of achieving proper melt flow in areas that may resist flow. Use of regrind without checking MW may contribute to failure.

Failure may occur as damage to material other than the plastic in a system, such as electrical insulation in which the conductor or other component is discolored or corroded by byproducts of processing such as hydrogen chloride (HCl). The damage may be superficial but may make the product unacceptable due to appearance. Unintentional processing may be continued crystallization or relaxation in service, causing shrinkage and possibly failure.

Service Conditions

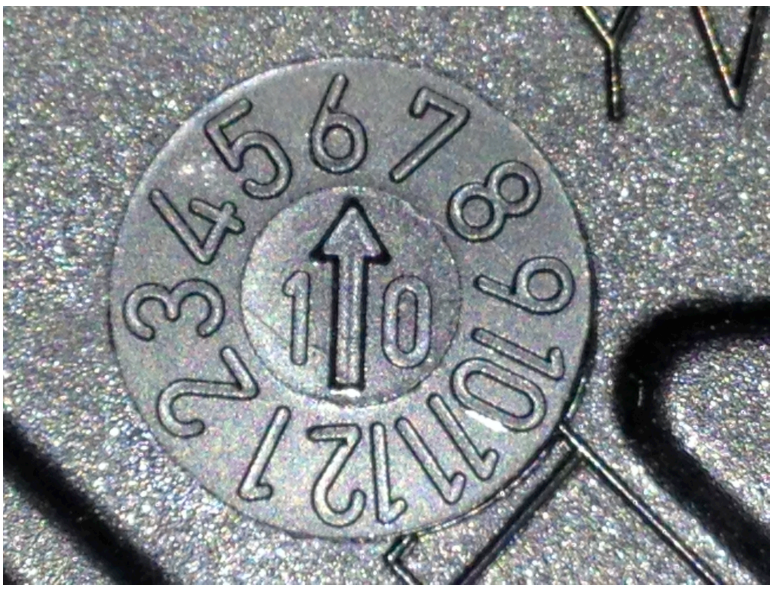
In spite of the built-in safety factors, warning labels, and user's instructions, failures arising from service conditions are common in the plastics industry. Five categories of unintentional service conditions are as follows.

Reasonable misuse
Use of product beyond its intended lifetime
Failure of product due to unstable service conditions
Failure due to service condition beyond reasonable misuse
Simultaneous application of two stresses operating synergistically

Most of the stresses imposed on plastics products in service can be grouped under the heading of thermal, chemical, physical, biological, mechanical, and electrical.

ANALYZING FAILURES

The main purpose of analyzing any type of failure is to determine the cause of the failure so that similar ones can be avoided in the future. Before proceeding with any analytical or microscopic tests, some basic information regarding the product must be gathered. If the product is returned from the field, basic information, such as the date of purchase, date of installation, date when the first failure encountered, geographic location, types of chemicals used with or around the product, whether the product was used indoors or outdoors, should be gathered from the end user. All this information is very vital if one is to analyze the defective product proficiently. For example, if the report from the field, and the defective product, indicate a certain type of chemical was used with the product, one can easily check the chemical compatibility of the product or go one step further and simulate the actual use condition using the same chemical. Recordkeeping also simplifies the task of failure analysis. A simple date code or cavity identification number placed on the product during manufacturing will certainly enhance the traceability.



Photograph showing a date code on a plastic injection molded part

Many types and styles of checklists to help analyze the failures have been developed. Seven basic methods are employed to analyze product failures.

Visual examination
Polymer Identification analysis
Stress analysis
Microtoming
Mechanical testing
Thermal analysis
Nondestructive Testing (NDT) Techniques

By zeroing in on the type of failure, one can easily select the appropriate method of failure analysis.

Visual Examination

A careful visual examination of the returned part can reveal many things. Excessive splay marks indicate that the materials were not adequately dried before processing. Splay Marks or Silver Streaks are usually caused by water vapor blisters at the flow front bursting and freezing on the wall of the molding surface. The failure to remove moisture from hydroscopic materials can lower the overall physical properties of the molded article and in some cases even cause them to become brittle. The presence of foreign material and other contaminants is also detrimental and can cause a part to fail.

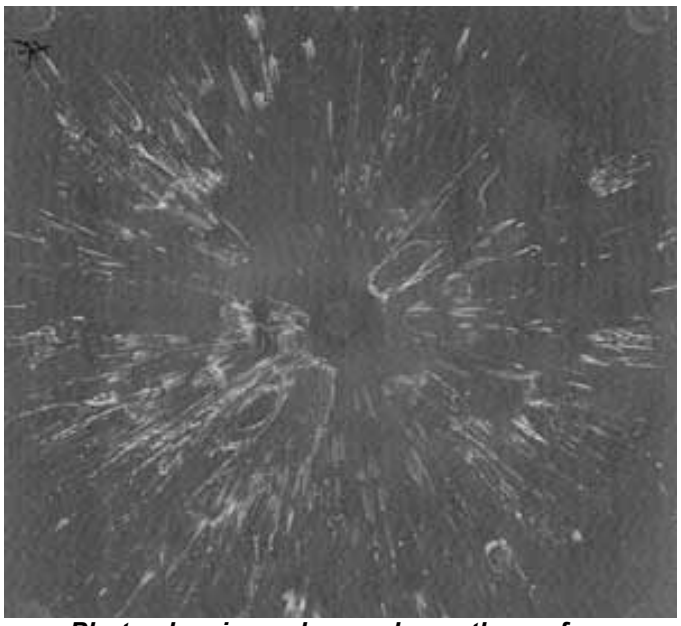


Photo showing splay marks on the surface

Burn marks on molded articles are easy to detect. They are usually brown streaks and black spots. These marks indicate the possibility of material degradation during processing causing the breakdown of molecular structure leading to overall reduction in the physical properties.

Sink marks and weak weld lines, readily visible on molded parts, represent poor processing practices and may be contributing factors to part failure. Sink Marks occur during the cooling process if certain areas of the part are not cooled sufficiently causing them to contract. They are caused by the outer skin of plastic solidifying while the material inside is still molten and viscous. The material compacts as it cools and solidifies. The best way to avoid these dimples is to design the part with a consistent wall thickness. However, many times the effect of the sink mark can be minimized by adjusting molding parameters such as injection pressure and time.



Photograph showing a sink mark

Blisters are hollows created on or in the molded part. In contrast to a void (vacuum) this entrapped gas can also appear near the walls. Decreasing melt temperature or extrusion screw speed and increasing mold temperature may help minimize blisters.

Cracks or crazes are caused by high internal molded in stress or by an external force imposed upon the part. They can also be caused by an incompatible external chemical being applied to the finished parts. The cracks often don't appear until days or weeks after the parts have been molded.

Short Shots occur when the part does not completely fill the mold. If too little plastic injection molding material flows into the mold, the cavity will not fill properly. This can be corrected by changing the plastic injection molding parameters.



Photograph showing a part exhibiting short-shot

When two halves of a mold come together, the sides of the cavities must press together tight enough not to allow any molten plastic to leak out of the cavity, resulting in a thin layer of plastic protruding from the part called flash. The plastic injection molding press must have enough tonnage, and the mold must be properly built and maintained to avoid this problem. However, some materials flash more easily than others. In fact, most thermoset materials will flash regardless of the press and mold. These parts need to be “deflashed” as a secondary operation. Excessive Flash is also seen out of vent grooves, or down ejector pins. It appears as thin or sometimes thick sections of plastic where it would not be on a normal part. Flash can very quickly (within a few cycles) damage the parting line surfaces.



Photograph of a part exhibiting flash

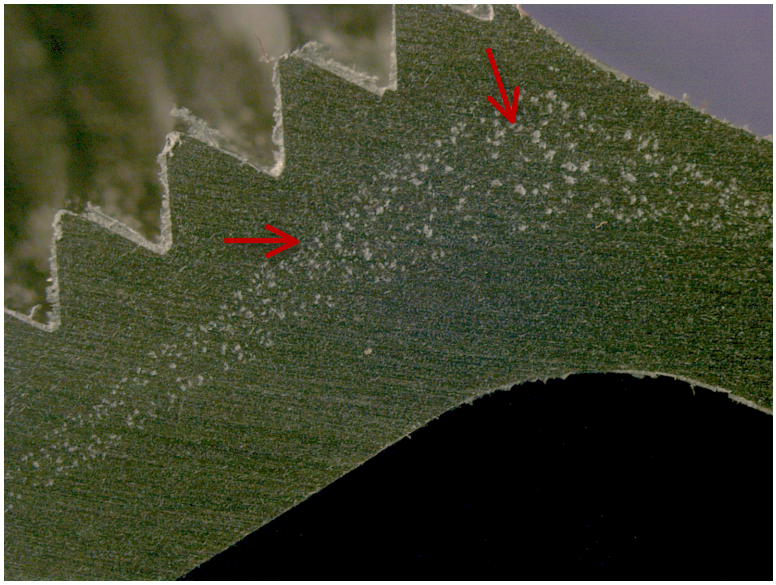
Warping or part distortion shows up as parts being bowed, warped, bent or twisted beyond the normal specification outlined on the drawing. Possible solutions are to adjust melt temperature (increase to relieve molded-in stress, decrease to avoid overpacking), check gates for proper location and adequate size, check mold knockout mechanism for proper design and operation, equalize/balance mold temperature of both halves, increase injection-hold or mold cooling time, relocate gates on or as near as possible to thick sections, and/or modify injection pressure.

Weld/Knit Lines are created when two or more melt flow fronts meet possibly causing a cosmetically visible line. They can also create a weakened area in the finished molded part especially with filled resins (i.e. glass filled). Possible solutions are to increase injection pressure, injection speed, melt or mold temperature, vent cavity in the weld area and to make sure part contains no sharp variation in cross-sections.

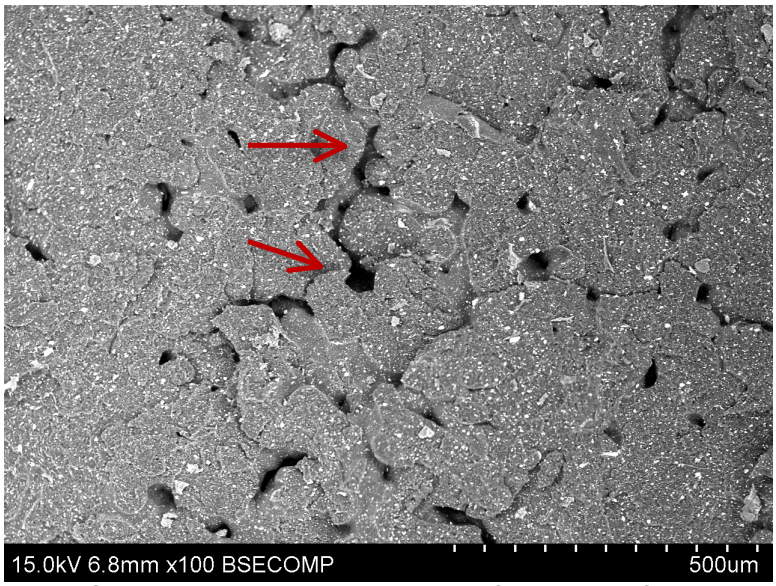
Differences in gloss are most conspicuous on textured surfaces. Irregular gloss may appear on the molded part even though the mold has a uniform surface texture. The problem is poor replication of the mold surface in some areas of the part. Pressure on the injected melt decreases with increasing distance from the gate. If the part is not fully packed at the point farthest from the gate, where the pressure is lowest, the mold surface texture will not be reproduced exactly, resulting in a glossy surface. Hence, unwanted gloss is least likely in the areas where cavity pressure is strongest-from the gate to about half way along the flow path. To fix this situation, raising the melt or mold temperature or the holding pressure should be considered. Extending the holding-pressure time may also increase the chances for accurate mold-surface replication. Part design can also contribute to gloss variations. For example, large changes in wall thickness can cause melt-flow irregularities and difficulties in mold-surface replication. Designing more uniform wall sections can alleviate this. Areas of excessive wall thickness or oversized ribs can also increase the risk of glossy marks. Another source for this surface appearance irregularity is insufficient venting at the flow line.

Besides manufacturing related defects, a careful visual examination will also reveal the extent of consumer abuse. The presence of unusual chemicals, grease, pipe dope, and other substances may give some clues. Heavy marks and gouges could be the sign of excessively applied external force.

The part should also be cut in half (using a sharp blade) to look for voids caused by trapped gas and excessive shrinkage, especially in thick sections during molding. A reduction in wall thickness caused by such voids could be less than adequate for supporting compressive or tensile force or withstanding impact load and may cause part to fail. Finally, if the product has failed because of exposure to UV rays or other environmental factors, a slight chalking, microscopic cracks, large readily visible cracks, or loss of color will be evident on its surface.



Cross section of a threaded part showing voids (arrows)



SEM image showing voids on a fracture surface

Polymer Identification Analysis

One of the main reasons for product failure is the use of the wrong material. When a failed product is returned from the field, material identification tests must be carried out to verify that the material used in the product is, in fact, the material specified on the product drawing. However, identifying the type of material is simply not enough. Since all plastic materials are supplied in a variety of grades with a broad range of properties, the grade of material must also be determined. A simple technique such as the melt index test can be carried out to confirm the grade of a particular type of material. The percentage of regrind material mixed with virgin material has a significant effect on the physical properties. Generally, the higher the level of regrind material mixed with virgin, the lower the physical properties. If during processing, higher than recommended temperature and long residence time is used, chances are that the material is degraded. This degraded material, when reground and mixed with virgin material, can cause a significant reduction in overall properties.

Part failures due to impurities and contamination of virgin material are common. Material contamination usually occurs during processing. A variety of purging materials are used to purge the previous material from the extruder barrel before using the new material. Not all of these purging materials are compatible. Such incompatibility can cause the loss of properties, brittleness, and delamination. In the vinyl compounding operation, failure to add key ingredients, such as an impact modifier, can result in premature part failure. Simple laboratory techniques cannot identify such impurities, contamination, or the absence of a key ingredient. More sophisticated techniques; such as Fourier Transform Infrared (FT-IR) analysis and gel permeation chromatography (GPC) must be employed. These methods can not only positively identify the basic material, but also point out the type and level of impurities in most cases.

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The following four techniques can be used for the FTIR analysis depending on sample properties.

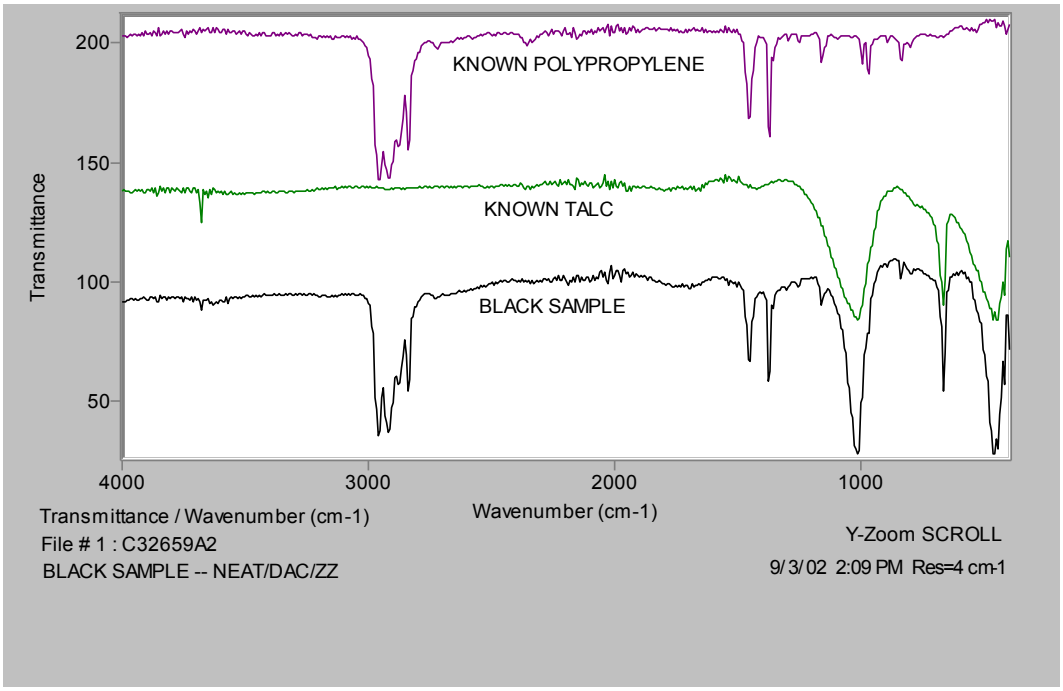
1. Microscope FTIR transmission mode: IR spectra are collected from the interested area of the sample using Microscope FTIR under transmission mode, using clean area as background. Sometimes, a small amount of sample needs to be carefully transferred onto a clean diamond window of Micro compression cell from the sample to flatten and thin for the Micro FT-IR analysis.

2. Microscope FTIR reflectance mode: IR spectra are collected from the interested area of the sample using Microscope FTIR under reflectance mode, with clean gold surface as background.

3. Microscope FTIR ATR mode: The Attenuated Total Reflectance Objective (ATR) provides non-destructive surface analysis. It can be used to analyze soft rubbers, coatings and highly absorbing materials. The ATR Objective uses a very high refractive index Zinc Selenide (ZnSe) crystal. Germanium (Ge) crystal is also available for the ATR Objective.

4. Microscope FTIR GAO mode: The Grazing Angle Objective (GAO) can perform the analysis of ultra-thin (sub-micron) coating on metallic substrates. The GAO can be used to perform infrared analysis of microscopic areas (about 50µm x 50µm) at grazing incidence.

FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum.



FTIR spectrum of talc-filled PP

By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds. There are several infrared spectral libraries including on-line computer libraries. To identify less common materials, IR will need to be combined with nuclear magnetic resonance, mass spectrometry, emission spectroscopy, X-ray diffraction, and/or other techniques.

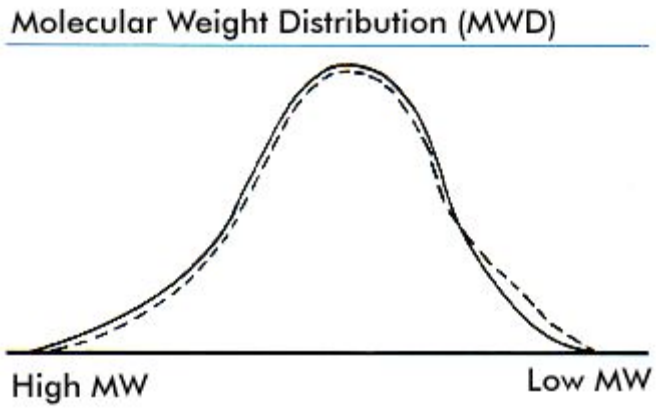
Gel permeation chromatography (GPC) is one of the most powerful and versatile analytical techniques available for understanding and predicting polymer performance. It is the most convenient technique for characterizing the complete molecular weight distribution of a polymer. GPC can determine several important parameters. These include number average molecular weight, weight average molecular weight, Z weight average molecular weight, and the most fundamental characteristic of a polymer, its molecular weight distribution. These values are important, since they affect many of the characteristic physical properties of a polymer. Subtle batch-to-batch differences in these measurable values can cause significant differences in the end-use properties of a polymer. Some of these properties include: Tensile strength, brittleness, impact strength, toughness, cure time, elastic modulus, melt viscosity, hardness, softening temperature, tear strength, stress-crack resistance, and coefficient of friction.

Two samples of the same polymer resin can have identical tensile strengths and melt viscosities, and yet differ markedly in their ability to be fabricated into usable, durable products. These differences can be attributed to subtle, yet significant variations in the molecular weight distributions of the two resin samples. Such differences, if undetected, can cause serious product defects. GPC separates molecules in solution by their "effective size in solution." To prepare a sample for GPC analysis the resin is first dissolved in an appropriate solvent. Inside the gel permeation chromatograph, the dissolved resin is injected into a continually flowing stream of solvent (mobile phase). The mobile phase flows through millions of highly porous, rigid particles (stationary phase) tightly packed together in a column. The

pore sizes of these particles are controlled and available in a range of sizes.

The distribution of different sized molecules in a polyethylene polymer typically follows the bell shaped normal distribution curve described by the Gaussian probability theory. The width of the individual peaks reflects the distribution of the size of molecules for a given resin and its components. The distribution curve is also known as the molecular weight distribution (MWD) curve. Taken together the peaks reflect the MWD of a sample. The broader the MWD, the broader the peaks become and vice versa. The higher the average molecular weight, the further along the molecular weight axis the curve shifts and vice versa.

As with other populations, the bell shaped curve can reflect distributions ranging from narrow to broad. A polymer containing a broad range of chain lengths is said to have a broad molecular weight distribution (MWD). Resins with this type of distribution have good Environmental Stress Crack Resistance (ESCR), good impact resistance and good processability. A polymer with a narrow MWD contains molecules that are nearly the same in molecular weight. It will crystallize at a faster, more uniform rate. This results in a product that will hold its shape.



You can see then how easily the MWD profiles of two resins can be compared. If the MWD profile of an incoming resin doesn't match that of the control resin (i.e. one that is known to process well) closely enough, the incoming resin can be modified or process conditions can be changed to make sure the resin processes properly. If the differences between the control resin and the incoming resin are too severe, the incoming resin can be returned to the supplier as unacceptable. MWD is dependent upon the type of process used to manufacture the particular resin. For polymers of the same density and average molecular weight, their melt flow rates are relatively independent of MWD. Therefore, resins that have the same density and melt index (MI) can have very different molecular weight distributions. The effects of density, molecular weight and molecular weight distribution on physical properties are summarized in Table below.

EFFECTS OF CHANGES IN DENSITY, MELT INDEX AND MOLECULAR WEIGHT DISTRIBUTION			
Property	**As Density Increases, Property:**	**As Melt Index Increases, Property:**	**As Molecular Weight Distribution Broadens, Property:**
Tensile Strength (At Yield)	Increases	Decreases	
Stiffness	Increases	Decreases Slightly	Decreases Slightly
Impact Strength	Decreases	Decreases	Decreases
Low Temperature Brittleness	Increases	Increases	Decreases
Abrasion Resistance	Increases	Decreases	
Hardness	Increases	Decreases Slightly	
Softening Point	Increases		Increases
Stress Crack Resistance	Decreases	Decreases	Increases
Permeability	Decreases	Increases Slightly	
Chemical Resistance	Increases	Decreases	
Melt Strength		Decreases	Increases
Gloss	Increases	Increases	Decreases
Haze	Decreases	Decreases	
Shrinkage	Decreases	Decreases	Increases

Gas Chromatography/mass spectroscopy is particularly useful as an analytical method for plastics failure analysis in cases where detection of an unknown contaminant or other compositional factor may be the cause or a contributor to failure. It takes advantage of the fact that GC is a method of separating compounds in a mixture, permitting their identification and possibly quantification.

MS is not only a very sensitive detector but also gives mass spectra of GC peaks, permitting their identification in many cases. In thermal desorption GC/MS compounds are transferred from the sample to the GC with heat. Completely nonvolatile materials are not detected. Using desorption temperatures up to 300-350°C, many components of plastics can be analyzed. In pyrolysis GC/MS the sample is decomposed at temperatures up to 900°C; GC/MS analyzes the pyrolyzate.

Plastics products often are not identified as to the company that sold the product. Failures

may occur years into the service history of a product. The customer may assume that the failed product was made by a particular vendor, while it could just as well have been made by another company. The accused company may want to confirm that the failed product was in fact made by them. That may be possible if there are distinguishable compositional factors between their product and the failed one. It may be possible to determine the source by analyzing for a distinctive material that is unique to a company's product.

Infrared spectroscopy (IR) is a useful method in plastics analysis. In many cases, however, it is not sensitive enough to detect trace materials. The spectrum may be of a complex mixture, making the spectrum of little value. Chromatography is a separation method from which compounds of a complex mixture can be identified and possibly quantified. In gas chromatography, for a material to be detected, it has to be sufficiently volatile to pass through a GC column at a temperature that may be as high as 300-400°C under helium gas flow.

Solvent extraction is a common way of separating extractable compounds from a mixture, followed by injection of the solution into the GC. In thermal desorption GC, also called thermal extraction GC, no solvent is used – only heat at a controlled temperature such as 2 minutes at 200-300°C. Use of heat alone without solvent provides a major increase in detectability.

Thermal desorption and pyrolysis gas chromatography/mass spectroscopy (GC/MS) are very sensitive, useful and versatile methods of analysis of plastics materials and products. Using heat to desorb or ''extract'' volatile materials from a sample gives much greater sensitivity than injection of solvent-extracted compounds. Some of the types of applications to various failure situations are: confirmation of source of failed product, competitive analysis, identification of contaminants causing failure, overcoming a problem in product development.

Stress Analysis

Once the part failure resulting from poor molding practices or improper material usage through visual examination and material identification is ruled out, the next logical step is to carry out an experimental stress analysis. Experimental stress analysis is one of the most versatile methods for analyzing parts for possible failure. The part can be externally stressed or can have residual or molded-in stresses. External stresses or molded-in stresses or a combination of both can cause a part to fail prematurely. Stress analysis is an important part of failure analysis. Detection of residual stresses has a different meaning than evaluation of stresses due to applied forces. It is possible of course to experience failure due to poor design, or underestimating of applied forces. These failures are usually detected in proof testing, or in early production. Residual stresses are altogether different: A molding process can generate residual stress just about anywhere. In such cases, photoelastic inspection can prove extremely helpful, allowing detection of defective molded parts or identification of failures in clear plastic products. Experimental stress analysis can be conducted to determine the actual levels of stress in the part. Five basic methods are used to conduct stress analysis:

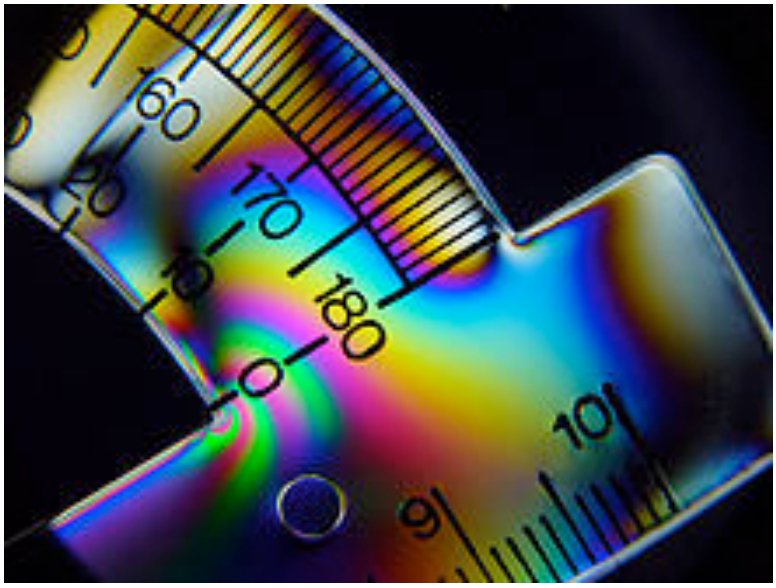
Photoelastic
Brittle coatings
Strain gauge
Chemical
Heat reversion

Photoelastic Method

The photoelastic method for experimental stress analysis is quite popular among design engineers and has proved to be an extremely versatile, yet simple technique.

If the parts to be analyzed are made out of one of the transparent materials, stress analysis is

simple. All transparent plastics, being birefringent, lend themselves to photoelastic stress analysis. The transparent part is placed between two polarizing mediums and viewed from the opposite side of the light source. The fringe patterns are observed without applying external stress. This allows the observer to study the molded-in or residual stresses in the part. High fringe order indicates the area of high stress level whereas low fringe order represents an unstressed area. Also, close spacing of fringes represents a high stress gradient. A uniform color indicates uniform stress in the part. Next, the part should be stressed by applying external force and simulating actual-use conditions. The areas of high stress concentration can be easily pinpointed by observing changes in fringe patterns brought forth by external stress as shown below.



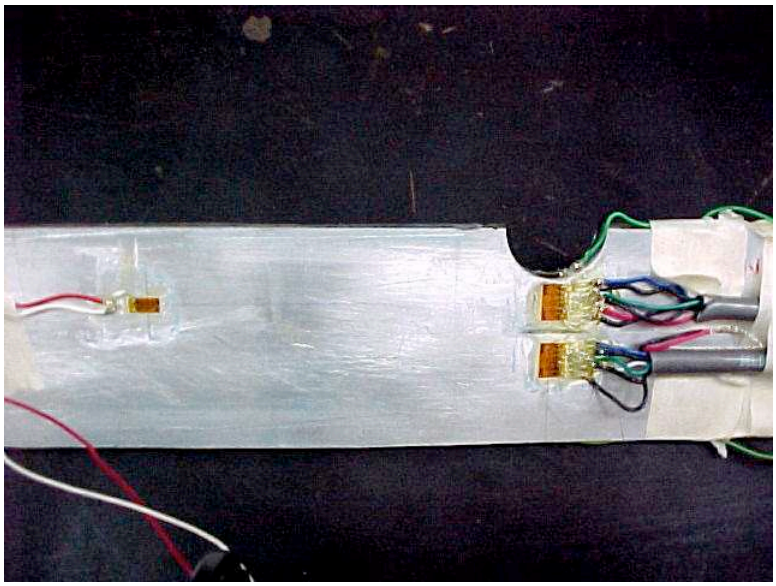
Another technique known as the photoelastic coating technique can be used to photoelastically stress-analyze opaque plastic parts. The part to be analyzed is coated with a photoelastic coating, service loads are applied to the part, and coating is illuminated by polarized light from the reflection polariscope. Molded-in or residual stresses cannot be observed with this technique. However, the same part can be fabricated using one of the transparent plastic materials. In summary, photoelastic techniques can be used successfully for failure analysis of a product.

Brittle-Coating Method

The brittle-coating method is yet another technique of conveniently measuring the localized stresses in a part. Brittle coatings are specially prepared lacquers that are usually applied by spraying on the actual part. The part is subjected to stress after air-drying the coating. The location of maximum strain and the direction of the principle strain are indicated by the small cracks that appear on the surface of the part as a result of external loading. Thus, the technique offers valuable information regarding the overall stress distribution over the surface of the part. The data obtained from the brittle coating method can be used to determine the exact areas for strain gauge location and orientation, allowing precise measurement of the strain magnitude at points of maximum interest. They are also useful for the determination of stresses at stress concentration points that are too small or inconveniently located for installation of strain gauges. The brittle-coating technique, however, is not suitable for detailed quantitative analysis like photoelasticity. Sometimes it is necessary to apply an undercoating prior to the brittle coating to promote adhesion and to minimize compatibility problems.

Strain Gauge Method

The electrical resistance strain gauge method is the most popular and widely accepted method for strain measurements. The strain gauge consists of a grid of strain-sensitive metal foil bonded to a plastic backing material. When a conductor is subjected to a mechanical deformation, its electrical resistance changes proportionally. This principle is applied in the operation of a strain gauge. For strain measurements, the strain gauge is bonded to the surface of a part with a special adhesive and then connected electrically to a measuring instrument. When the test part is subjected to a load, the resulting strain produced on the surface of the part is transmitted to the foil grid. The strain in the grid causes a change in its length and cross section, and produces a change in the resistivity of the grid material. This change in grid resistance, which is proportional to the strain, is then measured with a strain gauge recording instrument. In using strain gauges for failure analysis, care must be taken to test the adhesives for compatibility with particular plastics to avoid stress-cracking problems.

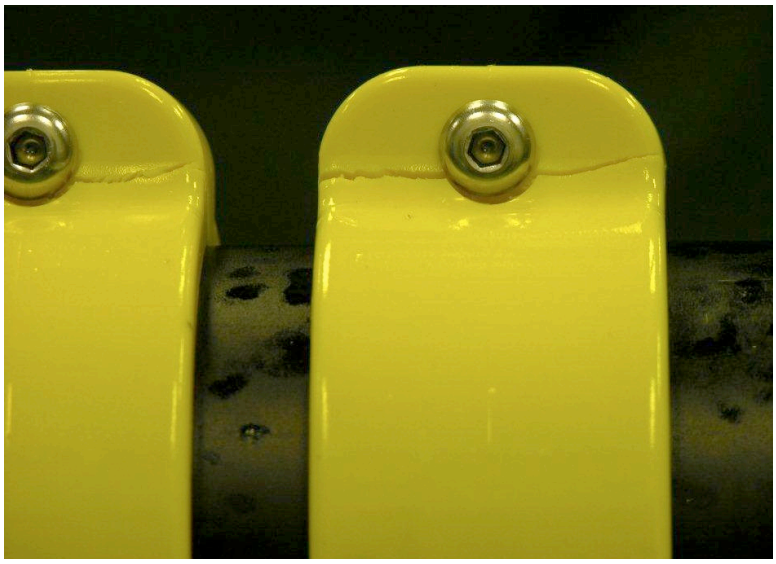


Residual or molded-in stresses can be directly measured with strain gauges using the hole drilling method. This method involves measuring a stress at a particular location, drilling a hole through the part to relieve the frozen-in stresses, and then remeasuring the stress. The difference between the two measurements is calculated as residual stress.

Chemical Method

Most plastics, when exposed to certain chemicals while under stress, show stress cracking. This phenomenon is used in stress analysis of molded parts. The level of molded-in or residual stress can be determined by this method. The part is immersed in a mixture of glacial acetic acid and water for 2 min at 73°F and later inspected for cracks that occur where tensile stress at the surface is greater than the critical stress. The part may also be externally stressed to a predetermined level and sprayed on with the chemical to determine critical stresses. Stress cracking curves for many types of plastics have been developed by material suppliers. If a defective product returned from the field appears to have stress-cracked, similar tests should be carried out to determine molded-in stresses as well as the effect of external loading by simulating end-use conditions. Failures of such types are quite common in parts where metal inserts are molded-in or inserted after molding. Three other tests, the stain-resistance test, solvent stress-cracking resistance, and environmental stress-cracking

resistance (ESCR), are also employed to analyze failed parts. ASTM D1693, Standard Test Method for Environmental Stress-Cracking of Ethylene Plastics is one such test. It is used for routine inspection purposes by subjecting a required number of specimens to the test conditions for a specified time and noting the number that fail. The cracking obtained with the test reagent is indicative of what may be expected from a wide variety of surface-active agents, soaps, and organic substances that are not absorbed appreciably by the polymer. Environmental stress-cracking is a property that is highly dependent upon the nature and level of the stresses applied and on the thermal history of the specimen. Under the conditions of the test method, high local multiaxial stresses are developed through the introduction of a controlled imperfection. Environmental stress-cracking has been found to occur most readily under such conditions.



Photograph showing cracking that developed around the high stress areas of a clamp upon exposure to a cracking agent

Heat Reversion Technique

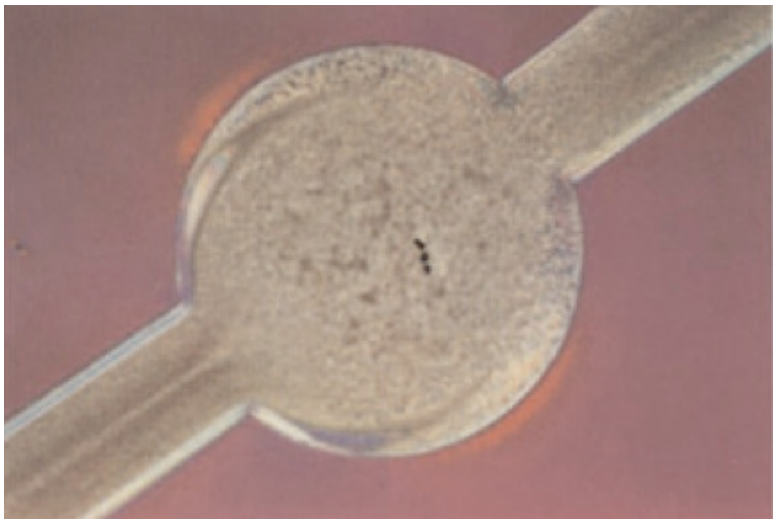
All plastics manufacturing process introduce some degree of stress in the finished product. The stresses in molded parts are commonly referred to as molded-in (residual) stresses. By reversing the process, by reheating the molded or extruded product, the presence of stress can be determined. The test is conducted by simply placing the entire specimen or a portion of the specimen in thermostatically controlled, circulating air oven and subjecting to a predetermined temperature for a specified time. The specimens are visually examined for a variety of attributes. The degree and severity of warpage, blistering, wall separation, fish-scaling and distortion in the gate area of molded parts indicate stress level. Stresses and molecular-orientation effects in the plastic material are relieved, and the plastic starts to revert to more stable form. The temperature at which this begins to occur is important. If changes start below the heat distortion temperature of the material, high levels of stress and flow orientation are indicated. The test has been significantly improved by new methods including the attachment of strain gages to critical regions of the part to carefully monitor initial changes in the shape. ASTM F1057 describes the standard practice for estimating the quality of extruded PVC pipe by the heat reversion technique.

Microtoming

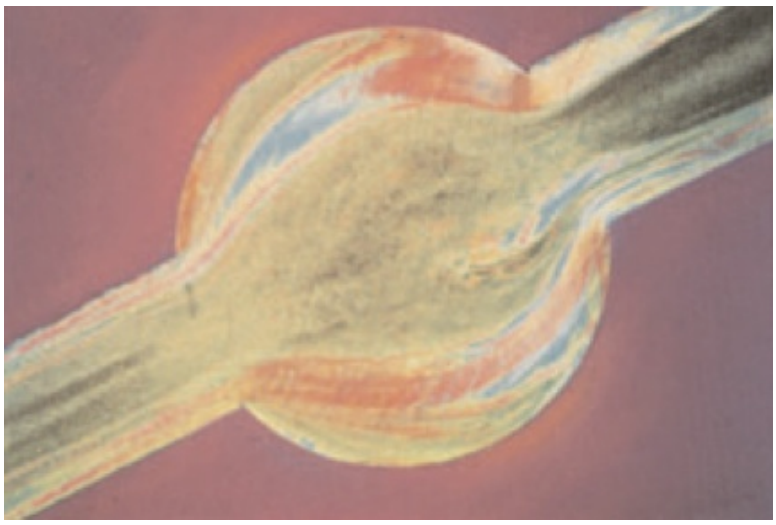
Microtoming is a technique of slicing an ultra thin section from a molded plastic part for microscopic examination. Biologists and metallurgists have used this technique for years, but only in the last decade has this technique been used successfully as a valuable failure analysis tool.

Microtoming begins with the skillful slicing of an 8-10 mm-thick section from a part and mounting the slice on a transparent glass slide. The section is then examined under a light transmission microscope equipped with a polarizer for photoelastic analysis. A high power (1000x) microscope, which will permit photographic recording of the structure in color, is preferred. By examining the microstructure of a material, much useful information can be derived. For example, microstructural examination of a finished part that is too brittle may show that the melt temperature was either nonuniform or too low. The presence of unmelted particles is usually evident in such cases. Another reason for frequent failures of the injection molded part is failure to apply sufficient time and pressure to freeze the gates. This causes the parts to be underpacked which creates center-wall shrinkage voids. Voids tend to reduce the load-bearing capabilities and toughness of a part through the concentration of stress in a weak area. Contamination, indicated by abnormality in the microstructure, almost always creates some problems. Contamination caused by the mixing of different polymers can be detected through such analysis by carefully studying the differences in polymer structures. Quite often, poor pigment dispersion also causes parts to be brittle. This is readily observable through the microtoming technique. In order to achieve optimum properties, additives such as glass fibers and fillers must disperse properly. Microtoming a glass fiber-reinforced plastic part reveals the degree of bonding of the glass fiber to the resin matrix as well as the dispersion and orientation of glass fibers. Molded-in stresses as well as stresses resulting from external loading are readily observed under cross-polarized light because of changes in birefringence when the molecular structure is strained. Microtoming technique can also be applied to check the integrity of spin and ultrasonic or vibration welds.

The sample images shown below illustrate how this technique can be utilized to demonstrate the quality of a molded part.



Homogeneous melt

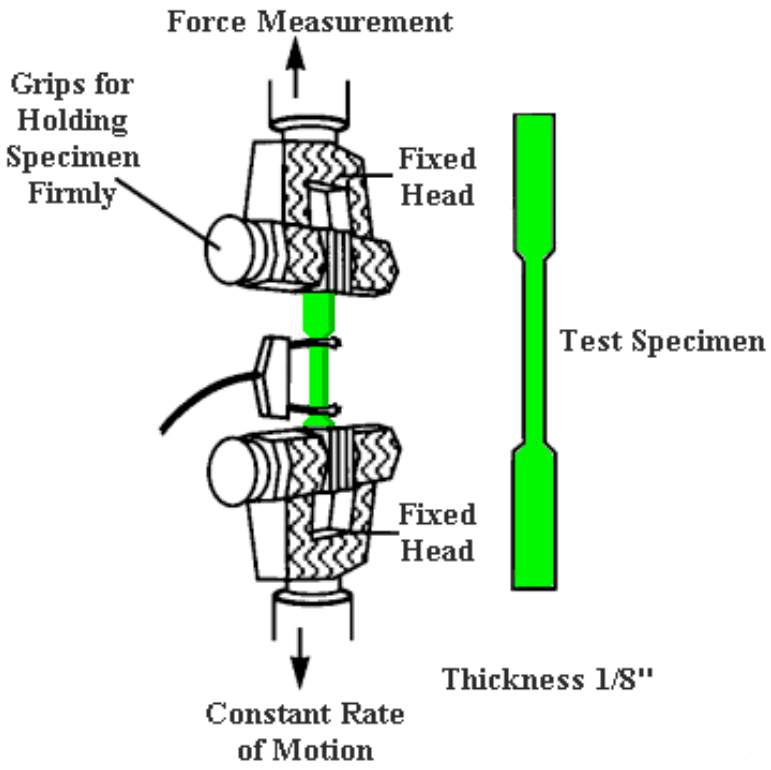


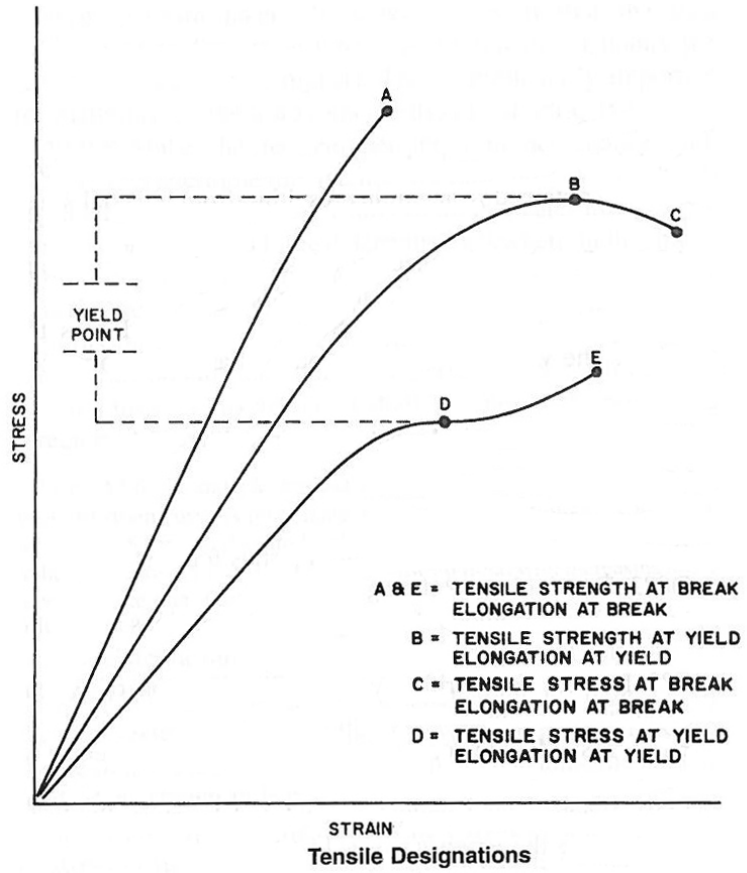
Inhomogeneous melt (brittle part)

Mechanical Testing

Defective product returned from the field is often subjected to a variety of mechanical tests to determine integrity of the product. Two basic methods are employed. First one involves conducting mechanical tests such as tensile, impact, flexural or compression on actual part or a small sample cut out from the part. The test results are then compared to the test results obtained from the retained samples. The second method requires grinding-up the defective parts and either compression or injection molding standard test bars and conducting mechanical tests. The test results, obtained by following either ASTM D638 or ISO are compared to the published data for the virgin material. The amount of material available for molding the test bars quite often precludes injection molding. The test data obtained from compression-molded samples are generally lower than injection molded samples. Fatigue failure tests such as flexural fatigue or tensile fatigue can be employed to determine premature failure from cyclic loading. The figures below show the typical tensile testing configuration and the various types of charts that are generated depending on the type of polymer and its behavior during the test.

Another common test is the deflection temperature, which is a measure of a polymer's resistance to distortion under a given load at elevated temperatures. The deflection temperature is also known as the 'deflection temperature under load' (DTUL), 'heat deflection temperature', or 'heat distortion temperature' (HDT). The two common loads used are 0.46 MPa (66 psi) and 1.8 MPa (264 psi), although tests performed at higher loads such as 5.0 MPa (725 psi) or 8.0 MPa (1160 psi) are occasionally encountered. The common ASTM test is ASTM D 648 while the analogous ISO test is ISO 75. The deflection temperature test results are a useful measure of relative service temperature for a polymer when used in load-bearing parts. However, the deflection temperature test is a short-term test and should not be used alone for product design. Other factors such as the time of exposure to elevated temperature, the rate of temperature increase, and the part geometry all affect the performance.





Tensile Designations

The ultimate elongation of an engineering material is the percentage increase in length that occurs before it breaks under tension. Ultimate elongation values of several hundred percent are common for elastomers and film/packaging polyolefins. Rigid plastics, especially fiber reinforced ones, often exhibit values under 5%. The combination of high ultimate tensile strength and high elongation leads to materials of high toughness.

The tensile modulus is the ratio of stress to elastic strain in tension. A high tensile modulus means that the material is rigid - more stress is required to produce a given amount of strain. In polymers, the tensile modulus and compressive modulus can be close or may vary widely. This variation may be 50% or more, depending on resin type, reinforcing agents, and processing methods. The tensile and compressive moduli are often very close for metals.

The table below lists average ultimate tensile strength, elongation at break, and tensile moduli values for some filled and unfilled polymers.

Polymer Type	Ultimate Tensile Strength (MPa)	Elongation (%)	Tensile Modulus (GPa)
ABS	40	30	2.3
ABS + 30% Glass Fiber	60	2	9
Acetal Copolymer	60	45	2.7
Acetal Copolymer + 30% Glass Fiber	110	3	9.5
Acrylic	70	5	3.2
Nylon 6	70	90	1.8
Polyamide-Imide	110	6	4.5
Polycarbonate	70	100	2.6
Polyethylene, HDPE	15	500	0.8
Polyethylene Terephthalate (PET)	55	125	2.7
Polyimide	85	7	2.5
Polyimide + Glass Fiber	150	2	12
Polypropylene	40	100	1.9
Polystyrene	40	7	3

The flexural strength of a material is defined as its ability to resist deformation under load. For materials that deform significantly but do not break, the load at yield, typically measured at 5% deformation/strain of the outer surface, is reported as the flexural strength or flexural yield strength. The test beam is under compressive stress at the concave surface and tensile stress at the convex surface. The test is described in ASTM D790 or ISO 178. These tests also give the procedure to measure a material's flexural modulus (the ratio of stress to strain in flexural deformation).

The table below lists average flexural strengths and flexural moduli values for some filled and unfilled polymers. These values are a measure of stiffness; flexible materials such as film grade polymers used have lower values than fiber reinforced engineering polymers used as metal substitutes such as polyimides or acetals.

Polymer Type	**Flexural Strength (MPa)**	**Flexural Modulus (GPa)**
ABS	75	2.5
ABS + 30% Glass Fiber	120	7
Acetal Copolymer	85	2.5
Acetal Copolymer + 30% Glass Fiber	150	7.5
Acrylic	100	3
Nylon 6	85	2.3
Polyamide-Imide	175	5
Polycarbonate	90	2.3
Polyethylene, MDPE	40	0.7
Polyethylene Terephthalate (PET)	80	1
Polyimide	140	3
Polyimide + Glass Fiber	270	12
Polypropylene	40	1.5
Polystyrene	70	2.5



Photograph of a universal test machine showing the flexural strength test set-up

A plastic's toughness determines its fracture behavior. If overloaded, structural and safety related parts should present a ductile fracture, so as to absorb energy in a crash, for example, and to reduce the risk of injuries from a brittle fracture. The broad term "toughness" encompasses properties of plastics, which are far more complex than strength or stiffness. Toughness is the property that governs a plastic's irreversible deformation before it breaks. A brittle plastic, in contrast, breaks almost without any deformation. Impact strength and notched impact strength describe a plastic's behavior under impact, that is to say, under the effect of rapid deformation. One major drawback regarding the standardized procedures to determine toughness properties is that they do not provide exact quantitative values, only comparative indications for the choice of suitable plastics.

In the Izod test, standardized under ASTM D256 and ISO 180, the notched or, unnotched standard test bar is held vertically at half of its length. For the notched test, the notch stands facing the hammer, just clear of the holding clamp. The impact strength or notched impact strength are determined as the impact energy absorbed relative to the cross-section of the test bar. Tests are usually carried out at room (+23˚C) and low (i.e. -30˚C) temperatures. Brittle fractures can be prevented by incorporating impact modifiers, such as elastomers, which are blended very intimately into the base material. Under impact stress, the elastomeric regions absorb additional energy and prevent brittle fracture of the part.

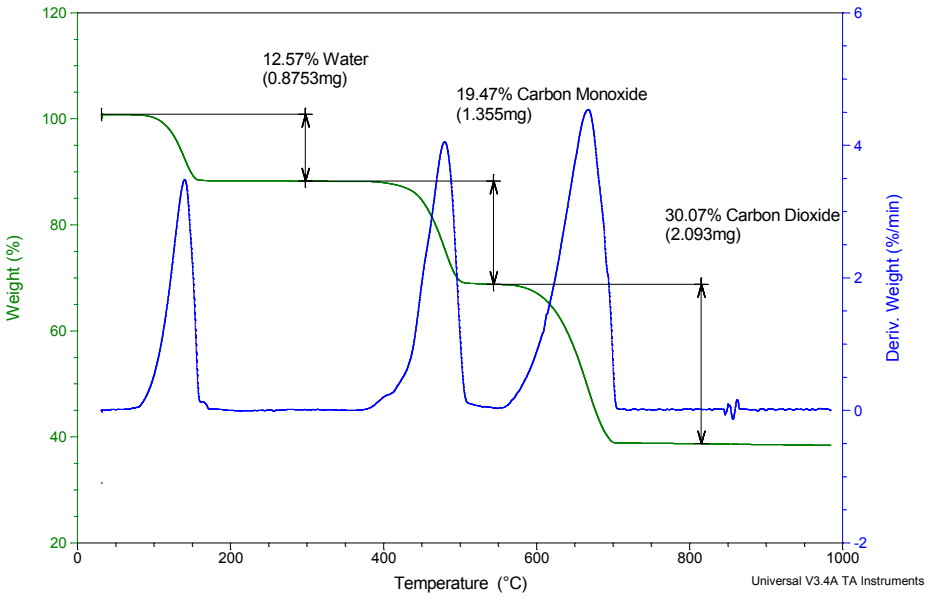
Thermal Analysis

Thermal Analysis techniques such as TGA, TMA, and DSC are used extensively in failure analysis. The thermomechanical properties of polymeric materials are defined as the mechanical properties that attain different values when subjected to different temperature levels. These material properties include, but are not limited to, the elastic modulus, thermal conductivity, thermal expansion coefficient, and the specific heat. The ability to measure the temperature-dependent material properties is critical for the determination of appropriate processing conditions and for the prediction of the behavior of polymeric components during service life.

TGA is commonly employed in research and testing to determine characteristics of polymer and plastic materials to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic, organic components, additives, decomposition points and

solvent residues. TGA measures the weight change as a function of temperature or time. The decomposition reaction at a constant temperature can directly be measured with TGA set at the target temperature. It covers the assessment of materials thermal stability through the determination of the temperature at which the materials start to decompose, react, or evaporate and the extent of the mass change using thermogravimetry.

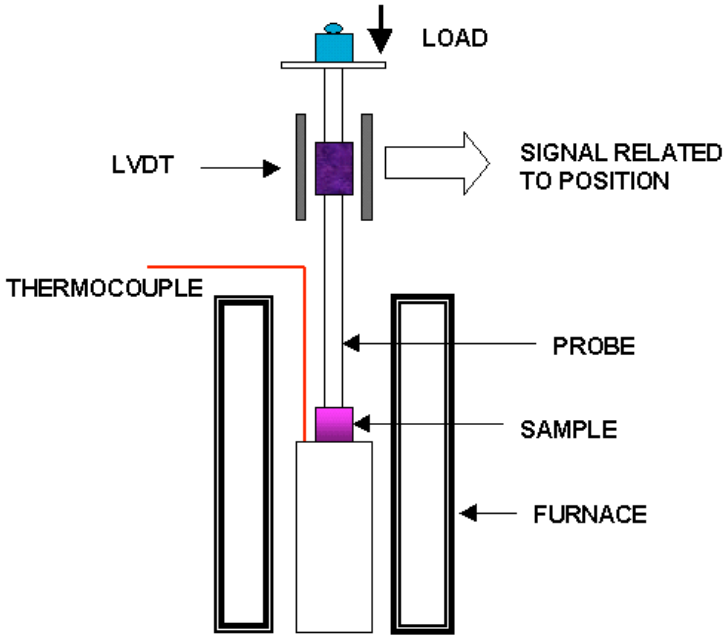
The results from thermogravimetric analyses are usually reported in the form of curves relating the mass lost from the sample against temperature. In this form the temperature at which certain processes begin and are completed are graphically demonstrated as shown below.



Thermomechanical analysis (TMA) is used to measure linear displacement of a material as a function of temperature. The technique provides information on various properties such as softening point, heat distortion, and transition temperatures, as well as the coefficient of linear expansion (CTE) as listed below:

- Expansion - used to determine CTE and to measure glass transitions
- Compression - used to measure compression modulus
- Penetration - used to evaluate coating softening points
- Three-Point Bending - used for distortion measurements
- Tension - primarily used for films and fibers, and for CTE in the machine and transverse directions

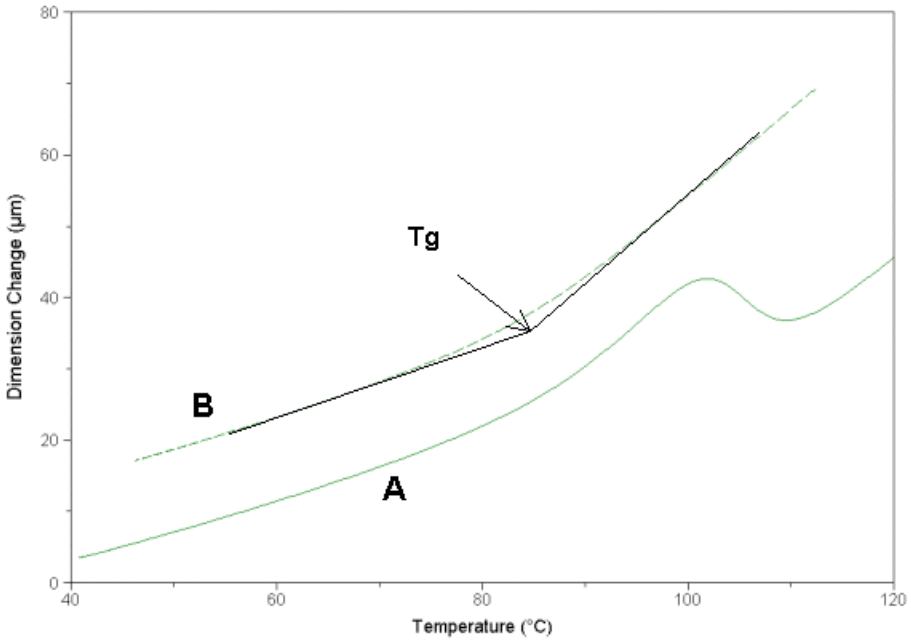
The sample sits on a support within the furnace. Resting upon it is a probe to sense changes in length, which are measured by a sensitive position transducer, normally a Linear Variable Displacement Transducer (LVDT). The probe and support are made from a material such as quartz glass (vitreous silica), which has a low, reproducible, and accurately known coefficient of thermal expansion, and also has low thermal conductivity, which helps to isolate the sensitive transducer from the changing temperatures in the furnace. A thermocouple near the sample indicates its temperature. There is usually provision for establishing a flowing gas atmosphere through the instrument, to prevent oxidation for example, and also to assist in heat transfer to the sample. Helium is effective in this respect. Sample sizes are commonly around 5-10mm in height and width. It is important to prepare samples with clean, flat and parallel faces to avoid artifacts in the recorded curves.



Schematic illustration of TMA

TMA applications are in many ways the simplest of the thermal techniques. However, they are also incredibility important in supplying information needed to design and process everything from chips to food products to engines. Because of the sensitivity of modern TMA, it is often used to measure Tg's that are difficult to obtain by DSC, for example those of highly cross-linked thermosets. While many other techniques exist for studying the important and informative region of the glass transition (Tg), TMA offers advantages for certain types of study. The indentation and penetration probes for instance, can follow transitions in very thin films, such as lacquer coatings on metals. Although quantitative mechanical properties (modulus) can in principle be derived from TMA measurements, this may be difficult in practice, and Dynamic Mechanical Analysis may be preferred. TMA is better suited to comparative measurements on a range of materials, and for measurements of transition temperatures and expansion coefficients on relatively small samples, in a conveniently short time.

In the below figure, curve A shows the dimensional changes around Tg when too great a load is used. The sample slumps after entering its softer state, making measurements doubtful. Whereas in curve B, data was obtained under a negligible load, allowing Tg to be measured as the intersection of the portions of the curve above and below Tg.



TMA instrumentation typically spans a temperature range from -150ºC to 1000ºC with controlled cooling from 400ºC to -60ºC, which is ideal for thermal cycling experiments. Programmed heating rates of 0.01ºC/min to 200ºC/min are possible.

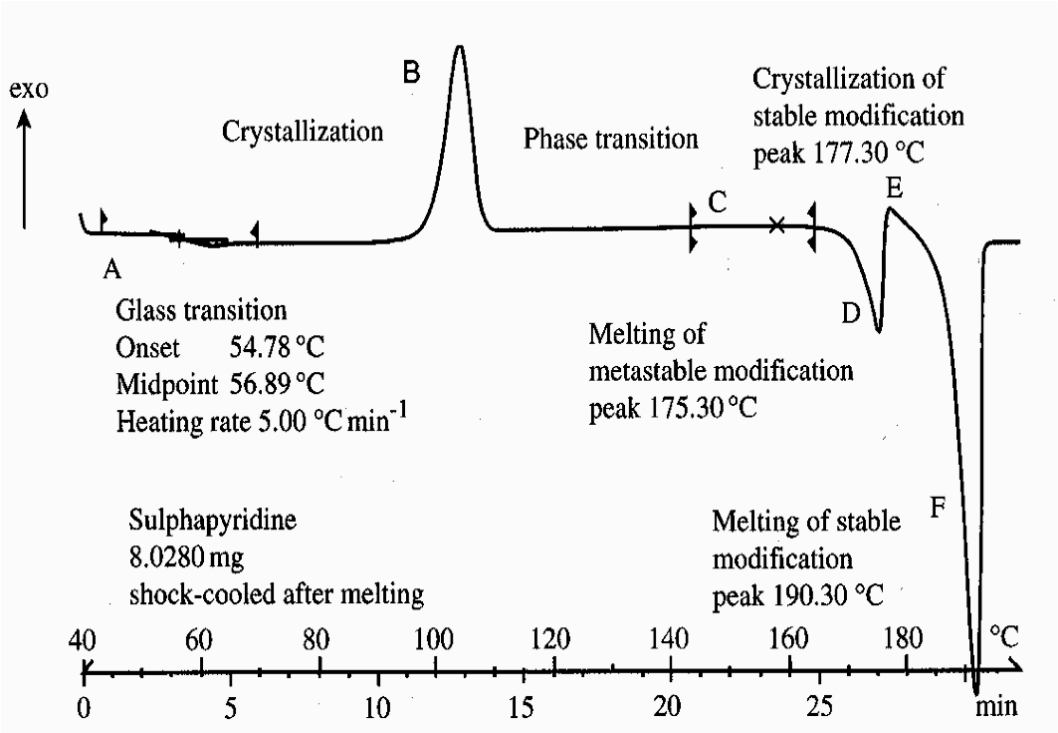
Dynamic Mechanical Analysis, otherwise known as DMA, is a technique where a small deformation is applied to a sample in a cyclic manner. This allows the materials response to stress, temperature, frequency and other values to be studied. The term is also used to refer to the analyzer that performs the test. DMA is also called DMTA for Dynamic Mechanical Thermal Analysis. Thermomechanical Analysis, or TMA, applies a constant static force to a material and watches the material change as temperature or time varies. It reports dimensional changes. On the other hand, DMA applies an oscillatory force at a set frequency to the sample and reports changes in stiffness and damping. DMA data is used to obtain modulus information while TMA gives coefficient of thermal expansion, or CTE. Both detect transitions, but DMA is much more sensitive. DMA can provide a quick and easy method of distinguishing between two ABS compositions; one containing a butadiene or SBR rubber, while the other containing a nitrile rubber. Identification can be accomplished by the difference observed between the Tg's of the two elastomers.

Differential Scanning Calorimetry (DSC) monitors heat effects associated with phase transitions and chemical reactions as a function of temperature. DSC is used to determine a wide range of physical properties of materials, including the glass-transition temperature Tg, the melting temperature Tm, and solid-solid transitions. In this technique, a sample and a reference material are subject to a controlled temperature program. When a phase transition such as melting occurs in the sample, an input of energy is required keep sample and reference at the same temperature. This difference in energy is recorded as a function of temperature to produce the DSC traces.
During the heating of a sample, for example, from room temperature to its decomposition temperature, peaks with positive and negative $\Delta dH/dt$ may be recorded; each peak corresponds to a heat effect associated with a specific process, such as crystallization or melting as the figure below illustrates.

The question arises as to what kind of information is obtainable from a DSC curve. The first and most direct information is the temperature at which a certain process occurs, for

example, the melting point of a polymer. The temperature at which a reaction, such as decomposition, may start is another important parameter. The peak temperature is associated with the temperature at which maximum reaction rate occurs.

A special case in which the temperature of a phase transformation is of great importance in polymers is the glass transition temperature, Tg. This is the temperature at which amorphous (noncrystalline) polymers are converted from a brittle, glasslike form to a rubbery, flexible form. This is not a true phase transition but one that involves a change in the local degrees of freedom. Above the glass transition temperature certain segmental motions of the polymer are comparatively unhindered by the interaction with neighboring chains. Below the glass transition temperature, such motions are hindered greatly, and the relaxation times associated with such hindered motions are usually long compared to the duration of the experiment. The operative definition of glass transition temperature is that at this temperature, or within a few degrees, the specific heat, the coefficient of thermal expansion, the free volume, and the dielectric constant (in the case of a polar polymer) all change rapidly. Since the mechanical behavior of polymers changes markedly at the glass transition temperature, it is an important characteristic of every polymer.



Nondestructive Testing (NDT) Techniques

NDT techniques are useful in determining the flaws, discontinuities and joints. Presently, many components are made from composite materials instead of metal in order to save weight. For example rotor blades of wind-powered devices or of helicopters are made of composite glass fiber materials. In order to ensure the safety of these objects, it is necessary to be able to test the material parameters ranging from the production of the raw material up to the finished structure and also after possible damages caused by aging or accident. Principally only few non-destructive techniques can be used to test composite glass fiber structures. These are modified ultrasonic or thermographic methods, both having their limitations.

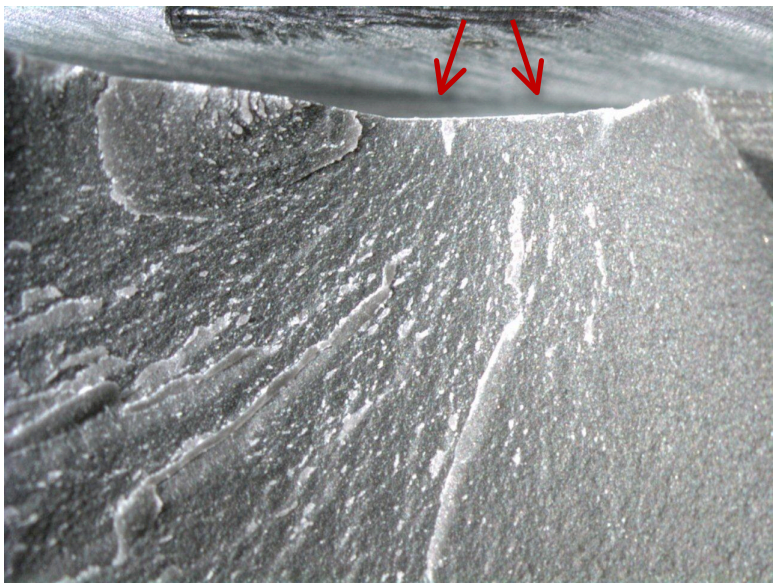
The problem of finding defects in composite materials is caused by inhomogeneity of the structure: composite material is plastic material with innumerable inclusions in filament form and boundary surfaces. Genuine defects such as foreign material inclusions, unbonds, voids and tears among other types of defects in the inhomogeneous structure have to be recognized. Obviously, more different types of defects can arise than within homogeneous materials. Only in the rarest cases the defects are visible with the naked eye. Furthermore, impact defects tend to be wider spread in the depth of the device than at its surface. That makes it necessary to use non-destructive testing techniques for inspection.

Fractography

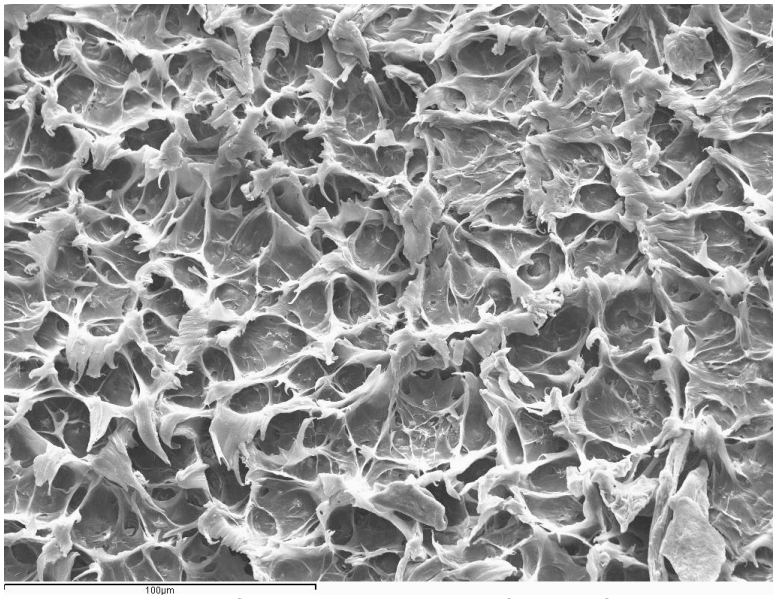
Fracture surface analysis is utilized to identify the fracture origin, direction of crack propagation, failure mechanism, presence of material defects, and environmental interaction. Some of the macroscopic and microscopic features employed by the failure analyst to evaluate fracture surfaces are described below. Note, however, that many of the fractographic features described for plastics are not observable for reinforced plastics and plastics containing high filler content.

On a macroscopic scale, all fractures fall into one of two categories: ductile and brittle. Ductile fractures, which are characterized by material tearing typically exhibit gross plastic deformation such as tearing. Fracture surface features are typically fibrillar in nature. Brittle fractures display little or no macroscopically visible plastic deformation and require less energy to form. Ductile fractures occur as the result of applied stresses exceeding the material yield strength mostly due to overload or under design. Brittle fractures, on the other hand, generally occur well below the material yield strength.

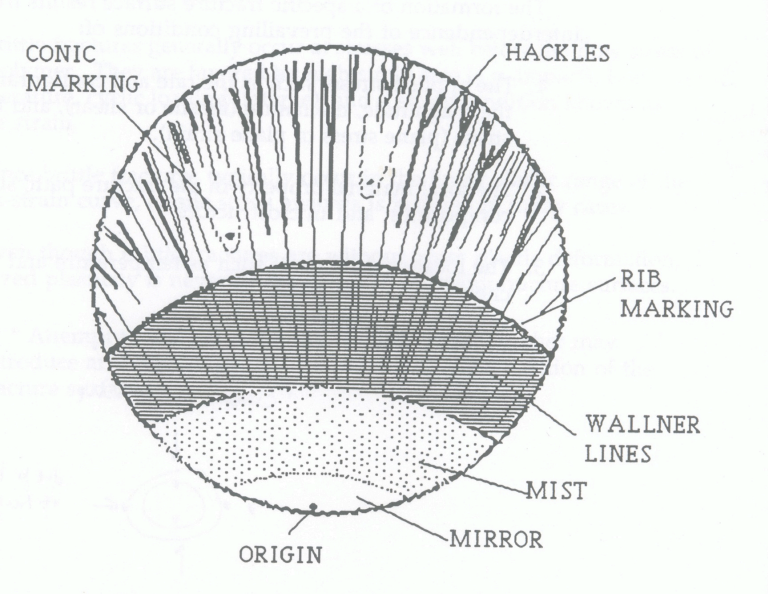
Many macroscopically visible fractographic features serve to identify the fracture origin(s) and direction of crack propagation, such as radial marks and chevron patterns. Radial marks are lines on a fracture surface that radiate outward from the origin and are formed by the intersection of brittle fractures propagating at different levels. Chevron patterns or herringbone patterns are actually radial marks resembling nested letters “V” and pointing towards the origin.



Fracture surface with chevrons pointing back to the origin



Fracture surface showing ductile fibrous features

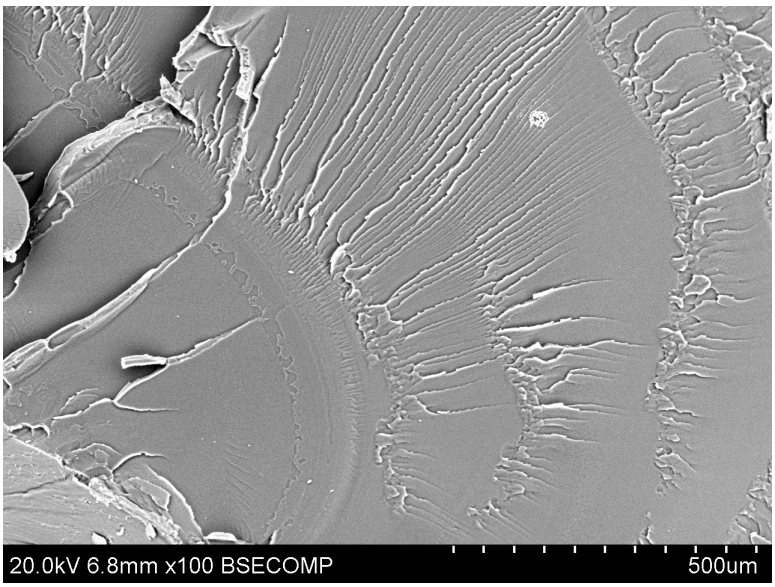


Characteristic fracture zones of a brittle failure

Brittle fractures in plastics exhibit characteristic features, several of which are macroscopically visible. These may include a mirror zone at the origin, mist region, and rib marks. The mirror zone is a smooth, flat, featureless region surrounding the origin and associated with the slow crack growth phase of fracture. In many polymers the mirror zone is the remnant of a ruptured craze. The size of the mirror zone depends both on the prevailing stress at the time of the fracture and the fracture toughness of the material. The mist region is located immediately adjacent to the mirror zone and displays a misty appearance. This is a transition zone from slow to fast crack growth. Rib marks are semi-elliptical lines resembling beach marks. Regions of the fracture surface containing hackle lines are typically rough in appearance. The hackles consist of divergent lines radiating outwards from the fracture origin. They are perhaps the most reliable features to use to locate the fracture origin by back tracing along the path of crack growth. Hackled regions are associated with high-energy dissipation due to localized plastic deformation on the fracture surface. They are regions of violent activities involving high crack velocity, rapid changes in the stress field, and non co-planar fracture paths. Hackles are commonly observed in the regions subjected to bending where the stresses change from compression to tension.

Wallner lines are faint striations on otherwise smooth fracture surfaces. They resemble fatigue striations with periodic spacing but are formed when stress waves reflected from the specimen boundaries interact with the propagating crack front. Subtle changes in the fracture surface texture result when the stress waves produce a slight perturbation of the stress field ahead of the crack front. Wallner lines are typically curved markings similar to crack front markings with the fracture origin located somewhere on their concave side. Even though they are not true crack front markings, they may be considered to be “snap-shots” of the crack front during crack propagation since stress wave velocities are much higher than crack velocities.

Rib markings are prominent curved crack front markings that are often visually observable. They occur during crack arrest or sudden changes in crack velocity and are typically randomly spaced. Their outward normal point to crack growth direction with the fracture origin located on their concave sides.

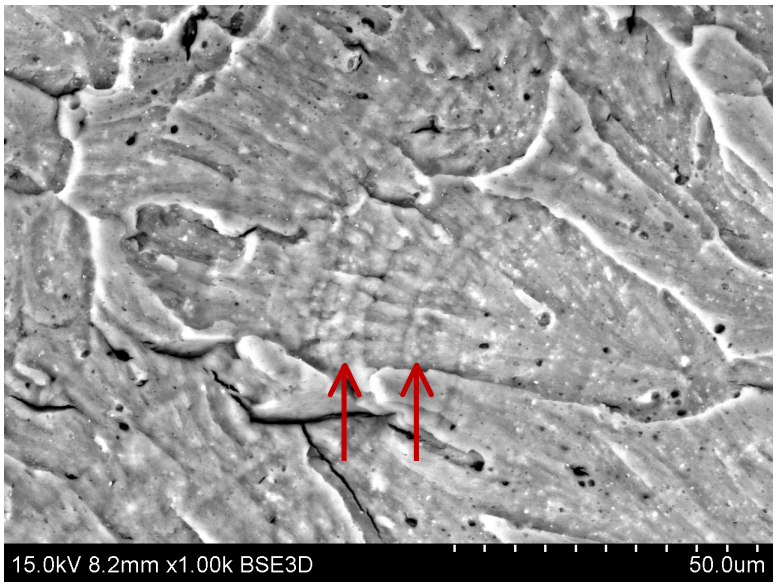


Fracture surface of an impact failure showing mirror and mist areas, rib markings, wallner lines and hackles

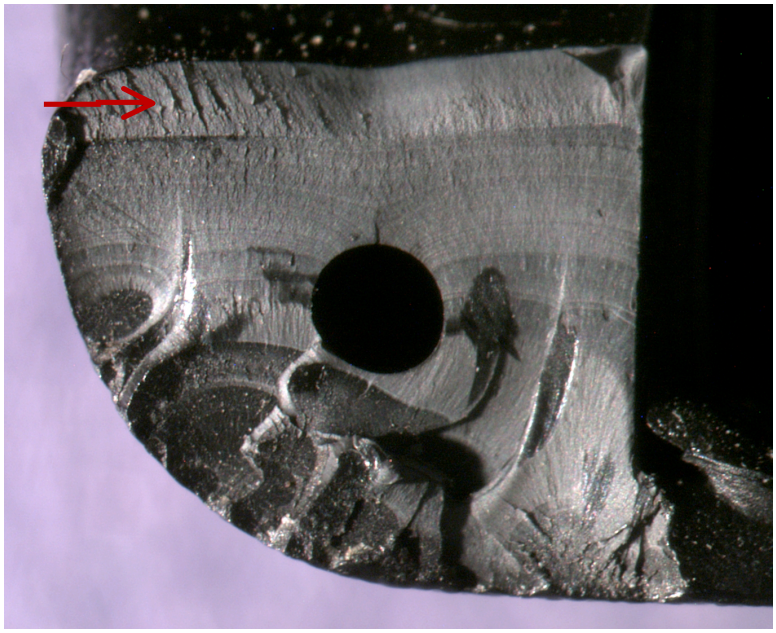
Fatigue failures display beach marks and ratchet marks that serve to identify the origin and the failure mode. Beach marks are macroscopically visible semi-elliptical lines running perpendicular to the overall direction of fatigue crack propagation. They mark successive positions of the advancing crack front. Fatigue striations are true crack arrest markings and are more distinct than Wallner lines. Typically each striation corresponds to one crack growth cycle. The spacing is usually regular if the stress level is uniform and gets wider with increasing stress. Hackles are not observed in the fatigue region since the crack grows at low velocity.



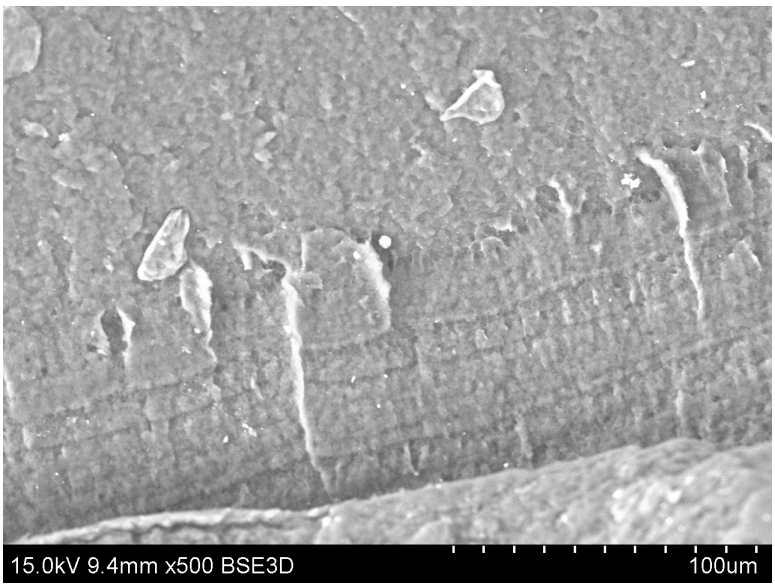
Fracture surface showing fatigue initiating at a stress concentration created by the indented lettering



Higher magnification SEM image showing fatigue striations



Close-up view of a failed PPO part. The initial cracks (dark areas) were formed due to ESC followed by cyclic loading (fatigue-light areas). Hackles are evident in the final overload area (arrow). The dark circle in the middle is a hole.



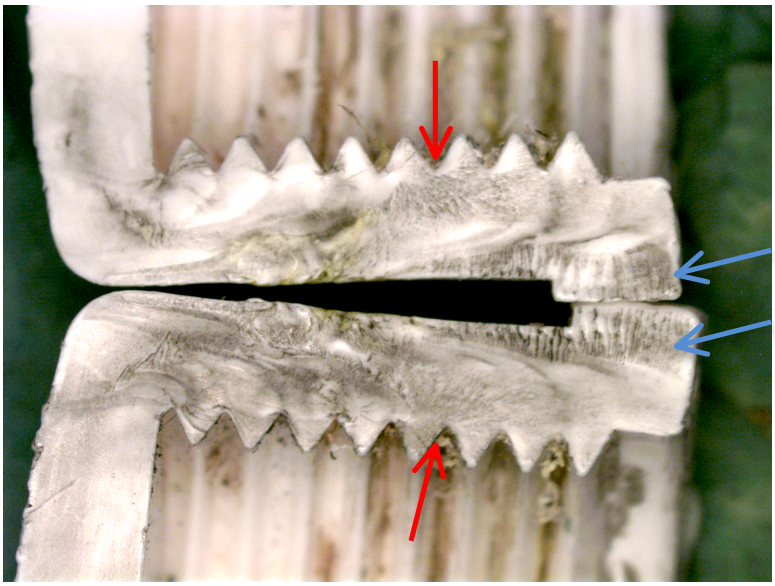
Higher magnification SEM image of the transition zone from ESC to fatigue striations

CASE STUDIES

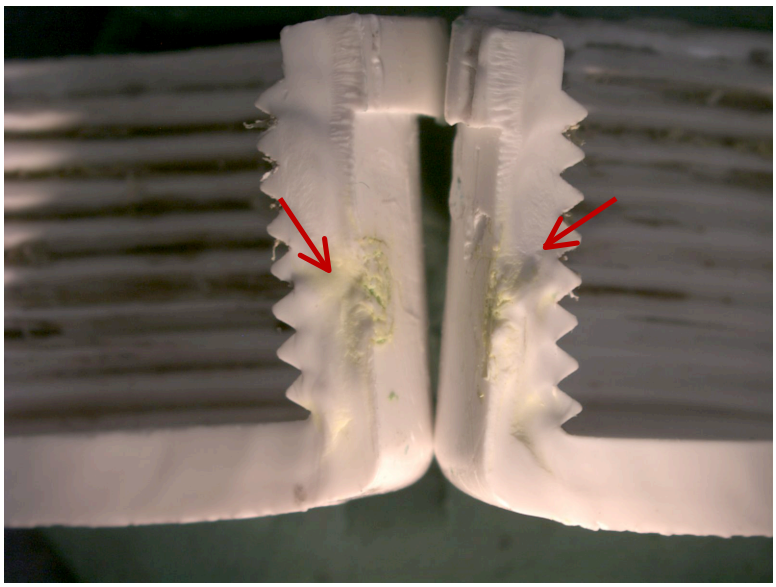
FAILURE ANALYSIS OF PVC END CAP

An end cap used on a multistory building to temporarily close off a showerhead at the end of a workday had failed some time during the off hours allowing water to escape. This caused water damage to the floors below including the lobby. Microscopic examination of the fracture surfaces did not reveal a single initiation point but rather several crack origination points on one side at the individual thread roots indicating the stress came from the opening of the cap using this side as the hinge. A series of small parallel shear ridges-hackles (blue arrows) mark the location of the final separation of the halves.

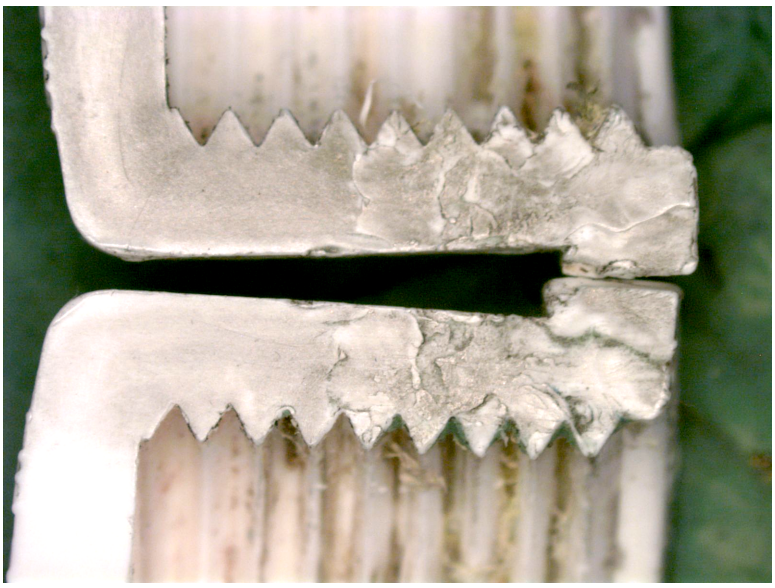
Rib markings progressing from the top of the cap to the side wall indicated the direction of crack propagation. A series of Wallner lines radiating away from thread roots 5 and 6 (red arrows) also suggested a change in the stress state at this location during final separation.



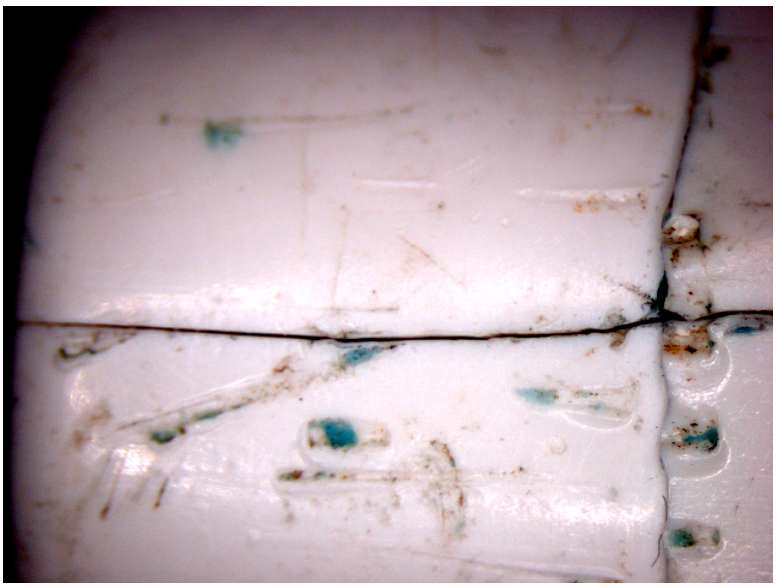
A view of the side opposite the ridge side revealed the features of a weld line failure. This weld line was where the initial failure occurred. A weak weld line would result from processing conditions (melt mold and/or core temperature too low). The crack initiated here and progressed up this side and across the top of the cap.



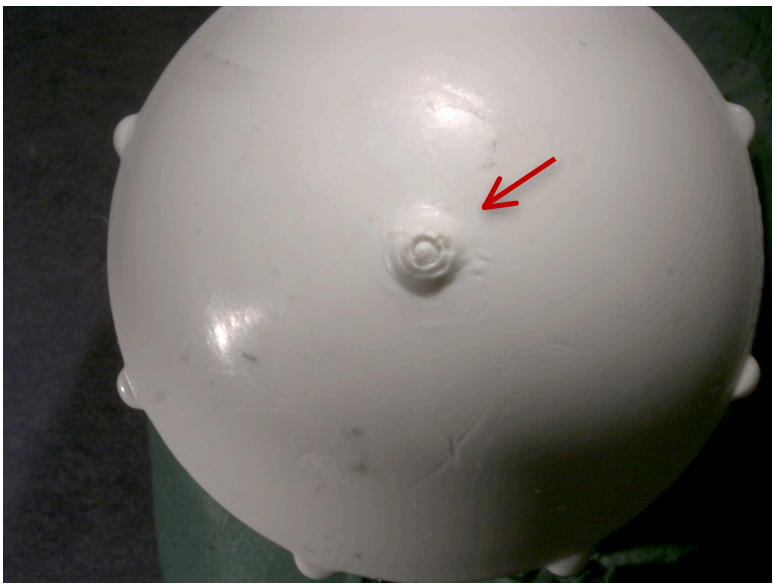
In this part the mold design had the gate on the side. The melt entering from the side split around and over the core rejoining at the weld line. The figure above shows the side with shear ridges before contrasting “coating” was applied to the surface to reveal fracture features. The gate location is visible (arrows).



Overall view of the end cap showing the side where the fracture initiated at the weld line. After the weld line failed the fracture traveled up and across at high speed causing the cap to completely separate into two with the aid of the water pressure. The fast travelling crack with high energy left very few features (shear ridges, etc.) on the fracture surface.



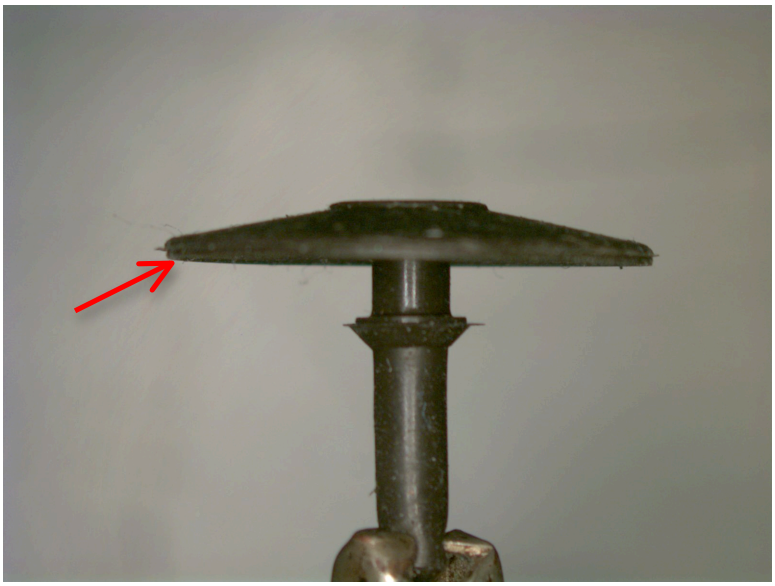
There was evidence of severe tool marks on the cap's exterior surface at the initiation point where the weld line was located. The installation practice and the undesirable location of the weld line combined to cause the failure under water pressure.



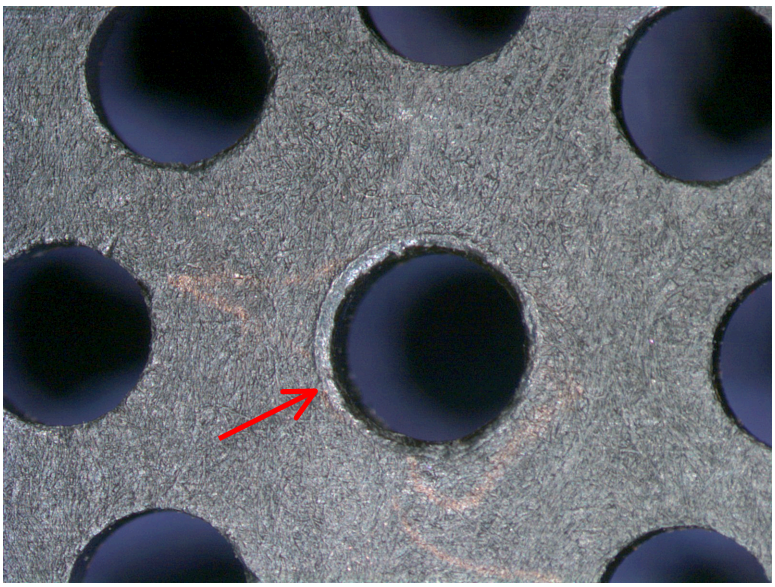
Photograph of an exemplar end cap showing an alternate mold design where the injection gate is located at the top instead of the side. With this design there would not be a weld line. The melt would enter at the top and flow down the sides of the part ending at the bottom without forming a weld line.

FAILURE ANALYSIS OF RUBBER CHECK VALVE

A medical device which employs an air compressor had a check valve that failed prematurely at less than 5% of the required service life. Samples of broken check valves, and some exemplars were provided for failure analysis. The valve body consisted of a mushroom shaped insert made from silicone rubber with 70-90 Shore A Durometer Hardness. It was designed to insert into a valve body where the mushroom head would act as a flapper valve, alternately covering and uncovering holes to provide one way flow from a reciprocating pump. The valve body consisted of a group of holes surrounding a central anchor hole through which the valve stem was inserted and locked in place by an anchor rib around the shaft.

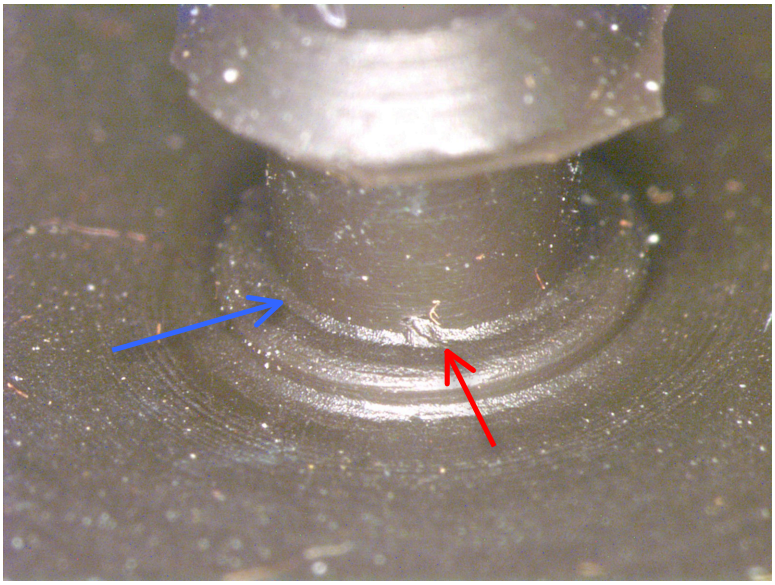


Photograph showing the mushroom shaped flapper head (arrow), anchor stem, and anchor rib. The anchor stem and anchor rib inserted into one end of the anchor hole in the valve head.



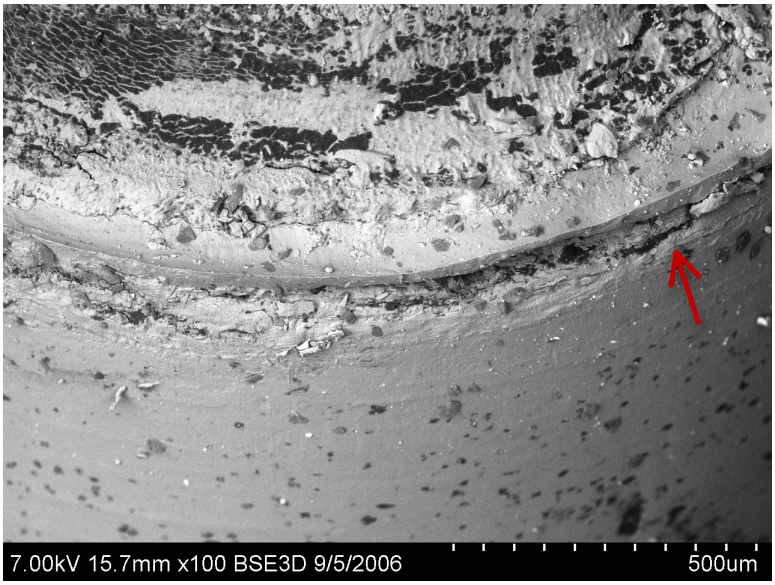
Compressor valve head with anchor hole (arrow) for the flapper surrounded by the air holes. Compressed air would lift the flapper to allow flow in one direction only.

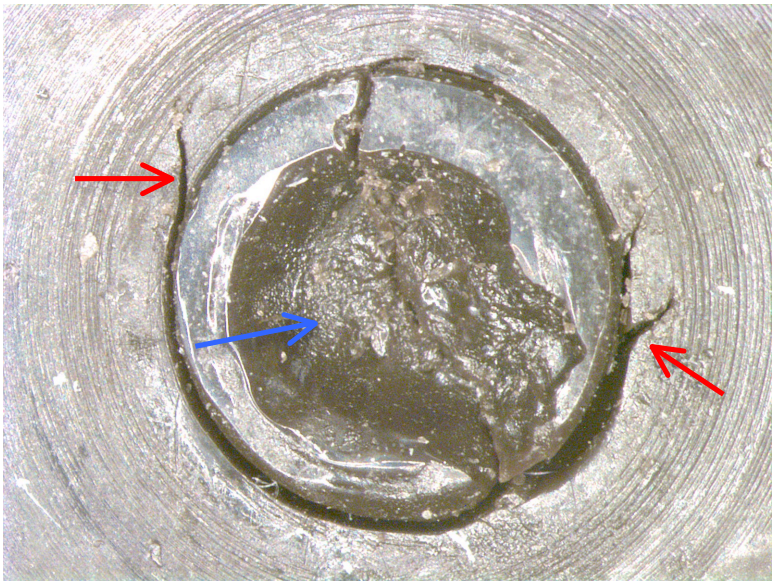
Stereomicroscopy of the exemplar revealed a manufacturing and a design flaw where the flapper and the stem joined as shown in figure below, which coincided with the failure location. The design flaw was a step ring at the junction between the stem and the flapper valve and the manufacturing flaw was a nick in the stem at the step ring junction. The nick and the step ring provided stress risers, which contributed to failure. The stresses developed in this area of the flapper head during the high frequency operation of the valve led to failure.



Junction between stem and flapper valve shows step ring (blue arrow) radius associated with failure and nick (red arrow).

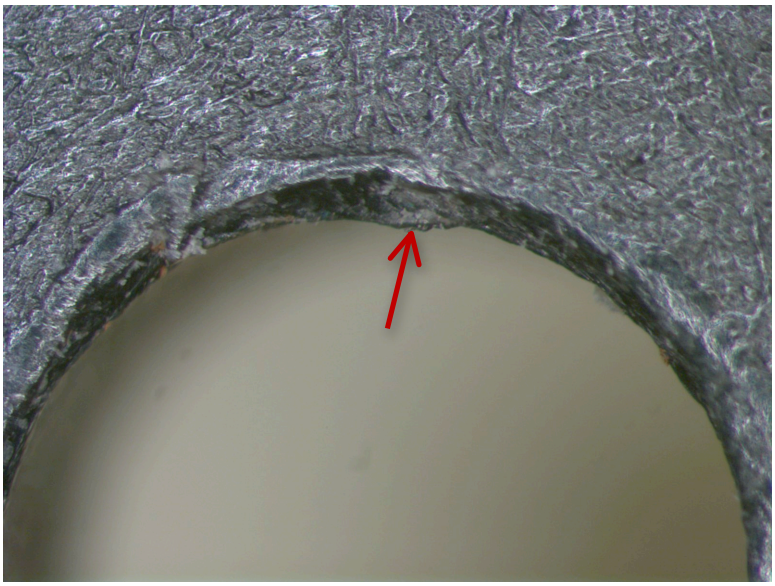
Examination of the fracture area with a Scanning Electron Microscope (SEM), revealed secondary cracks as shown below (arrow). These appeared to originate within rings of abrasion suggesting rubbing against the edge of the anchor hole.





Macrophotograph showing bottom of flapper where the stem separated. Primary failure (blue arrow) followed contour of step ring where it joined the stem. Secondary cracks (red arrows) developed following the contour where the step ring connected to the flapper.

Further examination of the anchor hole showed a relatively sharp edge and protrusions shown below, which most likely caused the abrasion observed on the stem.



FAILURE ANALYSIS OF POLYPROPYLENE FILTER HOUSING

A water filter in a residence failed approximately 2.5 years after installation causing water damage.

The location of the fracture was at the bottom section of the filter housing. Visual examinations did not reveal any evidence of external damage to the housing. Stereomicroscopic evaluation at magnifications of up to 40X indicated that the fracture had initiated on the internal diameter, at a geometric transition area. Detailed fracture surface examinations could not be performed since customer had requested to limit the evaluations to be nondestructive in nature and not disturb the failure area by opening the fracture.

A small shaving was removed from an area away from the crack and analyzed using Fourier Transmission Infrared techniques (FT-IR) to determine the material type of the housing. As shown in the spectra below, the material was determined to be polypropylene with talc filler.

The cap was removed to inspect the condition of the housing interior and the filter cartridge. No unusual conditions were observed upon disassembly. The o-rings on the cartridge sealing surface and the cap were found to be in position.

The design of the filter requires the cartridge to be clamped between the cap and the bottom of the filter housing. This causes the area of the housing where the crack initiated to be under continuous stress even without any water pressure. Further cyclic loading as a result of water pressure during normal operation will be additional and contribute to the overall stress level experienced in the cracked area of the housing.

An exemplar filter with a more recent manufacturing date was acquired from a local store and examined for comparison. Although the cartridge type was visually found to differ slightly, no significant dimensional variations were noted. The only noteworthy difference between the two filters was that the maximum operating pressure was reduced from 125 psig to 100 psig on the new filter.

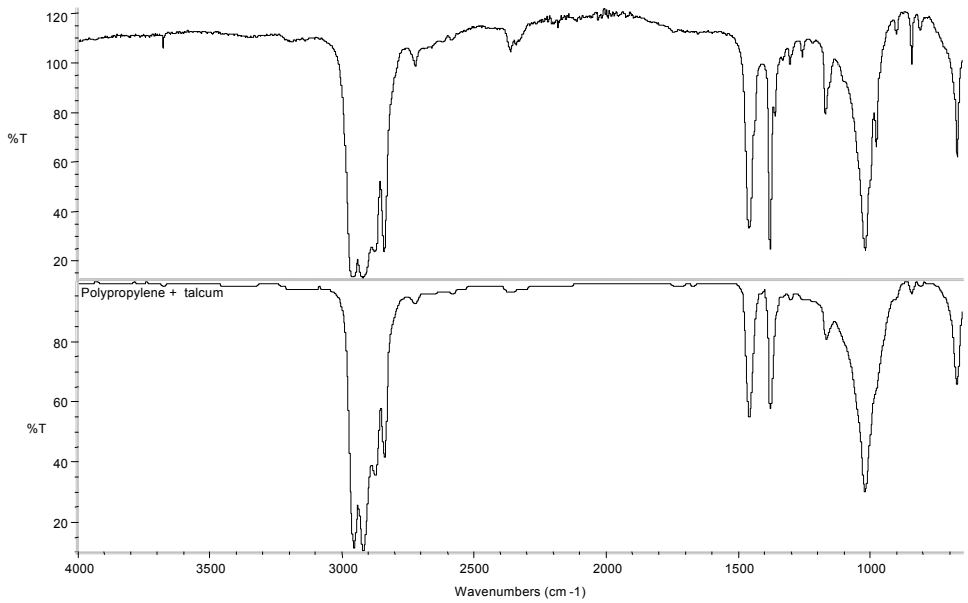
The filter housing failure most likely occurred in a progressive mode. The crack initiated at the high stress area at the bottom of the housing at a stress concentration point and propagated over time until final separation. Considering that the failure was related to the geometry of the part and the stress levels generated during normal use, the filter failure was attributed to inadequate design.



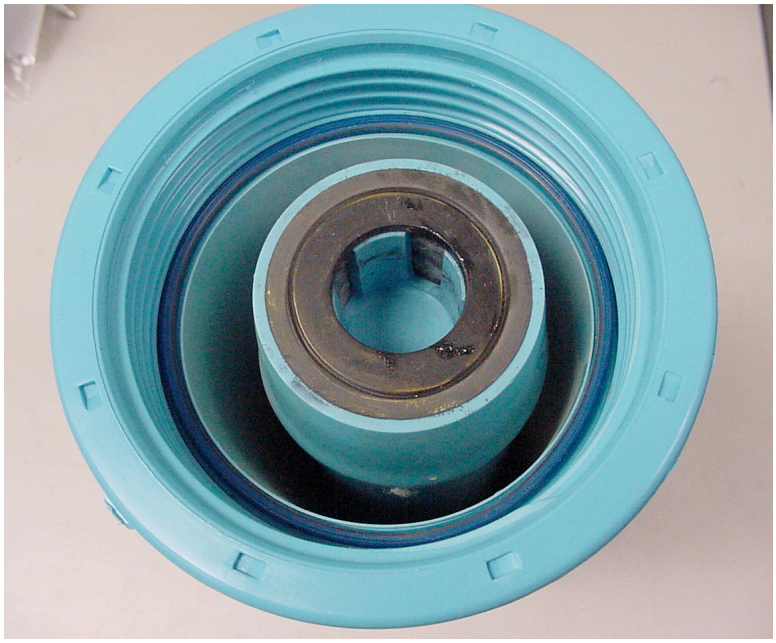
Photograph showing overall view of the cracked filter housing



Photograph showing a close-up view of the failure area



FT-IR spectra showing the housing material and matching reference standard



Photograph showing the cartridge and the housing interior after removing the cap

FAILURE ANALYSIS OF CPVC SPRINKLER PIPING

CPVC sprinkler piping was installed in a condominium complex and multiple failures were experienced upon pressurizing the system approximately a month after installation. A “failed” sample, removed by the contractor in the vicinity of a previous failure location, and four additional “unfailed” samples, removed from various units in the complex by the contractor were submitted for evaluation.

The pipe sections submitted exhibited ASTM F 442 as the standard designation. The longitudinal cracks, which caused the water leak, were located approximately 90° apart. Visual examinations did not reveal any evidence of external damage on the pipes. A section was removed from the failed sample and cut longitudinally to expose the internal diameter (ID). The crack pattern was suggestive of environmental stress cracking (ESC) as shown in figures below. The cracks were opened to facilitate evaluation of the fracture surfaces. Stereomicroscopic evaluation at magnifications of up to 40X indicated that multiple cracks had initiated on the internal surface. Higher magnification fracture surface examinations conducted using the electron microscope (SEM) confirmed multiple crack initiation points and features characteristic of environmental stress cracking whereas the lab-induced fracture zone exhibited fibrous ductile overload failure.

ASTM F442, *Standard Specification for Chlorinated Poly (Vinyl Chloride) (CPVC) Plastic Pipe*, covers pipe made in standard thermoplastic pipe dimension ratios and pressure rated for water. Included are criteria for material classification and requirements and test methods for materials, workmanship, dimensions, sustained and burst pressures, flattening and extrusion quality. Extrusion quality and flattening tests were selected to evaluate the materials conformance to specification.

The extrusion quality was determined using ASTM D 2152, *Standard Test Method for Adequacy of Fusion of Extruded Poly (Vinyl Chloride) (PVC) Pipe and Molded Fittings by Acetone Immersion.* Tested samples showed no evidence of attack and were found to be acceptable. Flattening tests were conducted on three samples one of which failed the test by cracking when tested per ASTM F 442. The crack appeared to have originated at a preexisting ESC location. Plastic pipe is manufactured by extrusion of molten CPVC resin through a die. The center mandrel is held in place with thin metal webs, which create the weld lines observed here. The polymer that flows through the die fuses back together after being sliced by the webs. The observed crack locations on the subject pipe samples indicate that these longitudinal knit lines, which are inherent to the extrusion process, were more susceptible to being attacked by the contaminant. The acceptable results obtained from the acetone immersion and the flattening tests indicate that the pipe was well fused.

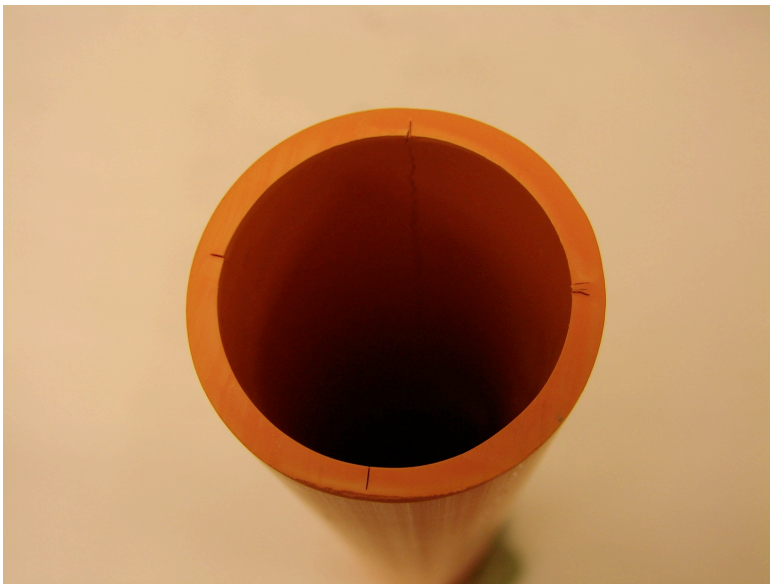
The interior surface of the failed pipe section was rinsed with a solvent (metlyl-tertiary butyl ether) and the extract was analyzed using gas chromatography/mass spectrometry (GC/MS) techniques to determine the nature of the contaminant (s). None were found; however, considering that the subject sample had been removed 5 months after the initial failures had occurred, it is quite conceivable that the contaminant has been flushed out.

The CPVC pipe failure occurred due to environmental stress cracking (ESC). The cracks initiated on the interior of the pipe at the high residual stress area created by the extrusion process and propagated into the pipe wall over time. The leaks most likely occurred when the remaining wall thickness separated from the normal water pressure generated during the system start-up.

Although no suspect ESC agent was detected in the tested sample, the physical evidence is consistent with this failure mode. CPVC is known to have high resistance to chemical attack by strong acids and other oxidizers, alkalis, salt solutions, and many other chemicals. However, it is attacked by non-ionic surfactants, some vegetable oils, and many organic chemicals such as polar solvents, aromatics and chlorinated hydrocarbons. It is possible that the pipes were exposed to some ESC agent after manufacturing during storage in a warehouse or at the job site.



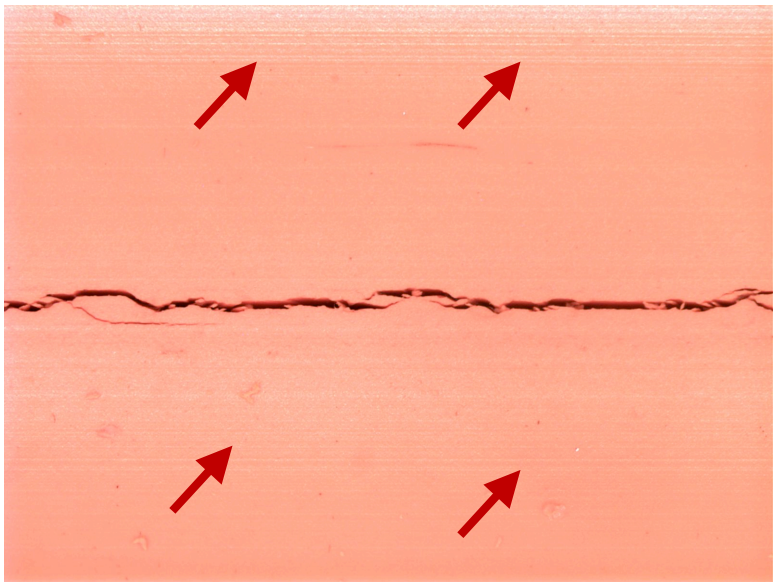
Photograph showing the "failed" sample



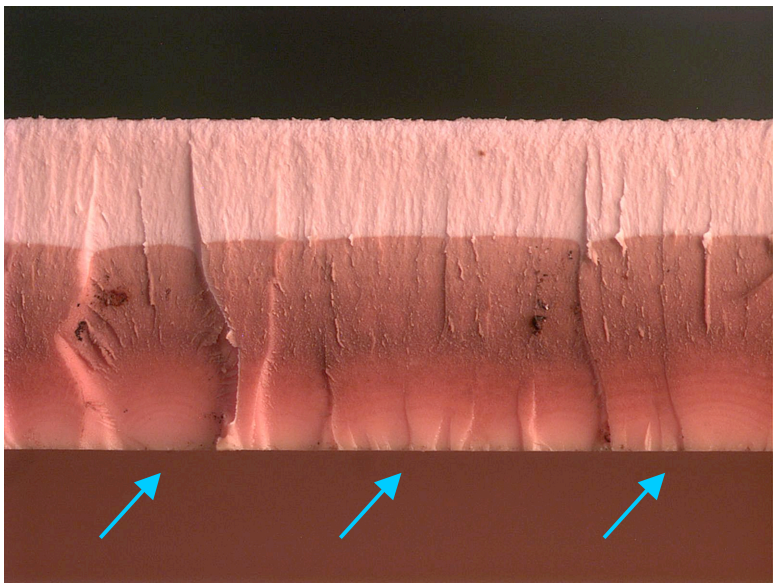
Photograph showing the end view of the failed pipe section, with cracks that are approximately 90° apart.



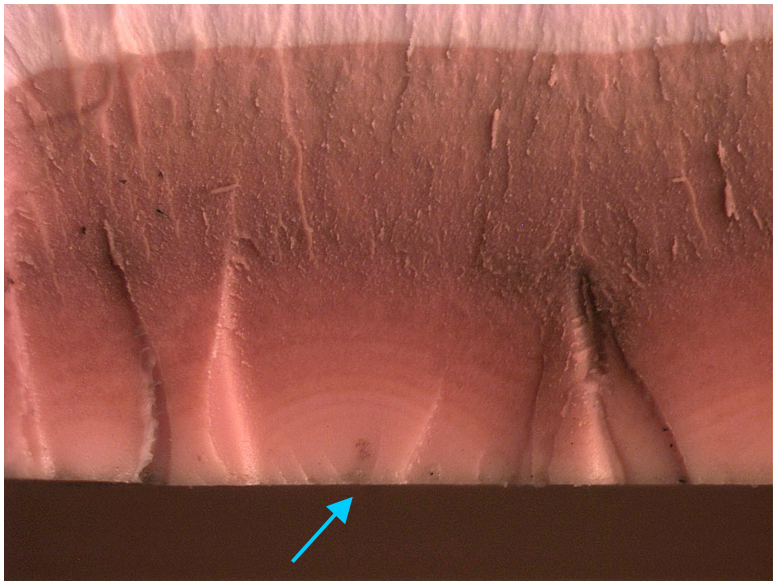
Close-up view of one of the longitudinal cracks in the failed section



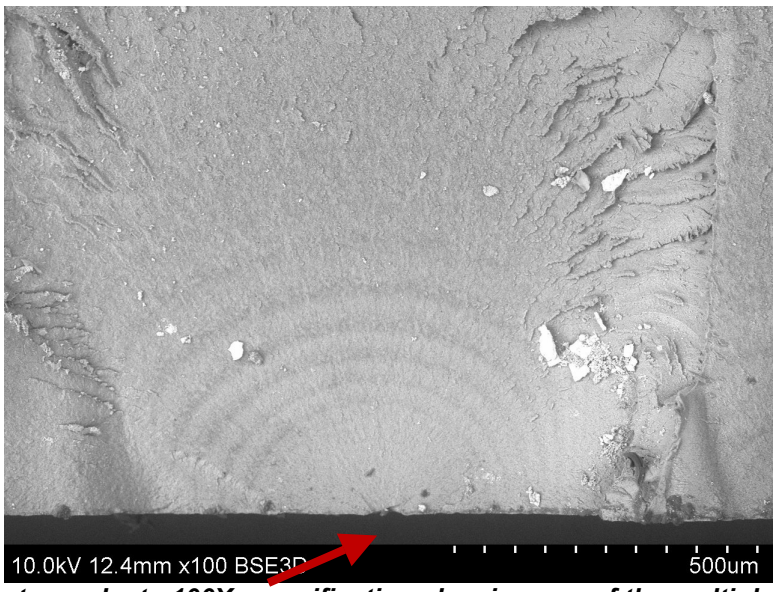
Macrophotograph at ~10X magnification showing a portion of the ID cracks. Note the arrows indicating extrusion lines running parallel to the crack.



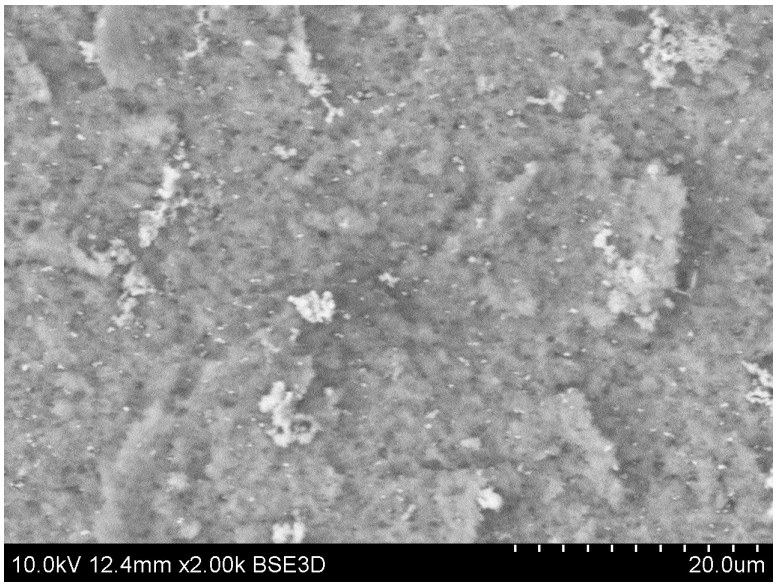
Macrophotograph showing the crack surface after opening it in the laboratory.The majority of the darker colored zone is the ESC area and the lightcolored final failure was induced in the laboratory. Note the multiple crack initiation sites on the pipe I.D. (arrows).



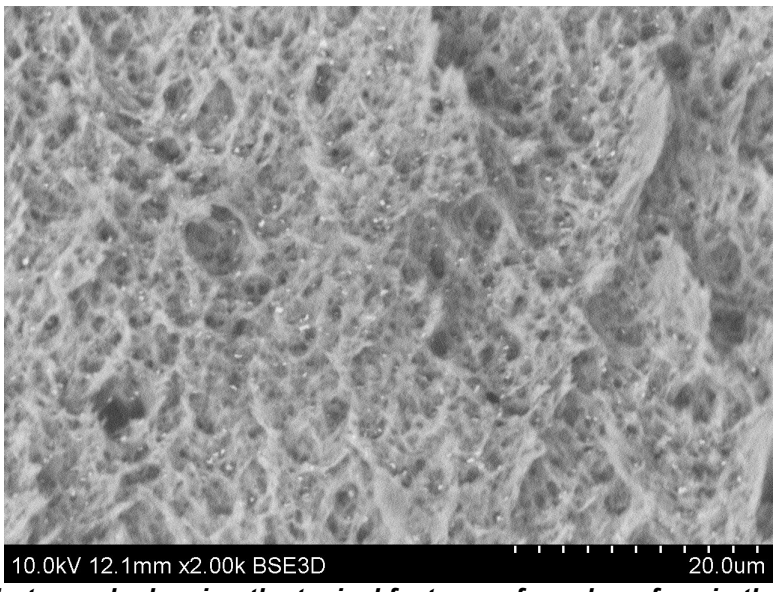
Higher magnification view showing one of the crack origins



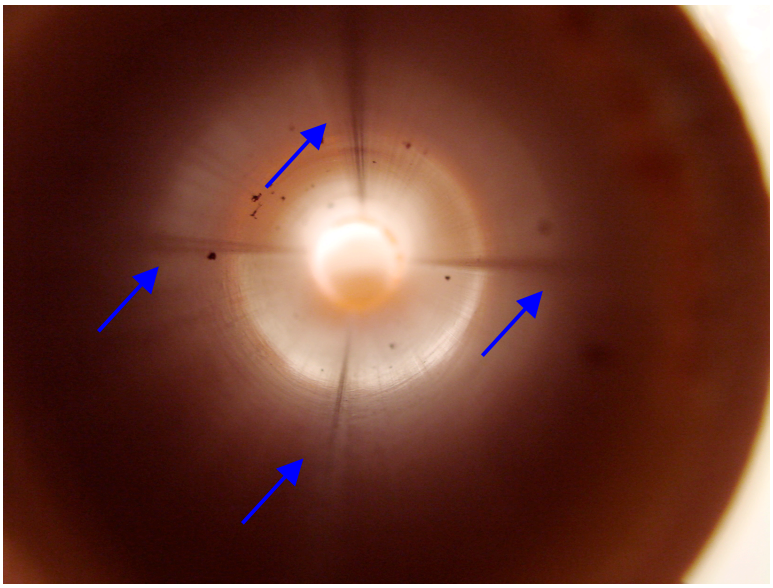
SEM microphotograph at ~100X magnification showing one of the multiple crack origins



SEM microphotograph showing the typical features of crack surface in the ESC zone



SEM microphotograph showing the typical features of crack surface in the lab-induced overload zone (Note the fibrous, ductile nature of the fracture)



A representative macrograph showing the extrusion knit lines (arrows) in one of the unfailed samples

FAILURE ANALYSIS OF A PLASTIC CHAIR

A person was injured while sitting in the plastic chair when the right front leg failed. The chair was new and had only been used for about two weeks. The injured person weighed less than 200 lbs., below the manufacturer's stated maximum load of 250 lbs.

Visual examination indicated the failure to be located at a transition area where the seat joined the leg/arm rest of the chair. This area is expected to be the high stress area as evidenced by the stress whitening observed on the opposite side of the fracture. The overstressing in this area of the left leg is believed to have occurred during the failure of the right leg. There was no evidence of misuse or abuse.

Low power stereomicroscopic and high magnification scanning electron microscopy examinations performed on the section of the fracture surface removed from chair revealed evidence of molding defects in the failure initiation area. Numerous voids (porosity) were observed at the fracture surface where the failure initiated. Polypropylene is known to have high resistance to crack initiation. However, its resistance to crack propagation is very low when there is a defect in the material.

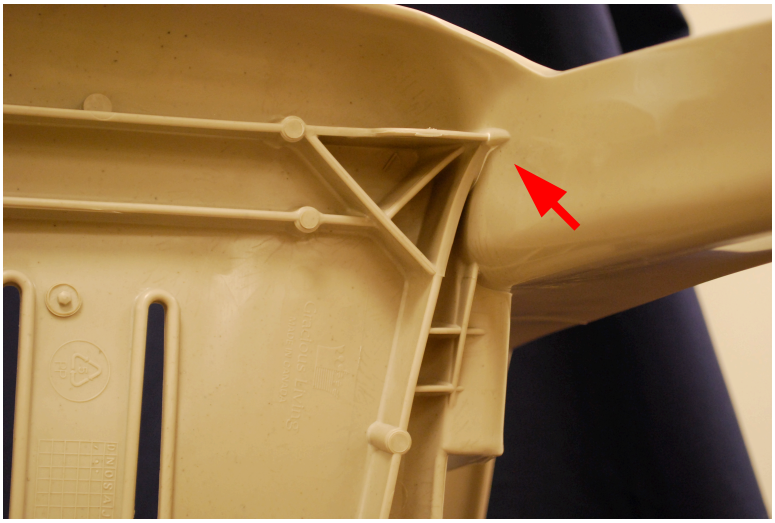
Although there is no industry standard specifying the type of material to be used, the material of construction was consistent with similar products analyzed by the author in the past. The ASTM standard applicable to plastic chairs, F1561-03, *Standard Performance Requirements for Plastic Chairs for Outdoor Use,* does not designate a specific polymer type. FTIR (Fourier Transform Infrared Analysis) indicated that the chair material was calcium carbonate filled polypropylene (PP). EDS analysis (Energy Dispersive X-Ray) also verified presence of mica particles.

Tensile test results, conducted per ASTM D638-03, *Standard Test Method for Tensile Properties of Plastics,* on samples removed from the back legs indicated that the strength was consistent with the type of material used, and within expected range. However, the low elongation values suggested that the mica addition has caused the material to have reduced ductility. Average maximum tensile strength at yield was 4,520 psi, whereas the % elongation at break was 10%. Past experience with this type of material indicates that elongation was less than half of typical values obtained on similar products.

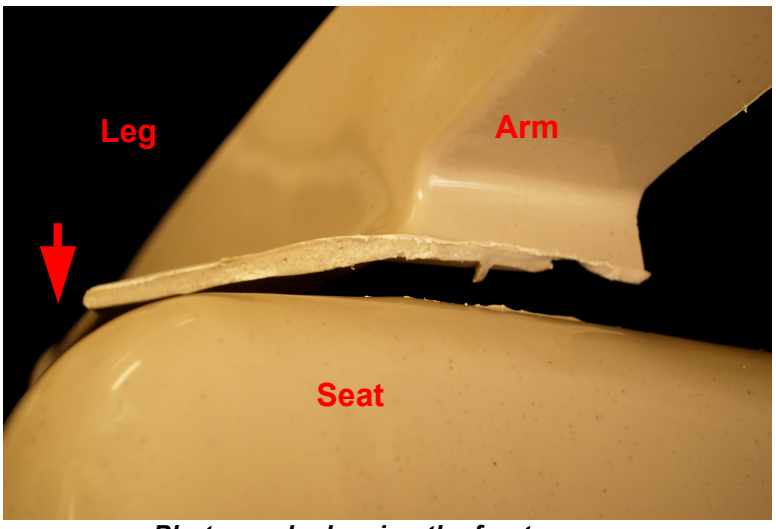
Fracture occurred at an area of high stress where molding defects were present. Material used for the chair was typical for material used for similar products. Tensile strength was adequate while elongation was insufficient. Presence of mica may have contributed to the failure; while its addition improves strength, ductility is reduced which can result in brittle behavior.



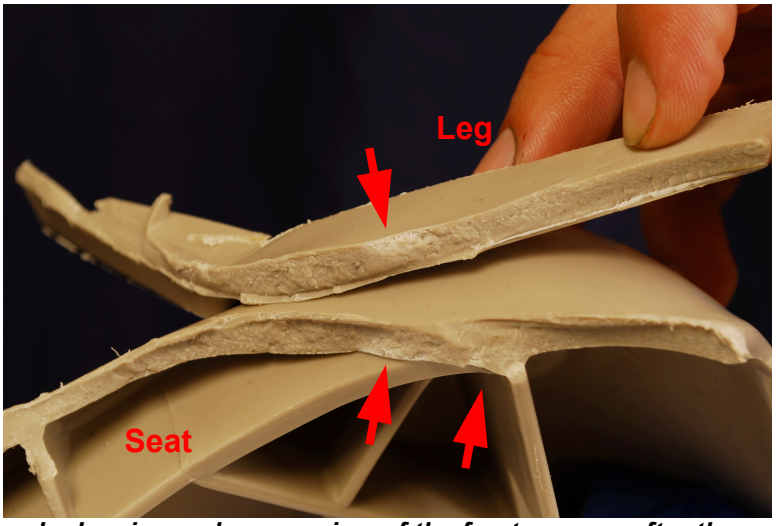
Photograph showing the chair, with arrow pointing to the fracture location



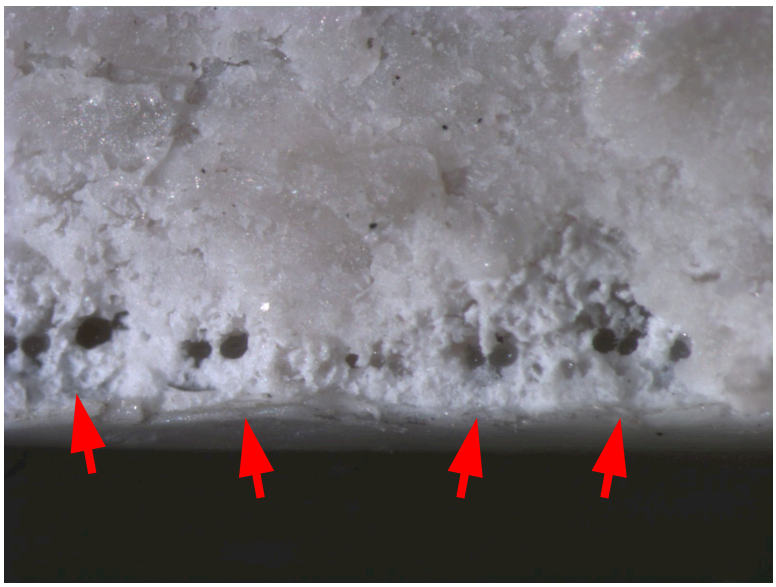
Photograph showing the left front leg, opposite the failed one.
Arrow points to the high stress area where stress whitening has occurred.



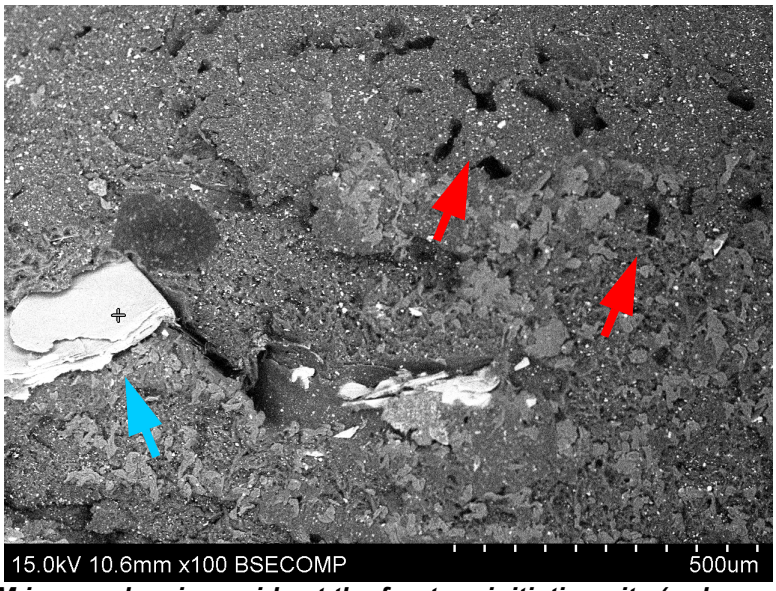
Photograph showing the fracture area



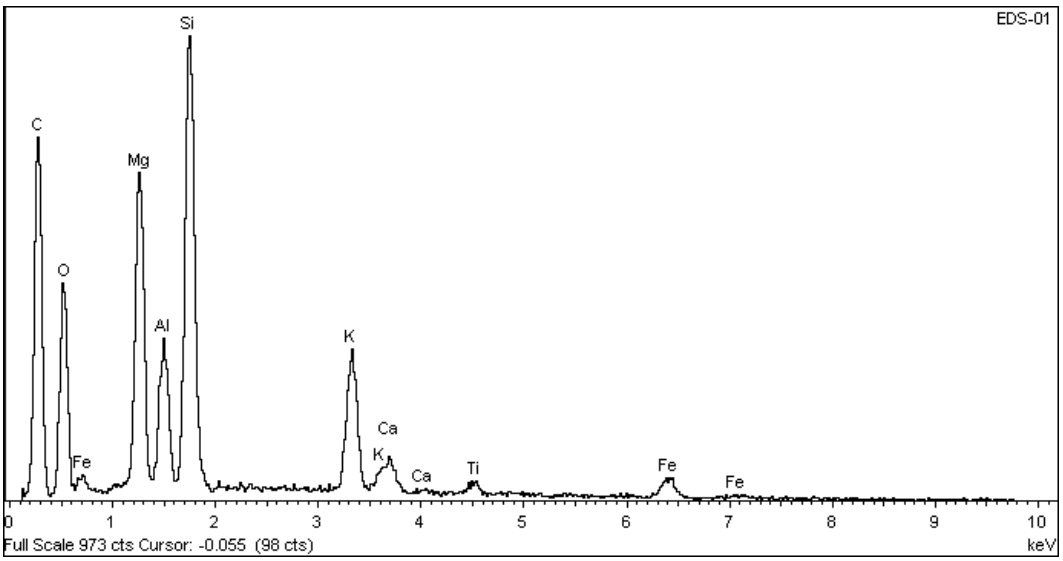
Photograph showing a close-up view of the fracture area after the sectioning. Arrows point to areas where defects were observed.



Macrograph showing voids at the fracture initiation site (arrows)



SEM image showing voids at the fracture initiation site (red arrows).
The "white" plate-like substance (blue arrow) was determined to be mica using EDS techniques.



EDS spectrum showing the elements detected in one of the large platelets near the fracture initiation site; the composition was consistent with mica.

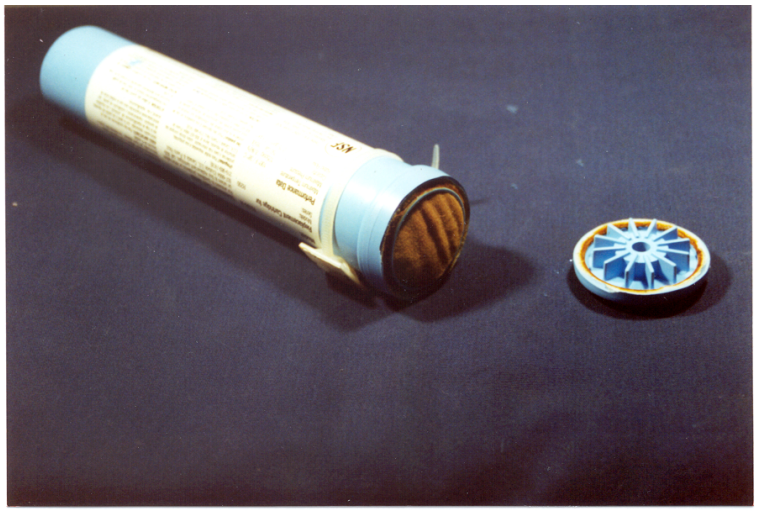
FAILURE ANALYSIS OF A WATER FILTER

A water filter used for an ice-maker failed causing water damage to the home. FTIR analysis determined that the material was talc filled polypropylene. The failure occurred on the inlet side of the filter while in service. Visual examinations and cross sectional analysis indicated that the end cap was bonded using electromagnetic or induction welding techniques using small (0.005-0.010") metal particles dispersed in a thermoplastic matrix. In these welding techniques the plastic parts to be welded are placed under pressure together, with a resin containing ferromagnetic particles or powder at the joint and subjected to an alternating electromagnetic field. The fluctuating field heats up the magnetic particles, which in turn heats up and melts the resin and/or underlying plastics.

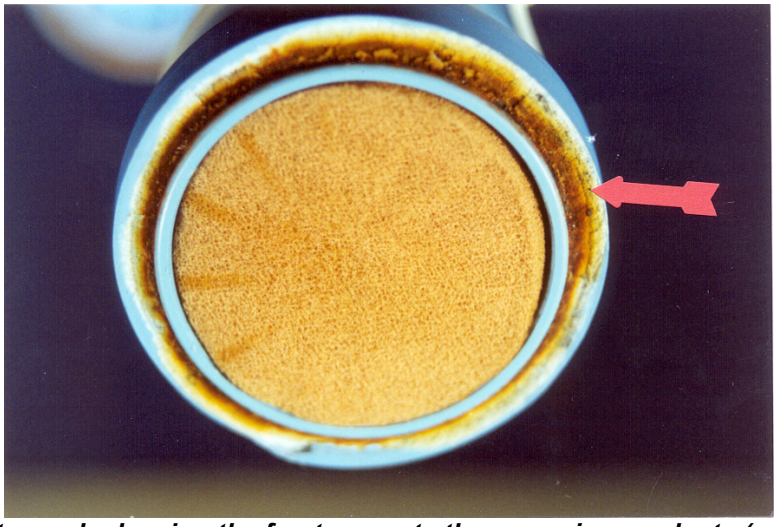
In this case the metal particles experienced corrosion due to exposure to water and the volume expansion of the corrosion products caused high stresses to develop in the radiused area of the cap causing it to fracture.



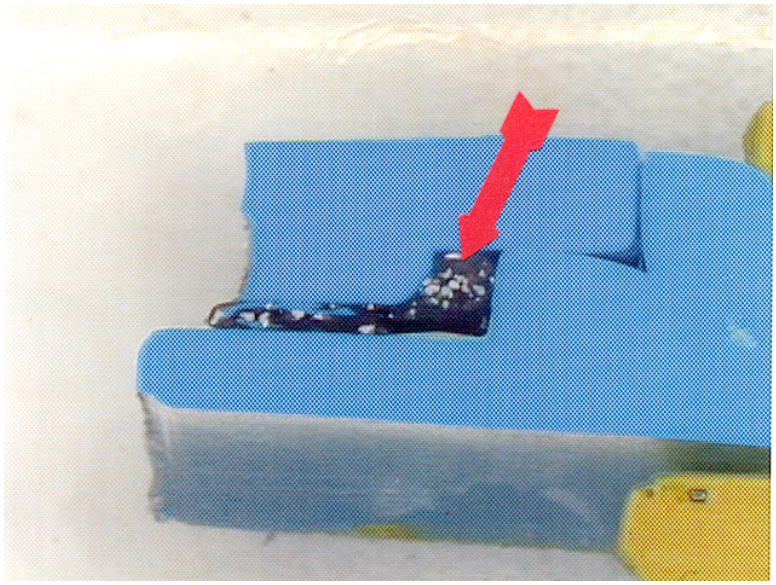
Photograph showing the fractured cap area of the filter



Photograph showing the filter body after the cap was separated for analysis



Photograph showing the fracture; note the corrosion products (arrow)

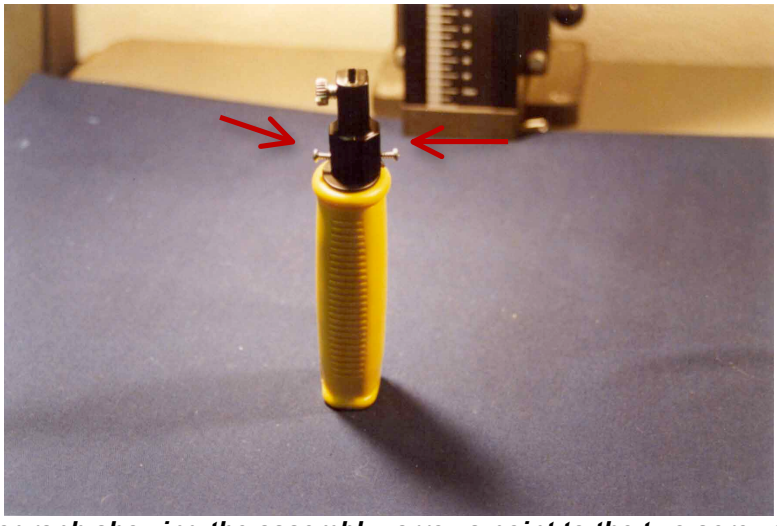


Cross sectional view showing the weld joint made using ferromagnetic particles

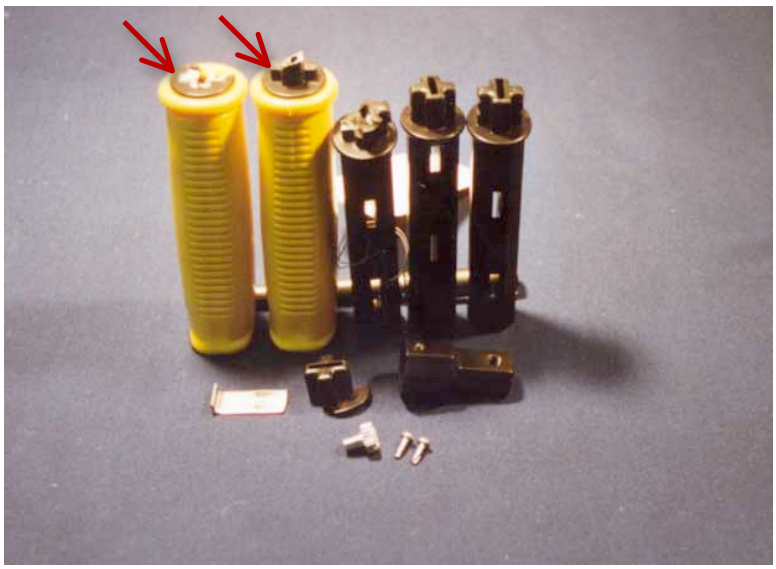
FAILURE ANALYSIS OF A SAW HANDLE

Molded ABS (Acrylonitrile Butadiene Styrene) insert for a Vinyl saw handle experienced delayed failures after assembly upon shipment to customers. Examination revealed that the metal component that holds the saw blade is secured in place with two screws as shown in the below figure. These screws extended into the handle causing deformation of the plastic. The cracks originated in these highly stressed areas.

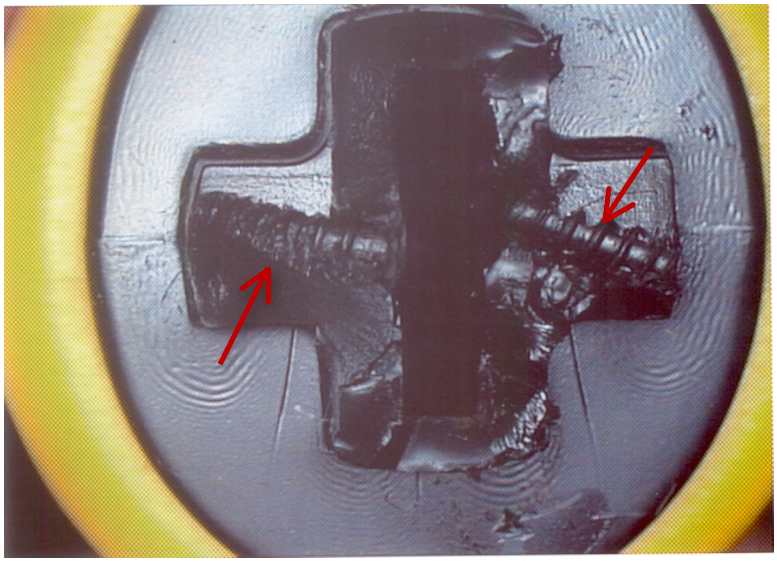
After reviewing the details of the assembly process, it was discovered that the inserts were immersed in a surfactant before assembly to make them slip into the vinyl handles easier. It is known that plastics can fail under very low stress, when they are in contact with particular chemical agents. This phenomenon is called environmental stress cracking (ESC). ABS is a co-polymer that is widely used in a variety of fields owing to its favorable cost/performance ratio, luster and resistance to impact. However, it is well documented in the literature through previous studies that certain kinds of chemical agents such as organic solvents and surfactants cause ESC of ABS. Laboratory ESC testing illustrated that a different type of surfactant, used at a much lower dilution ratio, could be utilized during assembly without causing any failures.



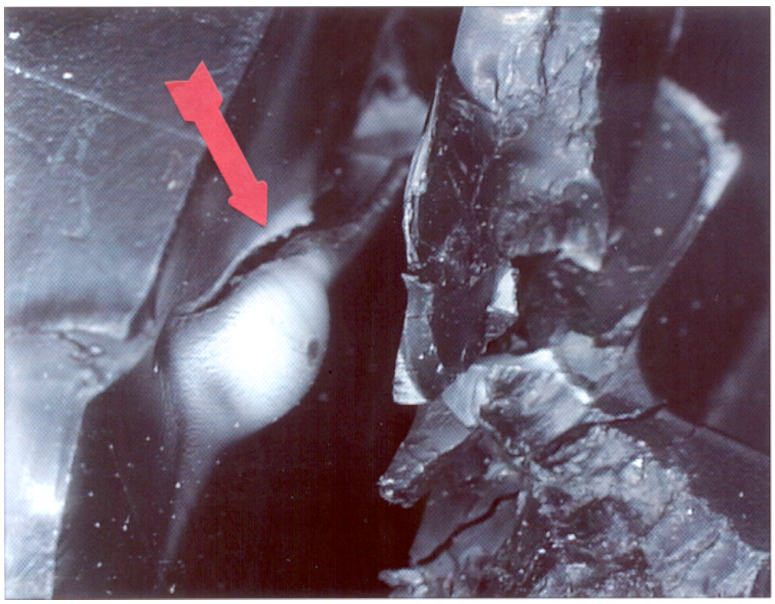
Photograph showing the assembly; arrows point to the two screws that secured the metallic piece, which held the blade in place.



Photograph showing the black inserts, with the yellow handles. Arrows point to the failures.



Photograph showing the screws that secured the metallic piece in place



Failure area with the crack initiating at the stressed area created by the overextended screw



Close-up view of cracked insert

FAILURE ANALYSIS OF PVC PIPE

Recently installed piping from an irrigation system at a country club started to experience splits and leaks. One failed section, removed from underground, was found to be split into two pieces, the crack running the entire 20-foot pipe length. Upon examination the pipe was observed to have areas of apparent delamination on the inner portion of the wall thickness and numerous blisters with sizes ranging between ½ inch and 3 inches in length.

An acetone immersion test, per ASTM D2152, Method for Adequacy of Fusion of Extruded PVC Pipe and Molded Fittings by Acetone immersion, was performed on the pipe to determine the presence of manufacturing defects. A cross section of pipe was taken and cut into pieces to fit in the acetone immersion tank. Although the smooth outer surface of the pipe was unaffected by acetone, the inner wall and sanded portions were severely affected by the acetone and exhibited peeling and flaking.

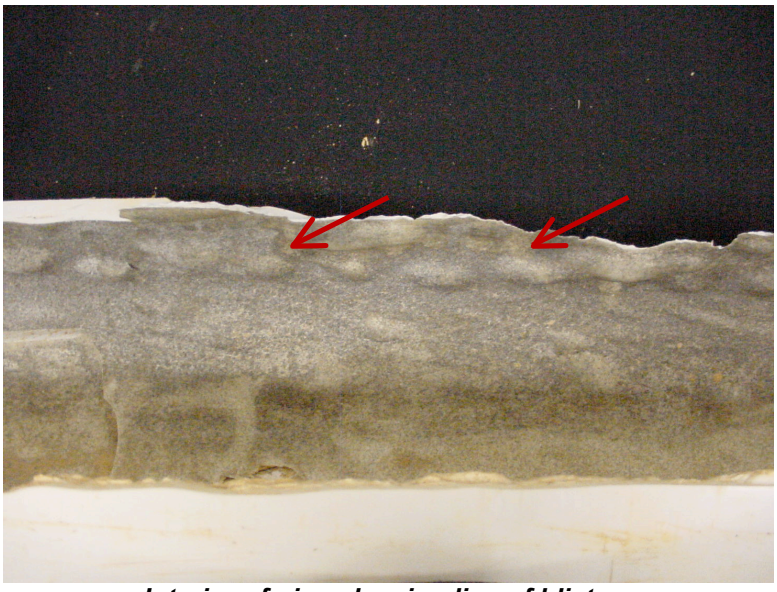
Microscopic examination was also performed and the wall of the pipe was observed to contain multiple voids and flaws that appeared like layers of delamination. Interior of the blisters also exhibited pronounced delamination between layers and a granular texture.

FT-IR was performed on the pipe material to confirm it was PVC. The sample, removed from the rough fracture surface, where contamination would have been most likely was found to be consistent with PVC without phthalate plasticizers.

The delamination and blistering of the pipe was due to manufacturing flaws. The acetone immersion test is designed to assess the adequacy of fusion by bringing out and accentuating any flaws that may be present in the walls of the pipe. The results indicated that while the smooth outer surface of the pipe was not attacked by the acetone, the interior surface with the clearly visible flaws and blisters was readily attacked by the acetone.

Entrained gases could cause the poor fusion seen in the walls of the pipe. With a porous structure, water can then penetrate the walls and cause the swelling and blistering observed on this pipe which would not have been normal for a PVC water pipe. Lack of discoloration on the blister interiors suggested that this condition was not caused by the combustion of foreign materials. The fracture occurred along a line weakened by numerous blisters.

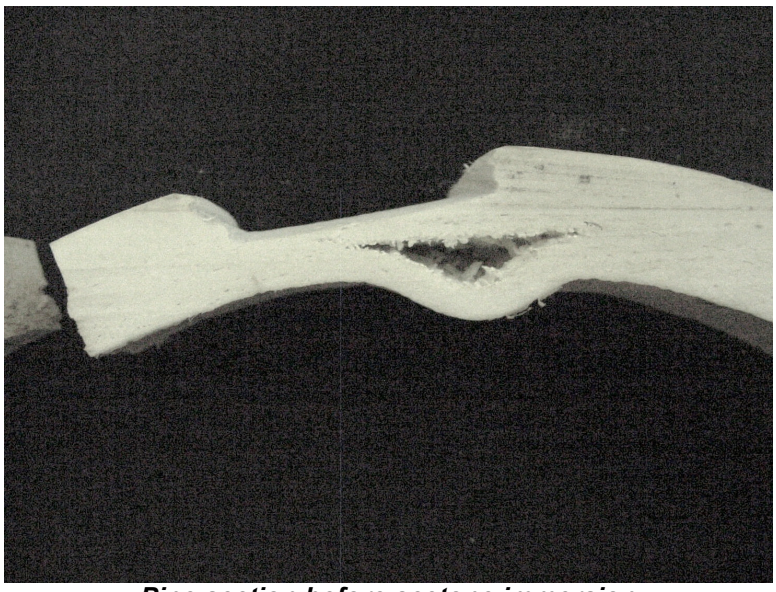
There are several ways that gas could have been entrained into the pipe during manufacture. Since PVC is thermally and shear sensitive, it can readily degrade to form HCl gas. If this gas is not vented properly, it will be trapped in the pipe walls. Thermal or shear degradation could happen if the extruder and die was not being run at the proper temperature, or if it was being run at too high of a speed. Also, since PVC is extruded from powder, it is possible to trap air into the molten polymer that, if not vented, can lead to the type of flaws observed, and lead to eventual failure of the pipe.



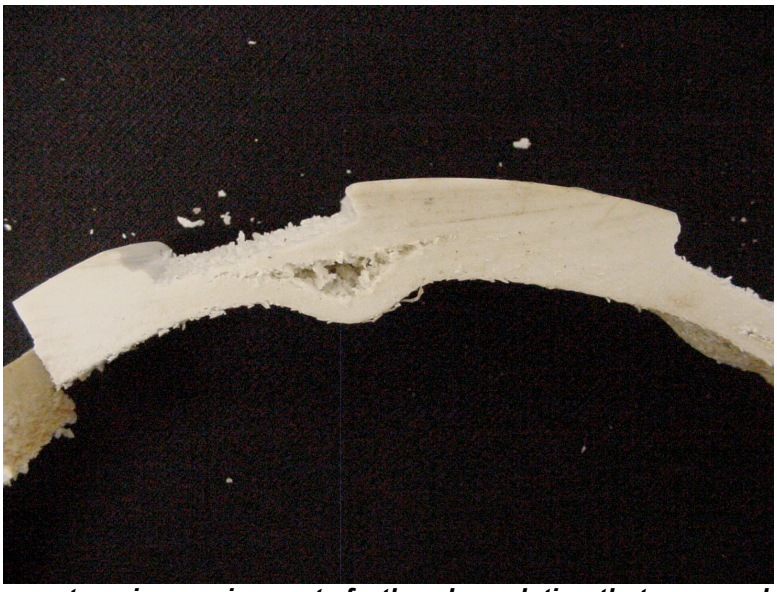
Interior of pipe showing line of blisters



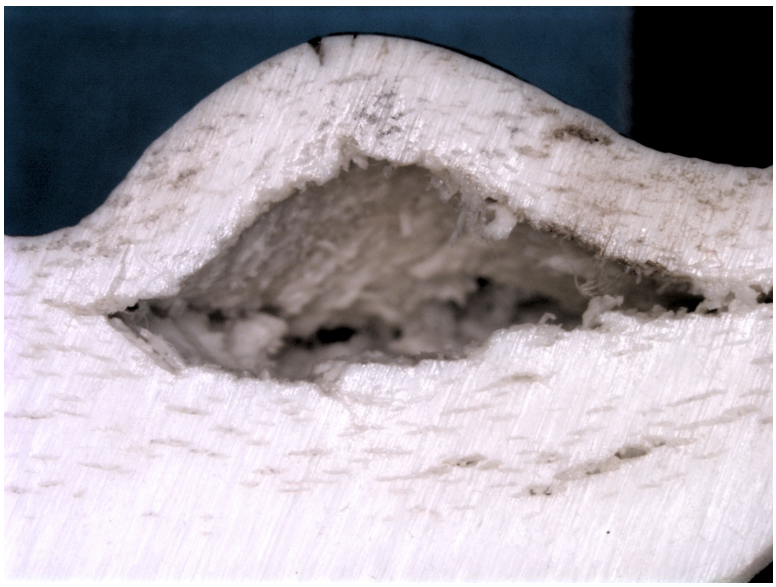
Interior of pipe showing the delamination along the fracture



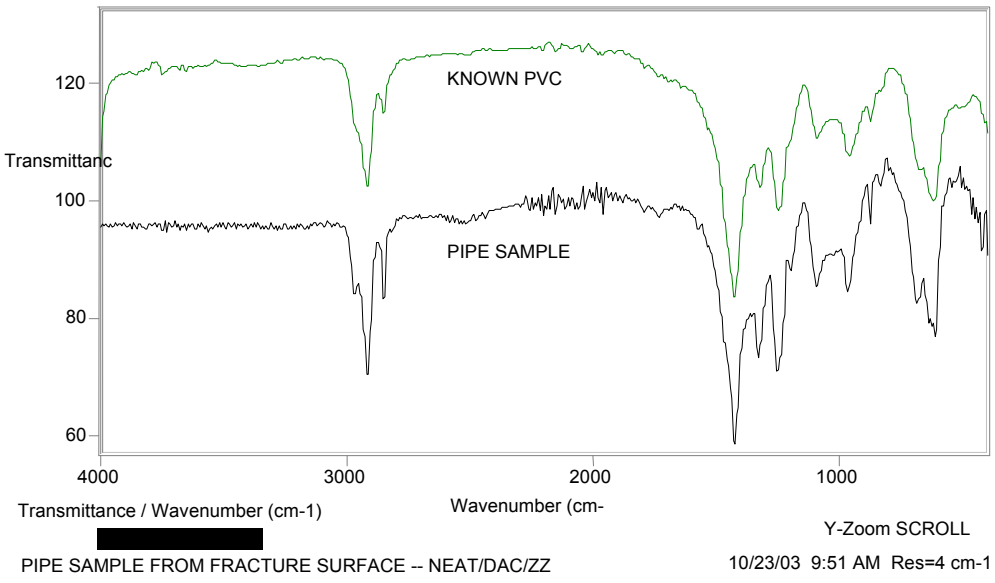
Pipe section before acetone immersion



Pipe section after acetone immersion, note further degradation that occurred during exposure



Close-up of blister and delamination across the pipe wall



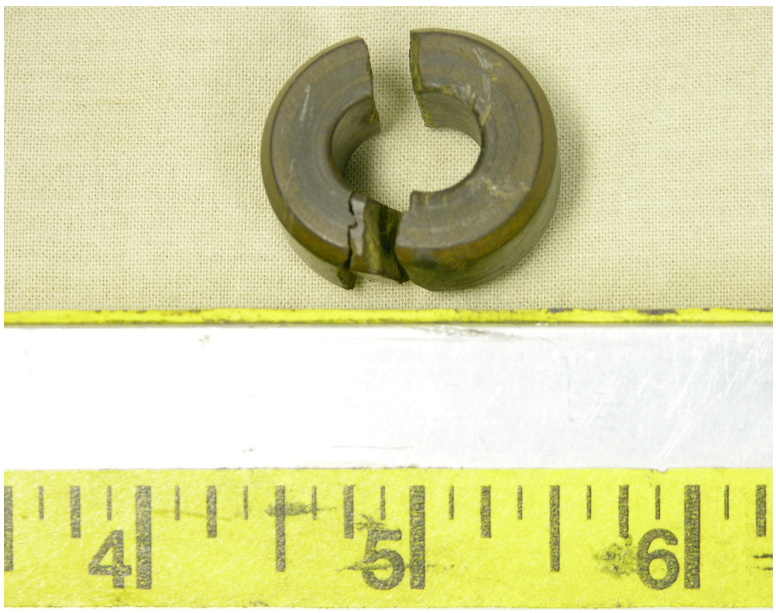
FT-IR spectrum of sample removed from pipe fracture surface.
The pipe sample is consistent with PVC without phthalates

FAILURE ANALYSIS OF CLUTCH ROLLER

A roller made of Torlon used as a guide in a snowmobile clutch mechanism had failed. Torlon® is a trademark name for polyamide-imide (PAI), which is a high strength plastic with the highest strength and stiffness of any thermoplastic up to 275°C (525°F). It has outstanding resistance to wear, creep, and chemicals – including strong acids and most organics – and is ideally suited for severe service environments.

Stereomicroscopic examinations of the roller revealed that the failure originated at the inner diameter of the part, near an inclusion. Although post-fracture mechanical damage in the vicinity of the inclusion prevented determination of the exact origin, it was clear that the fracture occurred on the same plane as the inclusion, indicating it was the primary cause of failure. The fracture on the surface opposite of the inclusion side propagated down through the height of the roller with no obvious fracture origin.

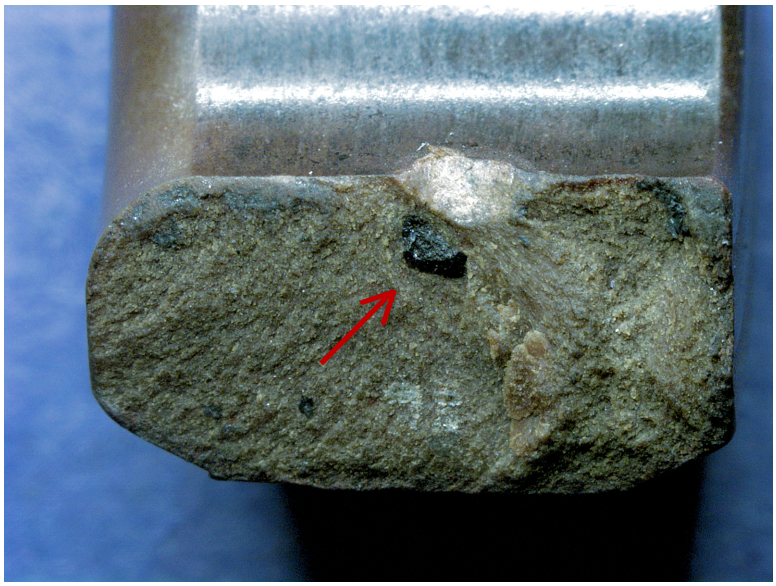
The make-up of the inclusion was not determined but it appeared to be nonmetallic, possibly oxidized (burnt) polymer. The oxidized polymer could have come from a dead spot in the injection molder or from the end of the injection nozzle. It could also have been caused if the injection temperatures were too high and there was a process interruption that allowed the polymer to overheat in the barrel. The inclusion could even be a different polymer from a previous run of the injection molder. FT-IR (Fourier Transform Infrared) spectroscopy would be the technique to use to verify its composition and state.



Photograph showing fractured roller



Photograph showing the fracture surfaces of the roller



Macrograph showing the inclusion on the fracture surface (arrow)



Higher magnification view of inclusion and origin area

FAILURE ANALYSIS OF A SUPERCHARGER DISK

An injection molded disk, used as a coupling disk in a supercharger had failed during a test. It was manufactured from a glass-filled nylon blend (PA6/PA66).

The disk was secured in place with pins that went through the holes and the entire assembly is oil cooled during operation. When the supercharger was disassembled, the disk showed extensive damage. The failed part and an unused part were submitted for analysis.

The initial inspection of the part showed extensive plastic deformation and significant thermal damage to the disk. Examination of the good part revealed weld lines running down through the disk at each pinhole. The weld lines coincided with the fractures in the failed part. The good part was sectioned to allow for examination of these areas. The good and failed parts were also submitted to Differential Scanning Calorimetry and glass content analysis, to verify the filler content and presence of any contaminants.

The failed part was cleaned of oil to allow the fracture surfaces to be microscopically examined. Several interesting features were observed. A number of the holes showed significant rounding of the fracture surface at the outer diameter of the disk. This rounding may have occurred due to excessive heat, or from erosion caused by broken parts rubbing against the surface after failure, or a combination of the two. Although there was some melting/softening of the fracture surface, some features could still be discerned indicating that all of the fractures originated from the inner diameter of the pinholes.

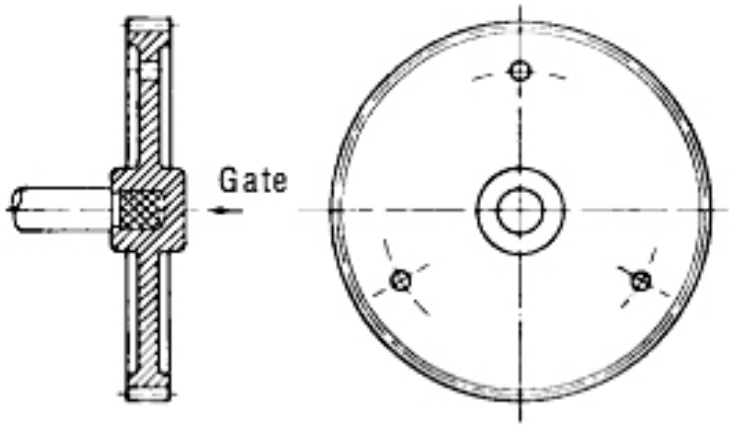
A couple of the holes were selected at random for examination of weld lines. The flow lines of the polymer were readily visible on the polished cross sections. At the weld lines the glass fibers were found to be oriented parallel to the top and bottom of the part, perpendicular to the load axis, creating a weak point in the part.

Each part was heated twice during the DSC analysis. The first heat would show the thermal transitions of the polymer (such as crystallization and melting) as they have been influenced by the thermal history of the part. The second heat will have a standardized heat history, without any service or molding effects, and show only the transitions inherent to the two polymers.

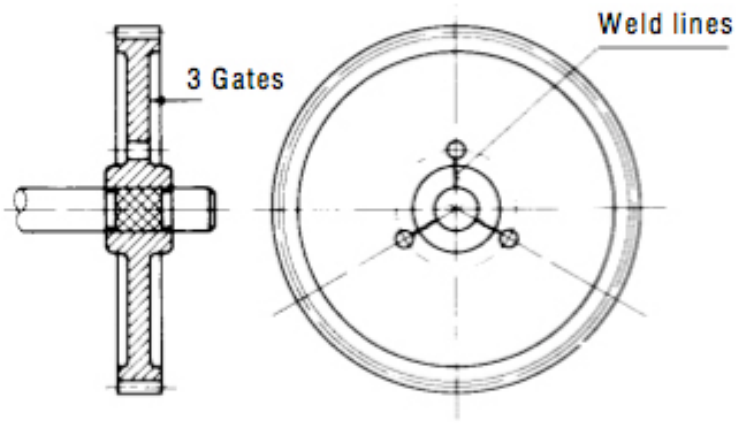
In the first heat, the scan of the failed part showed two distinct melting peaks, one for the PA6 component and one for the PA66 component, in the appropriate areas for each component of the blend. The first heat of the good part, however, showed only one melting peak. After the second heat, both showed two melting peaks, one for each component. The double peak seen in the first heat of the failed part occurred because it was subjected to heat sufficient to cause annealing of the part, which would have changed the physical properties of the part. Considering the normal service temperature of the part is mostly within the range of acceptable use for the material, the results indicated that the failed part was subjected to a higher temperature sufficient to soften one component of the material.

The glass content of both samples was verified to be 30% as specified, and determined not to have contributed to the failure.

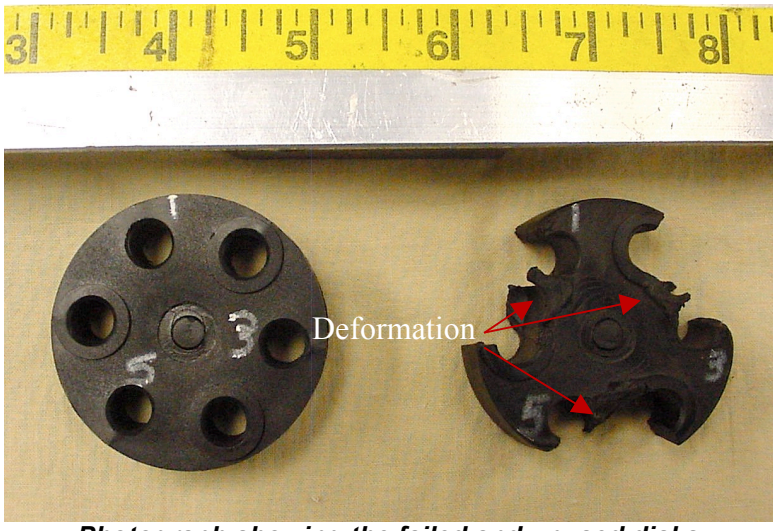
The disk failed through a combination of manufacturing and service related factors. The part was subjected to a temperature that exceeded its recommended operating temperature, which then caused a failure at a weak point in the part. In this case, the weak point was a weld line created during injection molding. Design and gating can have significant influence on a part's performance. In a similar situation, almost identical gears molded onto knurled shafts behaved differently in service. The gear shown below was center gated and did not create a problem.



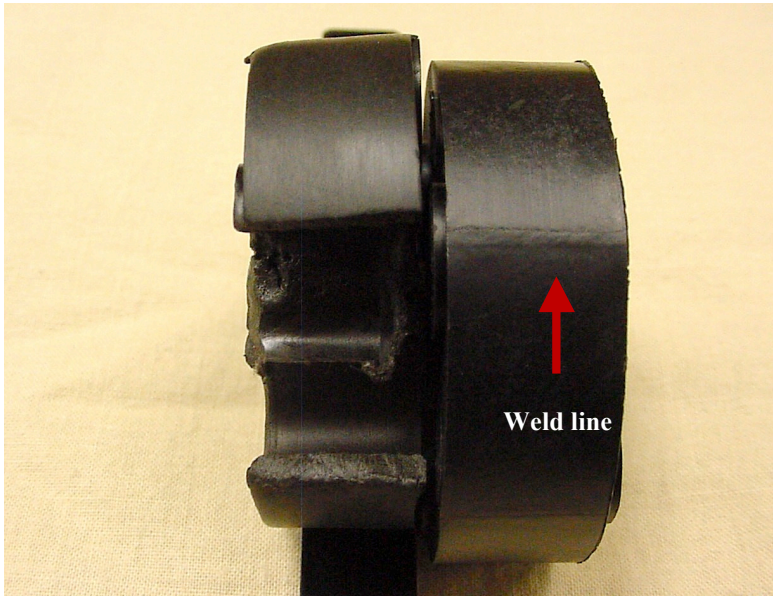
However, the gear shown in the below figure was filled through 3 pinpoint gates in the web. In addition, the three holes provided for attaching a metal disc were placed close to the hub. As a result, the thicker hub section was poorly filled and the three weld lines created weak spots, unable to withstand the stresses created by the metal insert and the sharp edges of the knurled surface.



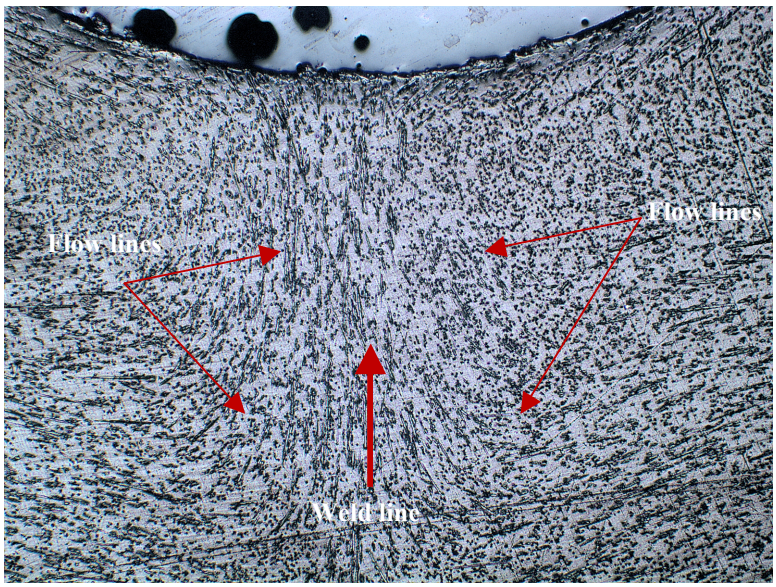
While eliminating the weld lines through modifying molding parameters is expected to improve the part's performance, it was also recommended that the customer conduct further studies to determine the cause of the overheating of the disk.



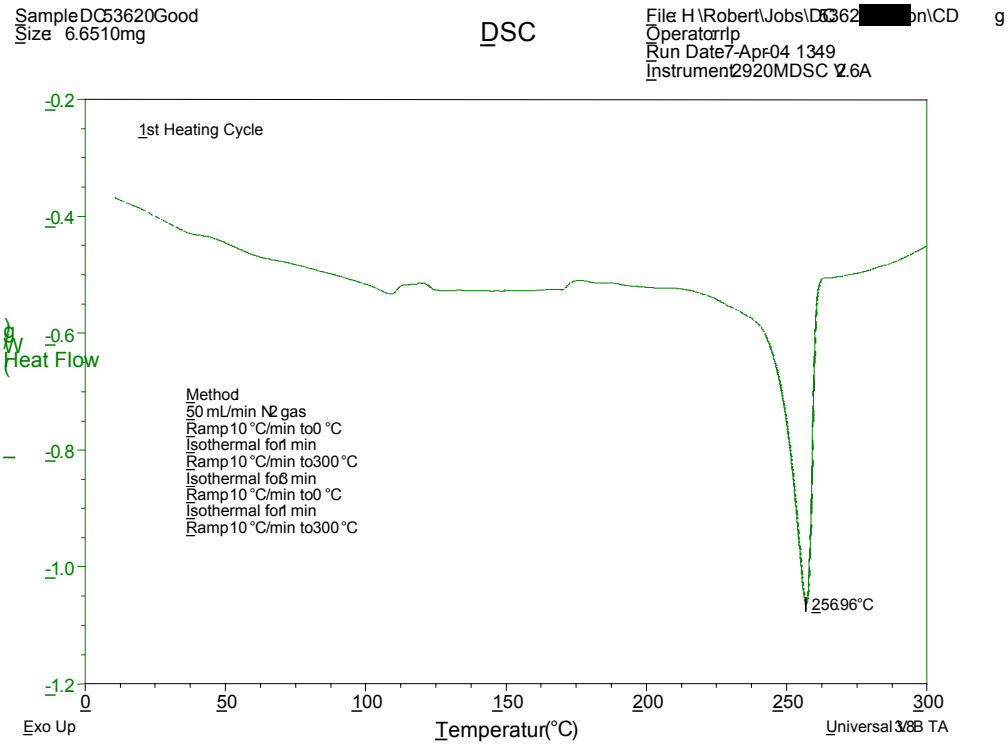
Photograph showing the failed and unused disks



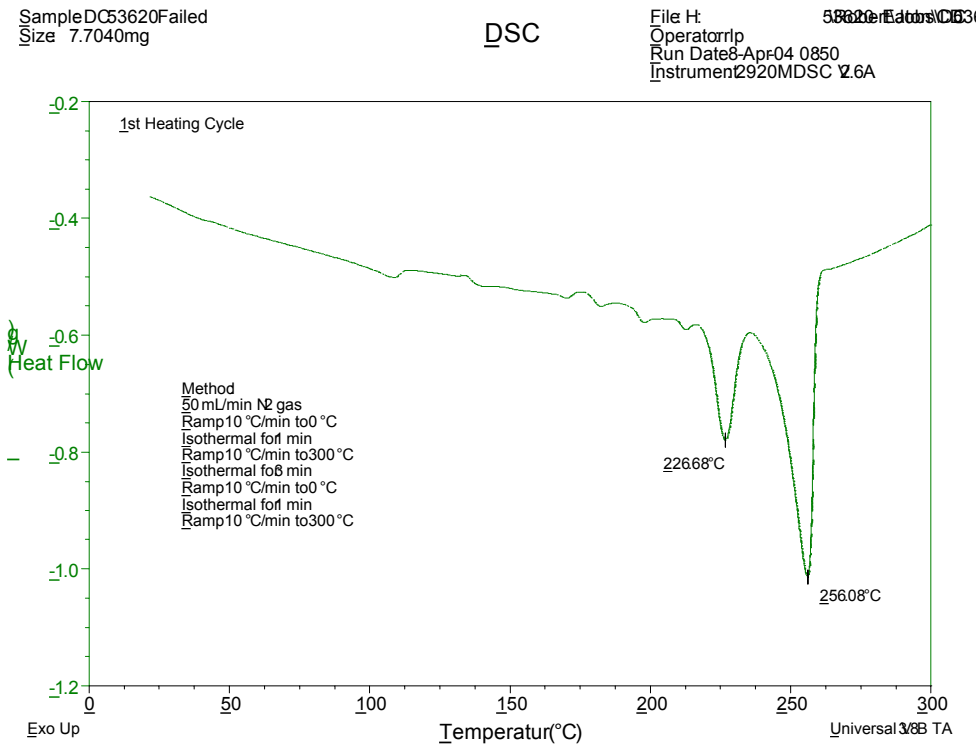
Photograph showing the weld line observed on the side of the disk



Orientation of the glass fibers clearly indicate the weld (knit) line formed during molding



DSC Thermogram of 1st heating cycle of Good part showing a single endotherm



DSC Thermogram of 1st heating cycle of Failed part showing two endotherms Nylon 6 and Nylon 66

FAILURE ANALYSIS OF A POLYCARBONATE BACKPLATE

The customer had received several returns that were discovered broken in their shipping containers even before the products were placed in service. These parts showed fractures at multiple areas. Because of the nature of the failure (before use) and the various failure locations on the part, a chemical attack was suspected. Two failed parts and one unused part were submitted for analysis. The material was 10% glass filled Lexan polycarbonate.

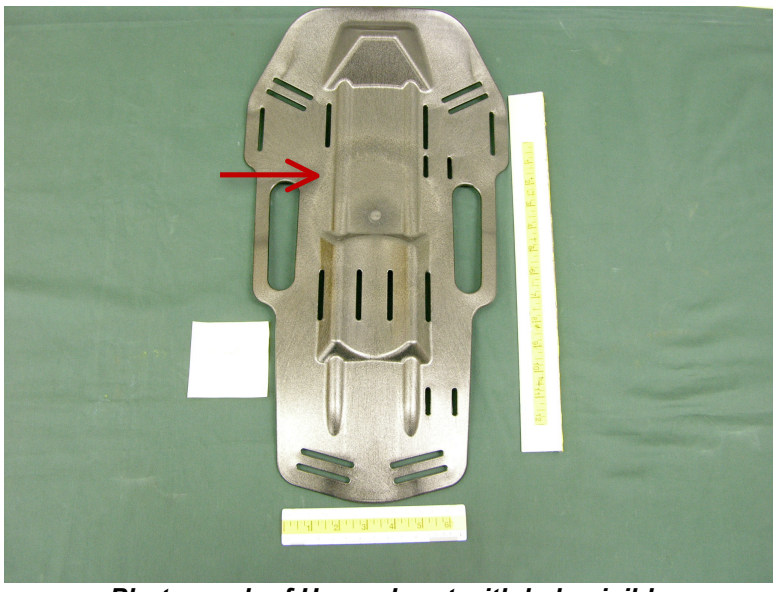
Visual examination of the parts revealed extensive cracking, mostly at the radii of the strapping slots. A 'halo' was also observed on the unused part, centered around the injection gate. The parts were then examined with a stereomicroscope to look for evidence of chemical attack or any chemical residue. None was found. Failures were observed to have occurred near the geometric transitions, in the vicinity of punch out marks, flow fronts or weld lines. The glass fibers were found to be randomly oriented; on the SEM images the holes visible were fibers perpendicular to the fracture surface, while the grooves visible were fibers parallel to the fracture surface. The glass fibers were all in intimate contact with the polycarbonate, as shown by the feathered pattern of cracks coming from the edges of the glass fibers, which indicated that the bonding was adequate. The fracture progression was rapid in nature, as indicated by the Wallner lines observed on many of the fracture surfaces.

Since there was no evidence of chemical attack, the possibility of molded-in stress was investigated using DSC techniques. Two scans were run, and each was examined for an exothermic transition that would indicate the relief of molded-in stress. A relatively high level of stress 0.4057 J/g was found in the part, as molded.

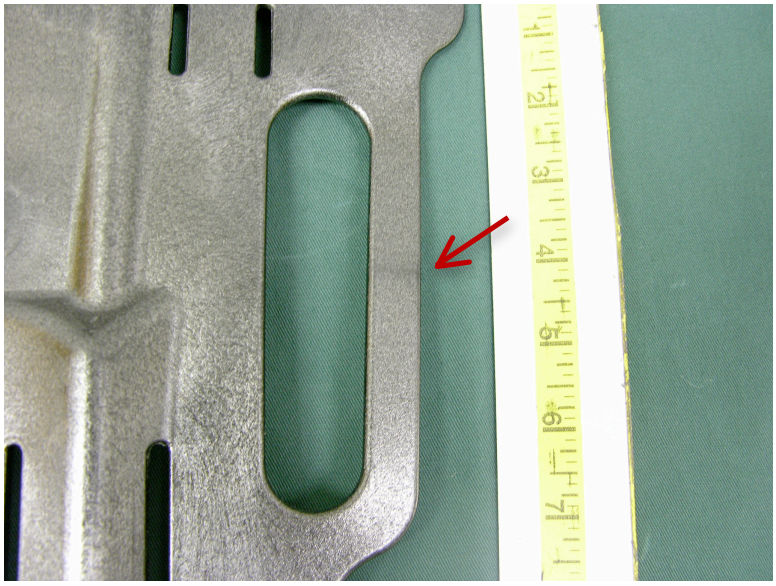
The parts failed through the sudden relief of molded-in stress. The extensive cracking observed indicated a high level of molded-in stress. This stress was quantified through DSC and found to be at 0.4057 J/g, which was significant considering the size of the part. The parts failed near transitions in shape (natural stress concentration areas), but not exactly at the transitions, suggesting that if the molded-in stress was reduced, the part would probably perform properly. The glass fibers were not preferentially oriented, indicating that the injection temperature was appropriate (not too cool). The fractures did not necessarily follow the orientation of the glass fibers. Although the glass fibers created microscopic defects in the polymer matrix that served as stress concentration points, they did not contribute to the failures.

The large size of the part and the thin walls necessitates a high melt temperature and a high injection pressure to fill the mold completely. If the mold was too cold, the material would have cooled rapidly and the polymer chains would not have been able to orient into lower stress conformations, leading to a large amount of molded-in stress. When the part is then subjected to a sharp blow, such as the ejection from the mold, the stress can be relieved suddenly, causing cracking and failure of the parts. Evidence of rapid cooling of the melt was observed at failure locations further from the injection point (the gate) through a rippled surface appearance. It was also evident in the weld lines visible at the midpoint of the outermost edge of the back plate.

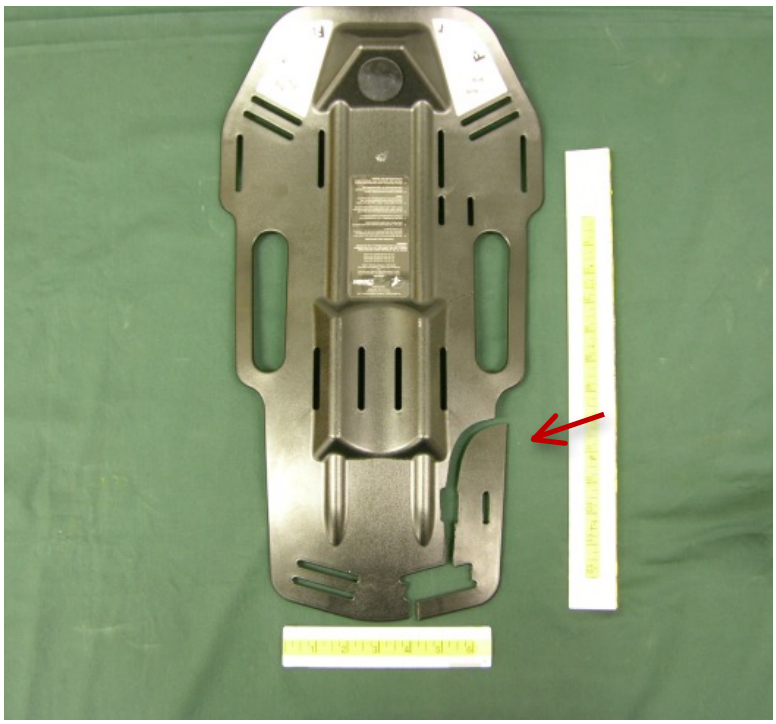
The 'halo' effect observed on the unused part could have been caused by a several different factors. An excessively high melt temperature could cause some degradation of the material, which would show up as streaks flowing from the injection point. In the case of this part, with a central injection point, the streaks would radiate from the gate, creating a halo. The streaks could also have been caused by the presence of water vapor. Polycarbonate is hygroscopic, meaning it can absorb water from the atmosphere. If the material was not properly dried, water vapor could be released during molding. This water vapor can also cause degradation of the polycarbonate, decreasing the strength of the part. It should be noted that the halo/streaking effect was not noticed on all of the examined parts.
The molded-in stress can be relieved through changes in the molding process or the mold itself. One solution would be to increase the mold temperature, allowing the polymer to cool at a slower rate. Polycarbonate typically needs a mold temperature between 80 and 120°C to minimize stress. Another solution would be to add a second injection point into the part so that the part can be filled from two directions.



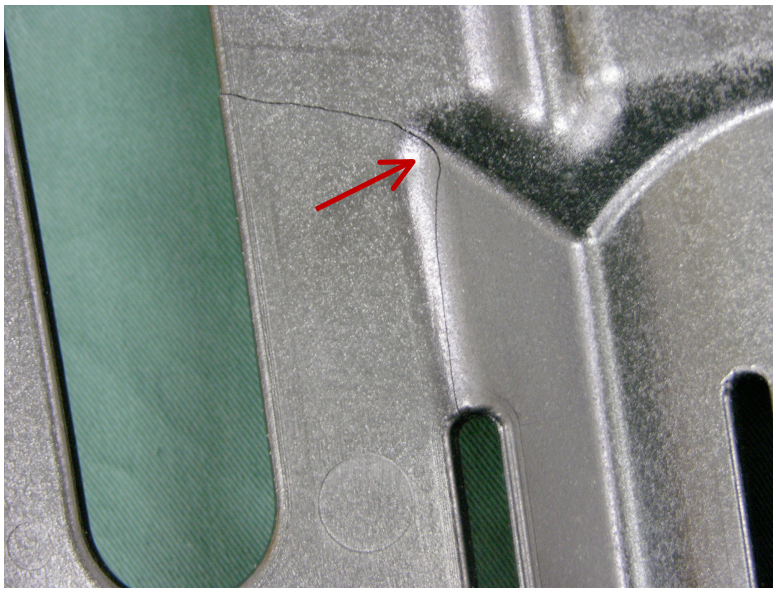
Photograph of Unused part with halo visible



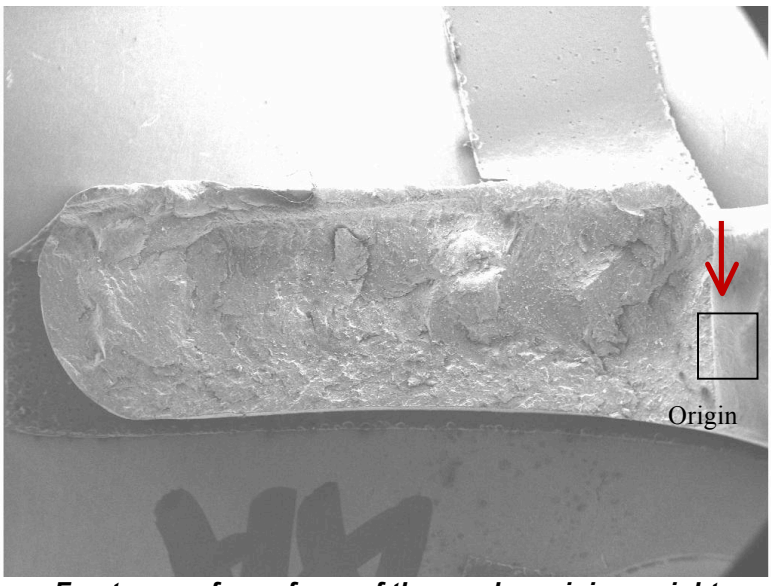
Photographshowing the weld line



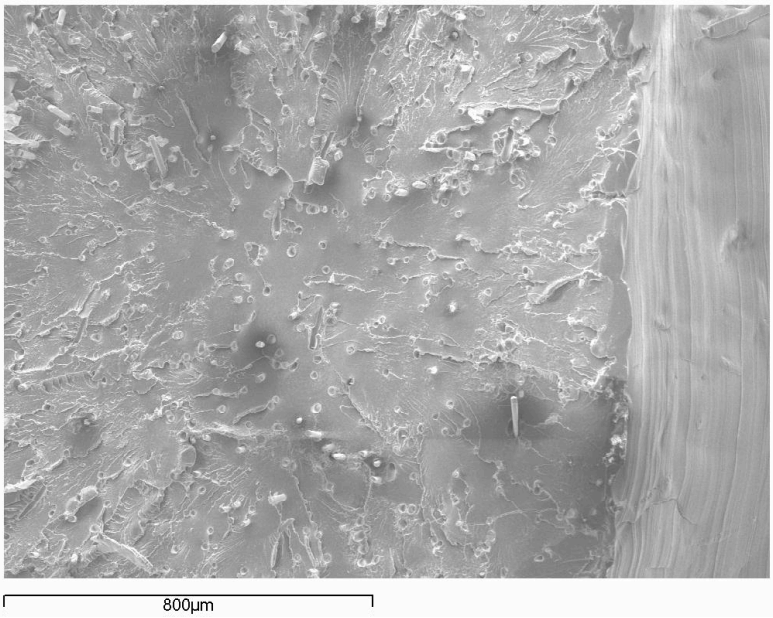
Photograph of the failed part (arrow points to the broken section)



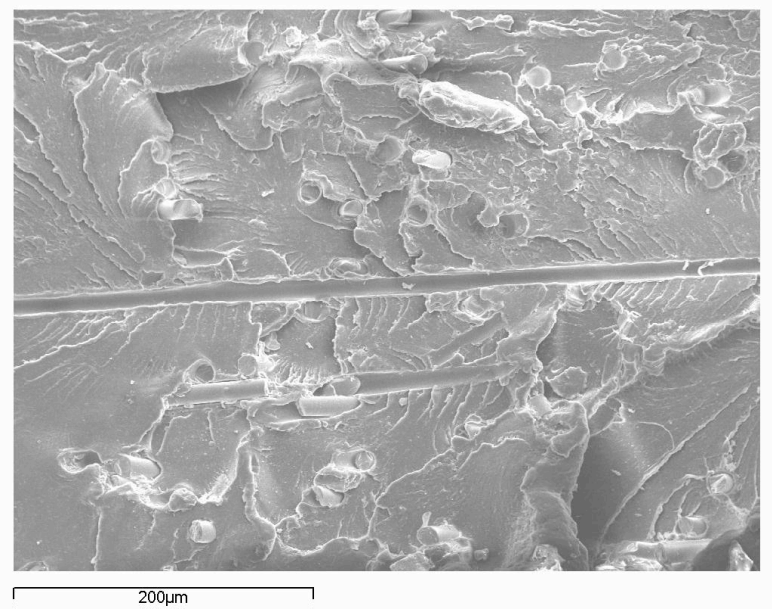
Photograph showing one of the cracked areas on the failed part



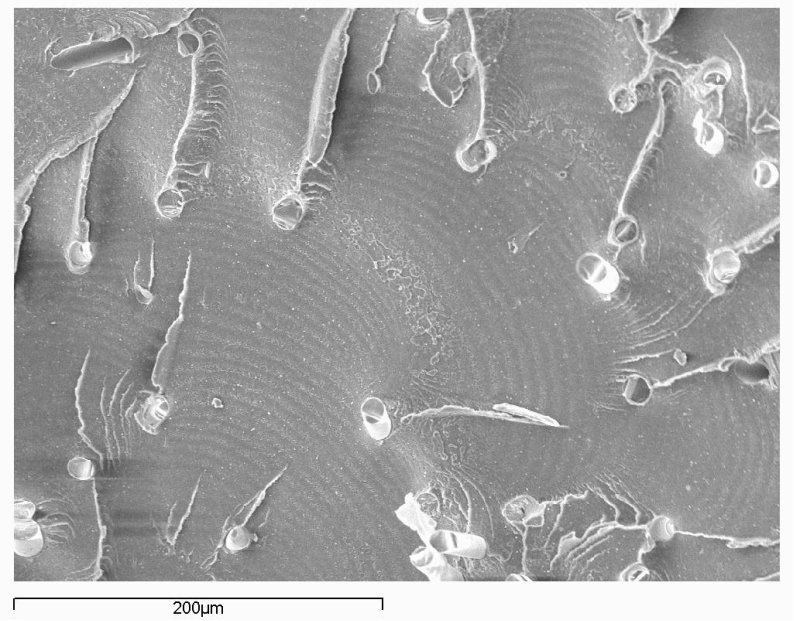
Fracture surface of one of the cracks, origin on right



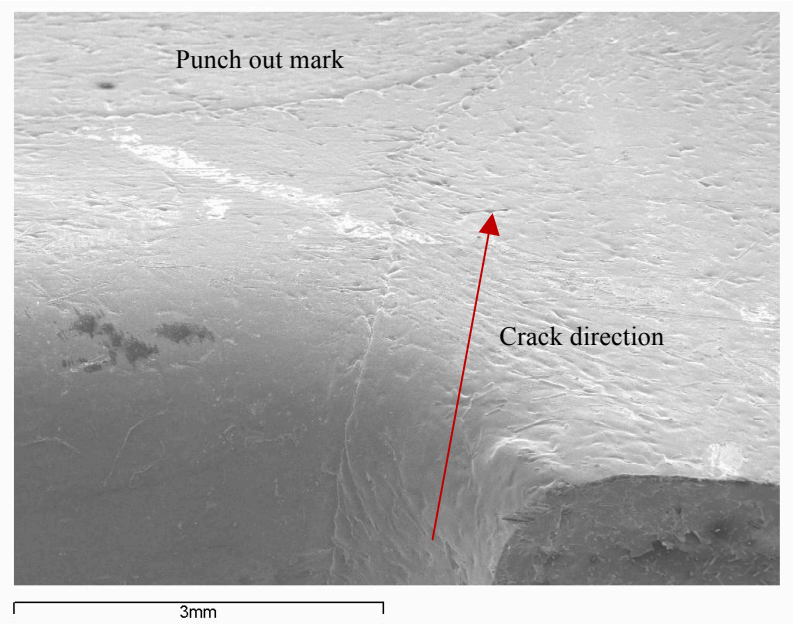
SEM image of origin area. The rippled molded surface visible on right indicates the melt front was partially solidified at this point in the mold and did not flow as well.



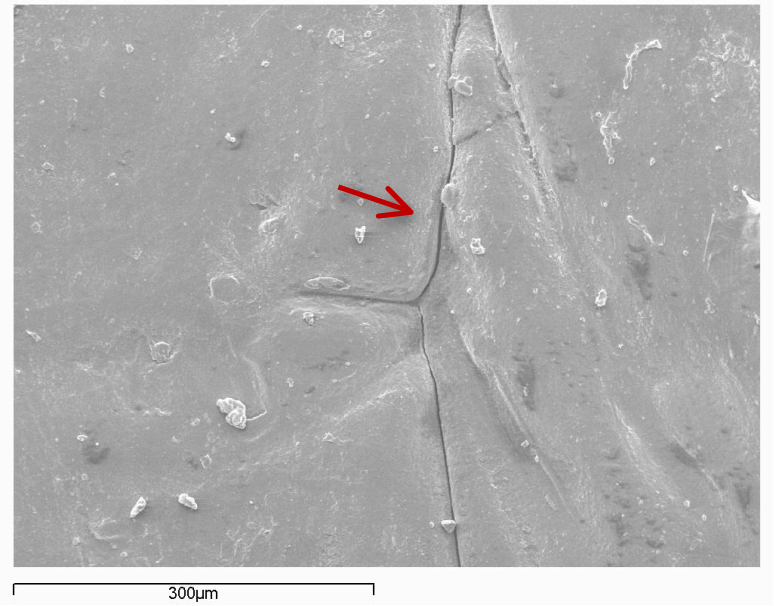
SEM image showing fiber pullouts (parallel to fracture surface)



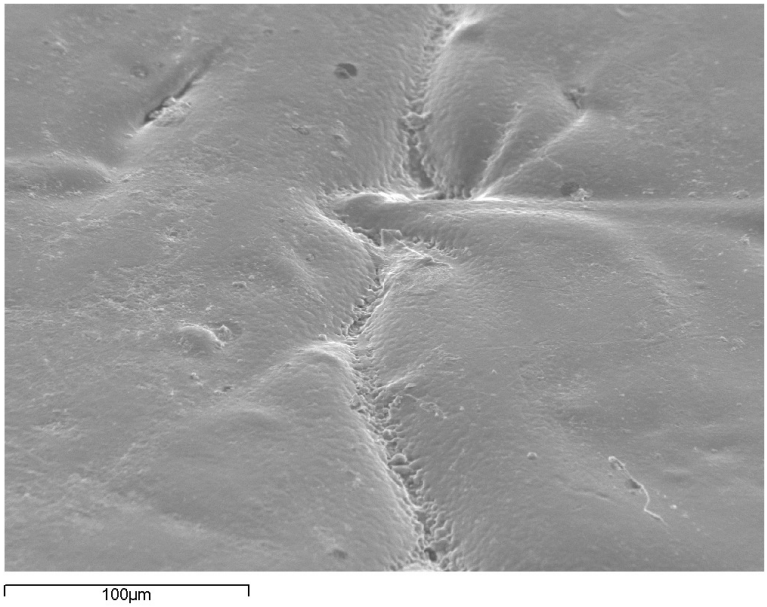
SEM image showing Wallner lines (fibers are perpendicular to fracture surface)



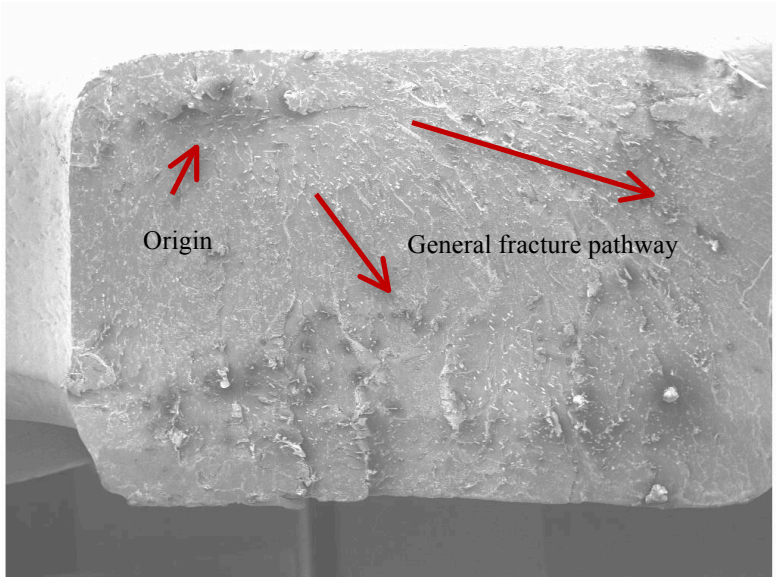
Fracture near geometric transition and punch out



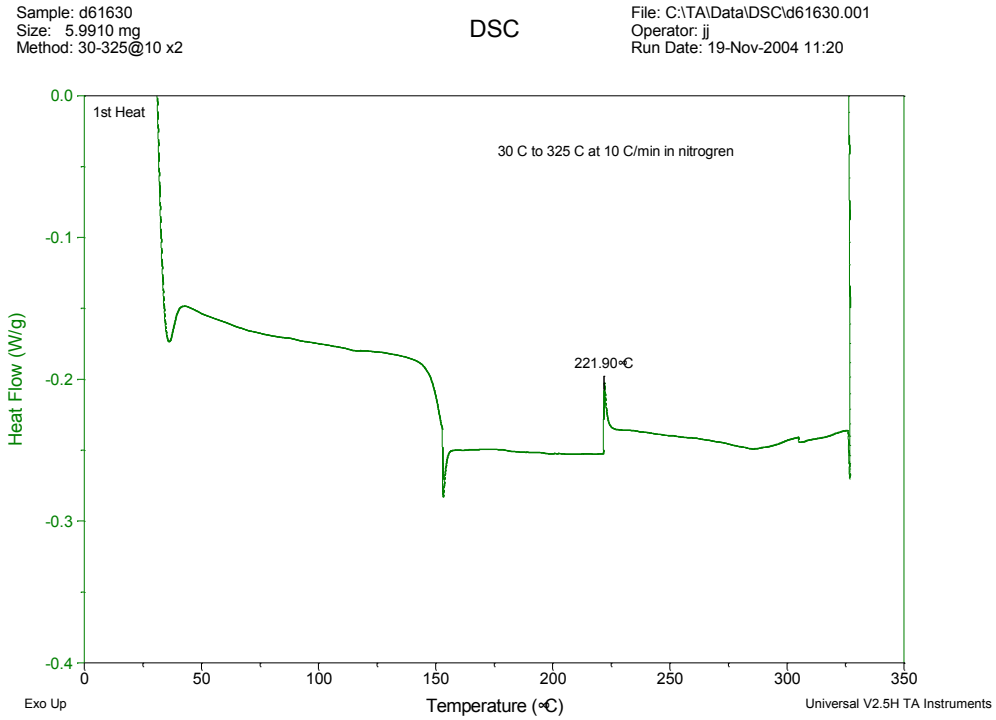
Surface crack observed near fracture



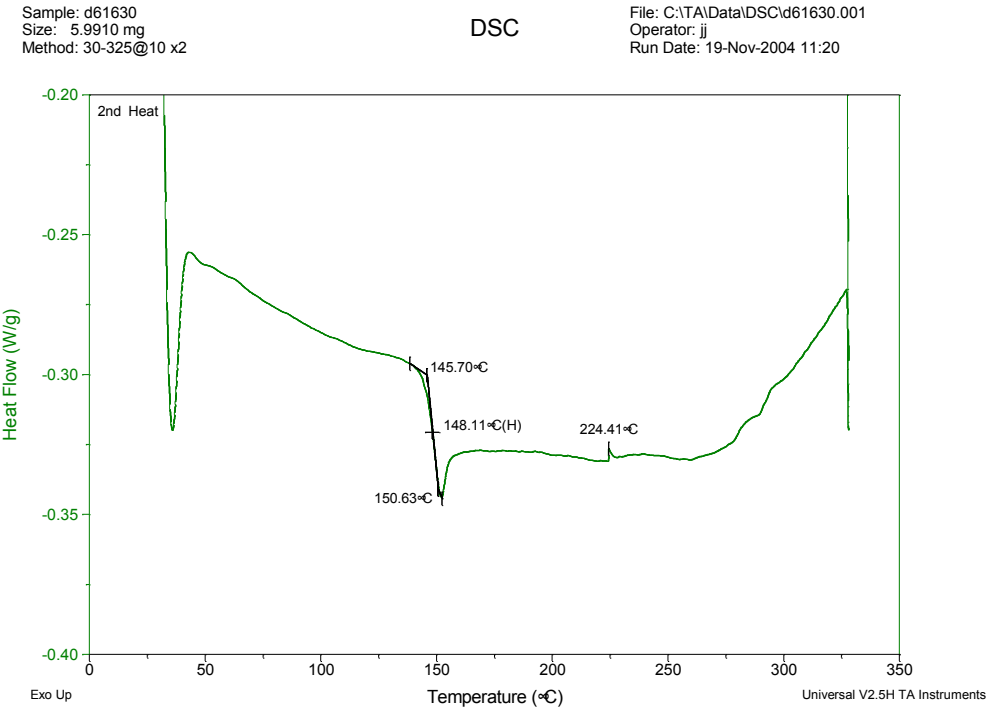
Surface defect observed near one of the fractures



One of the fracture surfaces showing the origin, wallner lines and hackles



DSC Thermogram, 1st run



DSC Thermogram, 2nd run

FAILURE ANALYSIS OF A RUBBER FUEL HOSE

Several sets of cracked and leaking rubber fuel line hoses used in riding lawn mowers were submitted for analysis along with a new hose sample. Chemical analysis using FT-IR techniques did not show any difference between the failed and new hose materials. However, it was noted that used hoses were very hard in comparison to the new hose, except for the ends. Hardness measurements were taken, and these confirmed that the used hoses were harder than the new hose. The ends of the used hoses were still soft because they were sealed from atmospheric ozone by the clamps. The cracking was most extensive on the outside portions of bends in the hose (the areas of highest strain). The insides of the bends did not show extensive cracking, although there was some.

From the morphology and location of the cracks it was evident that several factors contributed to the failure of the hoses. The branched nature of the cracks indicated that the failures occurred due to environmental stress cracking. The stress cracking occurred because the rubber oxidatively cross-linked after exposure to service conditions. Also, the cracking in hoses generally proceeded from the outside in, indicating that environmental factors such as heat and ozone contributed to the cover and tube cracking. However, the ends of some of the hoses showed significant branched cracking on the tube, but not the cover, indicating that the fuels being used also affected the hose and contributed to the failures.

The FT-IR results were consistent between the new and old hoses. There were no differences in the rubbers used for the new and old hoses, so the failures were not due to a defect in the manufacture of the materials. The outer cover was consistent with a chloroprene rubber (the same family as neoprene), and the inner tube was consistent with a nitrile rubber.

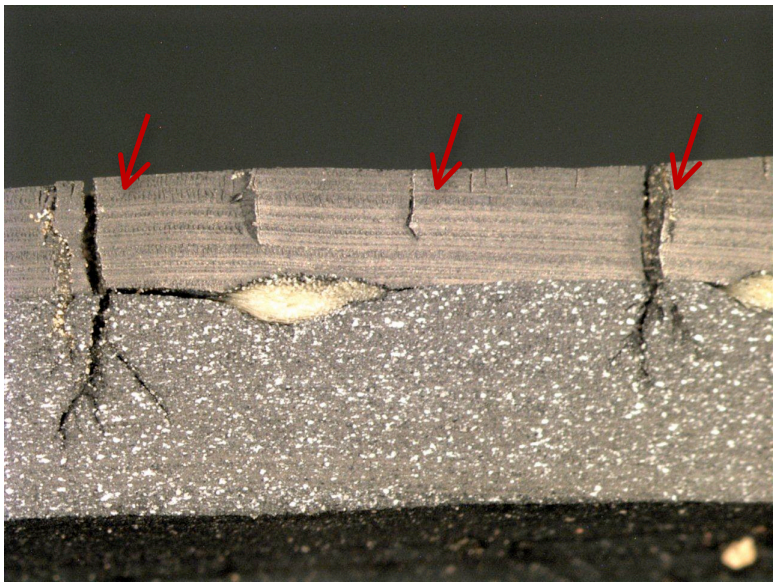
Chloroprene rubbers are generally resistant to heat and ozone but can be readily cross-linked (degraded) by aromatic and oxygenated solvents. Nitrile rubbers also have poor resistance to oxidized fuels in addition to being susceptible to ozone. Any fuel leak at the ends (under the clamp) would have caused the outer cover to be exposed to fuel leading to degradation. Cracking and splitting of the cover would then expose the tube to ozone, which would hasten the cross-linking (degradation). Once a rubber has fully cross-linked, it becomes hard and rigid. In an environment such as a lawn mower where there is a great deal of vibration, a hard and rigid hose will readily crack and eventually leak.

The hoses failed due to environmental stress cracking caused by oxidative cross-linking. The cross linking occurred due to a combination of heat, ozone, and the fuels being used. When a material cross-links, it loses elasticity and becomes more rigid. Once the material has lost enough elasticity, the combination of the inherent stresses in the material and the normal stresses applied in service (the engine vibration) will exceed the materials capacity, in this case causing a cracked, leaking hose.

It should also be noted that the types of hoses used have a maximum recommended operating temperature of 100°C, which can readily be approached under the hood of an operating lawnmower during summer. Therefore, hoses that conform to SAE J30R7 specifications, which have a maximum recommended operating temperature of 125°C and are rated for oxidized fuel use, may be more appropriate for use in this type of service environment. The higher operating temperature and the resistance to oxidized fuels should greatly reduce or eliminate the observed failures.



Environmental cracking was observed on the fuel hoses



Cross sectional view of the hose showing cracks initiating on the exterior layer and progressing to the interior (arrows)