

CHEMICAL RESISTANCE IN PLASTICS: KEY CONSIDERATIONS FOR MATERIAL SELECTION



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■ **Table of Contents**

<i>Introduction</i>	3
<i>Physical Attack</i>	4
<i>Chemical Attack</i>	12
<i>Considerations For Temperature, Concentration, and Exposure Time</i>	17
<i>Environmental Stress Cracking</i>	20
<i>Chemically Resistant Plastics</i>	21
<i>Conclusion</i>	23

Simple descriptions of "good" or "poor" chemical resistance do not provide sufficient information to anticipate performance, as polymer behavior is governed by a number of factors.

The chemicals that a plastic part will encounter in an operating environment are an important consideration during material selection. Simple descriptions of "good" or "poor" chemical resistance do not provide sufficient information to anticipate performance, as polymer behavior is governed by a number of factors. A particular plastic may be completely unaffected by a chemical, experience complete degradation, or its resistance may lay somewhere in between.

The purpose of this paper is to explore factors that impact the chemical resistance of plastic materials. The references listed at the end may be utilized to gain a deeper understanding of chemical compatibility.

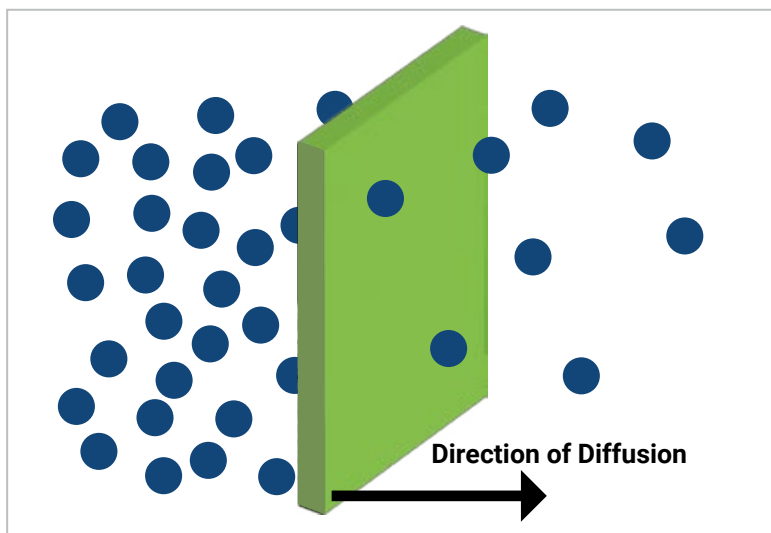
INTRODUCTION

A polymer typically experiences a combination of physical and chemical processes when exposed to an incompatible chemical. The following sections will cover mechanisms of attack, along with the roles played by polymer structure, chemical type, chemical concentration, thermal stress, exposure time, and mechanical stress.

PHYSICAL ATTACK

Physical attack, or solvent effects, refers to the diffusion of a chemical into the polymer matrix. At the most basic level, these transport processes are driven by the existence of a concentration gradient. Fluid molecules will naturally move from an area of high concentration to an area of low concentration, as illustrated by Figure 1.

Figure 1: Simple Diffusion of Atoms or Molecules Through a Solid



Source: Adapted from Grote & Antonsson, 2009

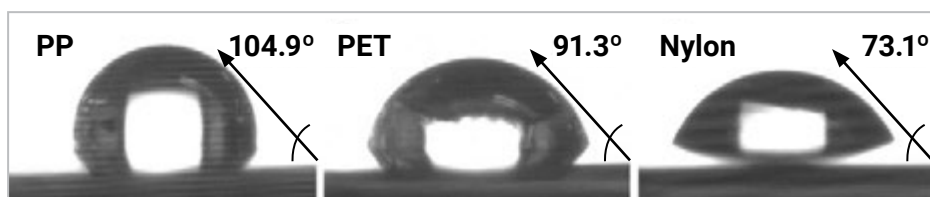
Polymers are complex solids consisting of long, repeating chains of monomer units. From molecular weight to crystallinity, polymer structure is defined at the atomic level. We will soon see some implications of this on the observable, macroscopic scale.

Polarity is one characteristic that greatly influences diffusion. When the atoms of a molecule do not evenly share electrons with each other, there will be an uneven distribution of charge. This creates two distinct areas (poles) of negative and positive charge. Electronegativity (electron affinity) refers to the degree that an atom attracts electrons. The larger the electronegativity difference between two atoms, the stronger and more polar the chemical bond will be. Atoms of similar electronegativities will share electrons evenly, forming a nonpolar bond [7]. Polymers are typically nonpolar materials, consisting mainly of nonpolar covalent C – C and C – H bonds. Although, other atoms within the backbone or polar side groups can create a polymer that has relatively more polarity. As for common atoms found in polymers, their relative electronegativities rank as follows [12]: $F > O > Cl > N > Br > C > H$.

The electronegativities of carbon and hydrogen are so close, they form a nonpolar bond despite a slight difference. The amounts and locations of polar bonds impact attractive forces between a polymer and chemical. Generally, dissimilar bonds do not like to interact with each other. As a rule of thumb “like dissolves like” – this concept helps to explain why oil (nonpolar) and water (polar) will not readily mix or why water is more attracted to some polymer surfaces than others.

The mechanism of physical attack first involves adsorption, or the wetting of the polymer surface [10]. The more that a chemical is attracted to the surface, the more it will adhere. Polar substances like water are repelled by nonpolar, hydrophobic polymer surfaces to different degrees, depending largely on the presence of polar groups. Figure 2 illustrates the water contact angles of three different polymers that vary in polarity.

Figure 2: Water Contact Angles of PP, PET, and Nylon Films

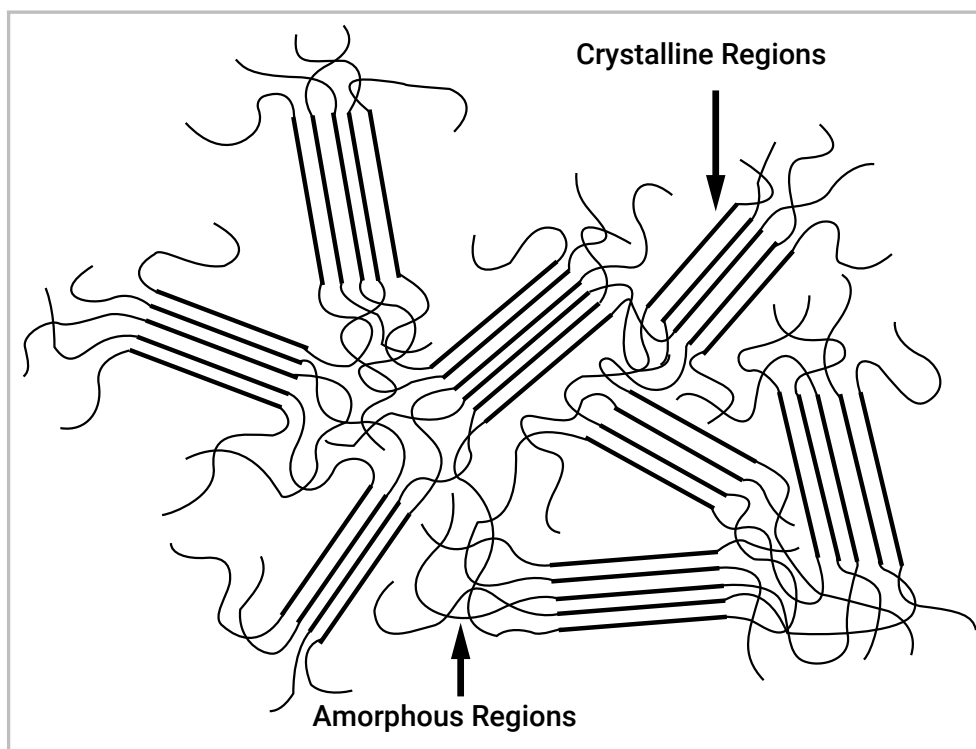


Source: Adapted from Choi, 2019

Different degrees of wetting are observed, based on the relative polarity of each material [3]. Nylons are highly polar compared to many other plastics, due to the presence of very polar amide groups. A water contact angle of 73.1° has been observed upon testing. PET is a (less) polar material, containing polar ester groups. A higher contact angle of 91.3° is reported. PP consists of nonpolar carbon and hydrogen bonds, making it a highly nonpolar material. One can almost imagine the PP surface pushing the water away, with a high water contact angle of 104.9°. Less repulsion is generally seen with increasing polarity, due to the attractive forces between polar groups and water [3, 12]. The droplet lays much flatter on a polar surface, with a smaller contact angle.

Diffusion refers to the entry of a chemical into the polymer structure. Polymer chains and chemical molecules can be imagined as dynamic, rather than static objects. Small chemical molecules move through space in random molecular motion, while larger polymer chains also have some mobility. Polymers contain areas of open space in between their chains, known as free volume. This space forms through small fluctuations in local density and chain packing. A chemical molecule may enter the polymer when it contacts a “hole” that is large enough to fit through [1]. Amorphous regions within a polymer matrix are less densely packed than crystalline regions, leaving more accessible free volume for chemicals to enter. Figure 3 provides an illustration of these different regions.

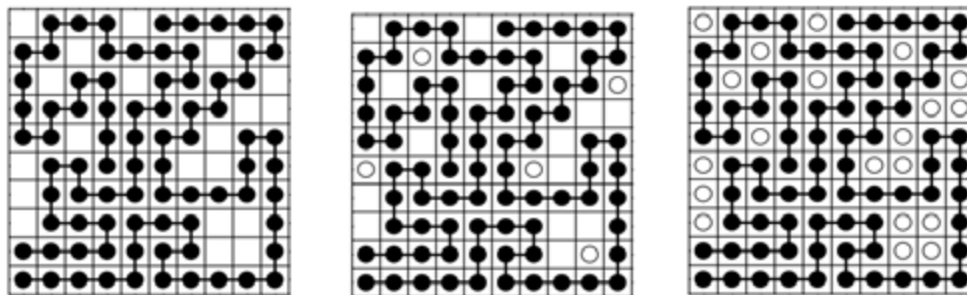
Figure 3: A Semi-Crystalline Polymer Structure, Containing Both Crystalline and Amorphous Regions



Source: Ebnesajjab, 2016

A large number of amorphous regions, impurities, or other physical defects can allow for molecules to enter and move more easily through a polymer structure [5]. A higher degree of wetting provides a larger contact area – if a chemical is attracted to the material’s surface, then it is more likely to find one of these entry points. Figure 4 shows a general overview of the diffusion process.

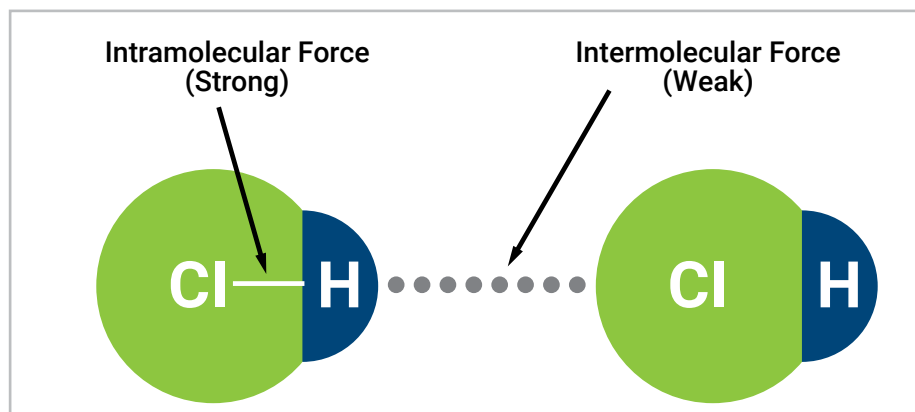
Figure 4: Representation of Chemical Molecules (White) Entering a Polymer Matrix (Black)



Source: Adapted from Karimi, 2011

The polymer can experience varying degrees of absorption and swelling. As a substance absorbs into the polymer matrix, filling the spaces between chains, the material will grow in size like a sponge absorbing water. The attractive interactions between polymer chains are weakened, leading to plasticization and strength reduction. Under the right conditions, the polymer may be completely dissolved. Note that no primary (intramolecular) chemical bonds are broken during the transport processes described. Secondary (intermolecular) bonds, or the interactions occurring between two separate molecules, are the ones being disrupted [16]. This is the distinction between purely physical attack mechanisms versus chemical ones. Figure 5 can be used to better visualize the differences between intra- and intermolecular interactions.

Figure 5: The Distinction Between Intermolecular and Intramolecular Forces



Source: Flowers, 2015

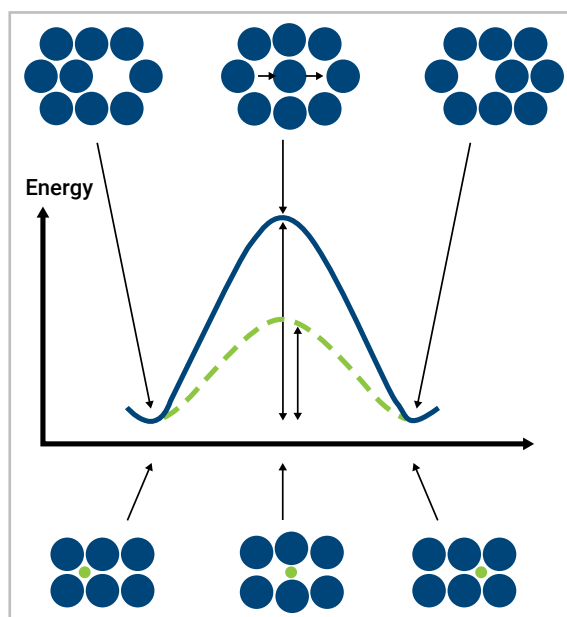
A detailed look at intermolecular forces is beyond the scope of this paper. Although, they do have notable influences on polymer properties. The strength of these forces plays a role in determining physical and mechanical properties of a polymer, as well as resistance to solvent absorption [7, 16]. These forces are weaker than chemical bonds, but they are also additive. For example, increasing the molecular weight of a polymer is one way to increase the strength of intermolecular forces.

The extent of molecular transport depends on the properties of the diffusing species compared to that of the polymer. We know that chemicals with polarities similar to the polymer will diffuse more easily. Smaller diffusing species will also typically move more easily through the matrix. Large or bulky molecules will experience more steric hinderance, or restrictions on movement [5]. Picture an elephant trying to move through a crowded room, compared to a mouse. The mouse will move through the crowd with ease, finding small gaps to travel through.

Temperature is another factor that impacts transport processes. The glass transition temperature represents the temperature that a polymer will transition from a glassy, ridged state to a rubbery, flexible one. As temperature increases above the glass transition temperature, a polymer will have a more liquid-like structure. The chain mobility and free volume of the polymer, as well as the mobility of diffusing species will increase as atoms and molecules become increasingly energetic [11].

In order to move from one stable position to another, a diffusing species may be required to overcome a barrier in the form of activation energy. Heat can provide the required energy input for a diffusing species to break secondary bonds. The molecule is then able to move to a near open position, even if this would not normally occur at lower temperatures. This general idea is visualized in Figure 6, where relative activation energies are shown for two scenarios. Larger diffusing species or more densely packed structures will tend to experience higher activation energies, or more resistance to diffusion [10].

Figure 6: Activation Energies of Diffusion: (Top) a Large Diffusing Species Through an Opening (Missing Atoms) in the Material Matrix, and (Bottom) a Small Diffusing Species Through Atomic Gaps of a Filled Matrix



Source: Adapted from Grote & Antonsson, 2009

For example, there are no solvents capable of dissolving polyethylene at room temperature. Swelling is able to occur, but only at about 30°C below the melting point, are certain solvents able to induce dissolution. Increased molecular mobility at higher temperatures allows the solvent molecules to have more contact with polymer chains. They also have the energy required to overcome internal forces holding the chains together. When the solubilities of the chemical and polymer are similar and there is exposure to elevated temperatures, partial or complete dissolution can occur.

Chemical incompatibility may be loosely anticipated, in some cases, with predictive models. Experimentally determined solubility parameters for select polymers and solvents can be seen in Tables 1A and 1B. The closer a polymer solubility parameter is to that of a given solvent, the more physical attack is expected occur [5].

Table 1: (A) Solubility Parameters (δ) of Common Polymers and (B) Solubility Parameters (δ) of Some Common Solvents

(A)

Polymer	δ (MPa ^{1/2})	Polymer	δ (MPa ^{1/2})
Polytetrafluoroethylene	12.6	Polymethyl methacrylate	18.8
Polychlorotrifluoroethylene	14.7	Polyvinyl acetate	19.2
Polyethylene	16.3	Polyvinyl chloride	19.4
Polypropylene	16.3	Polyvinylidene chloride	20.0–24.9
Polybutyl acrylate	18.0	Acetal resins	22.6
Polystyrene	18.8	Nylon 66	27.7

(B)

Solvent	δ (MPa ^{1/2})	Solvent	δ (MPa ^{1/2})
Hexane	14.9	Carbon disulfide	20.4
Octane	15.5	Acetone	20.4
Methylcyclohexane	15.9	Octanol	21.0
Cyclohexane	16.7	Hexanol	21.8
2,2-Dichloropropane	16.7	Pyridine	22.2
Piperidine	17.7	Butanol	23.3
Xylene	18.0	Cyclohexanol	23.3
Toluene	18.2	Propanol	24.3
1,2-Dichloropropane	18.4	Hydrogen cyanide	24.7
Ethyl acetate	18.6	Acetic acid	25.7
Benzene	18.8	Ethanol	25.9
Trichloromethane	19.0	Formic acid	27.5
Tetrachloroethane	19.2	Methanol	29.6
Chloromethane	19.8	Phenol	29.6
1,2-Dichloroethane	20.0	Glycerol	33.7
Cyclohexane	20.2	Water	47.7

Source: Adapted from Ebnesajjad, 2016

We see that the solubility parameters for xylene and polyethylene are $18.0 \text{ MPa}^{1/2}$ and $16.3 \text{ MPa}^{1/2}$ respectively. Since the difference is small (less than $2 \text{ MPa}^{1/2}$), xylene acts as a good solvent at elevated temperatures. This prediction is shown to be true in experiments, as shown by Figure 6.

Figure 6: Solvent (xylene) Containing Dissolved HDPE After Heating for 5 Minutes at 104°C



A small sample of HDPE was able to be completely dissolved in a short time by the nonpolar solvent at elevated temperatures. Dissolution would have not occurred to this extent at room temperature.

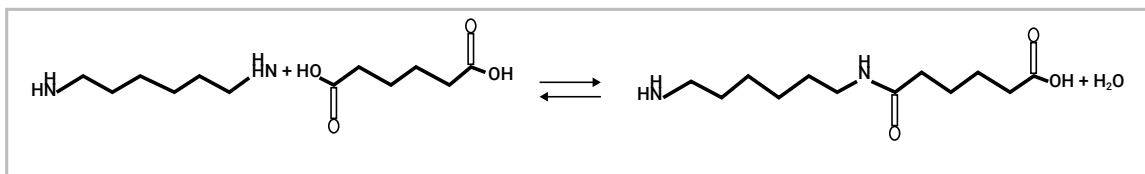
CHEMICAL ATTACK

When a polymer is being chemically altered by reactions, chemical attack (degradation) is occurring. Compared to dissolution, which disrupts secondary bonds, chemical reactions impact primary chemical bonds [16]. Chemical attack typically begins with initial steps of wetting, diffusion, and absorption as described in the previous section [10]. Reactions may impact the main polymer chain (molecular degradation), side groups, or both. The following section summarizes some common mechanisms of chemical attack seen in plastics.

Solvolysis

Solvolysis refers to interactions with solvent molecules that lead to substitution or elimination reactions. Hydrolysis is one form that is seen often, where water is the reagent. Hydrolysis reactions are common in condensation polymers like polyamides and polyesters. In condensation polymerization, monomers are linked together by the release of small molecules like water. The hydrolysis of nylon is the reverse of the polymerization reaction that the material is formed by [13]. Figure 7 shows the polymerization of nylon 6,6, however the double arrows indicate that this is a reversible reaction. Hydrolysis occurs when the reaction progresses from right to left.

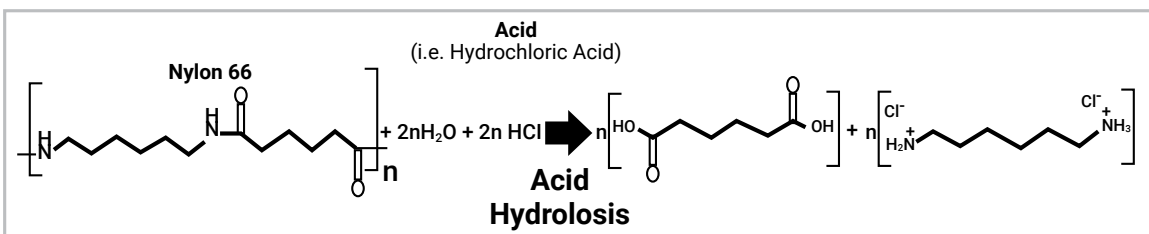
Figure 7: Condensation / Hydrolysis of Nylon 6,6



Source: Adapted from McNeely, 2025

The polymer chain is broken down into individual monomer units, with water being used to stabilize the chain ends. This will occur until an equilibrium is reached. The breaking of these bonds and the reduction in molecular weight leads to a loss in strength and embrittlement of the polymer. Hydrolysis can be accelerated by the presence of strong acids or bases. For example, quicker reaction times and higher yields of monomers are observed for acid catalyzed hydrolysis of nylon 6,6 [2, 13]. The reversible reaction that we previously saw is pushed even further to favor hydrolysis, as visualized by Figure 8.

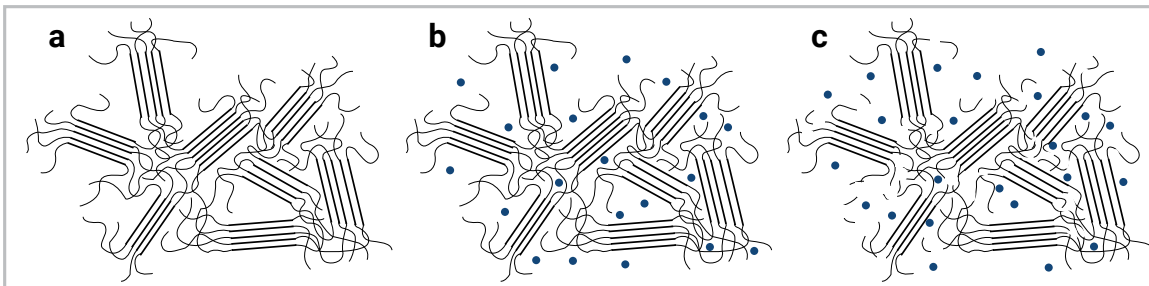
Figure 8: Hydrolysis of Nylon 6,6 in the Presence of Hydrochloric Acid



Source: Adapted from McNeely, 2025

Solvents other than water can cause similar reactions to occur, like ammonia in ammonolysis or acetone in acetolysis. Condensation polymers are typically more susceptible to attack [13]. Plasticization usually occurs as the solvent molecules enter the matrix. Solvolysis reactions result in the formation of monomer units and other small products. The material experiences softening and an overall property loss as a result [2]. Figure 9 provides a visual for the hydrolysis process in nylon 6.

Figure 9: Changes Occurring Within a PA6 Matrix While Aging in Water (a) Crystalline and Amorphous Phases Before Immersion, (b) Plasticization, (c) Chain Scission Due to Hydrolysis

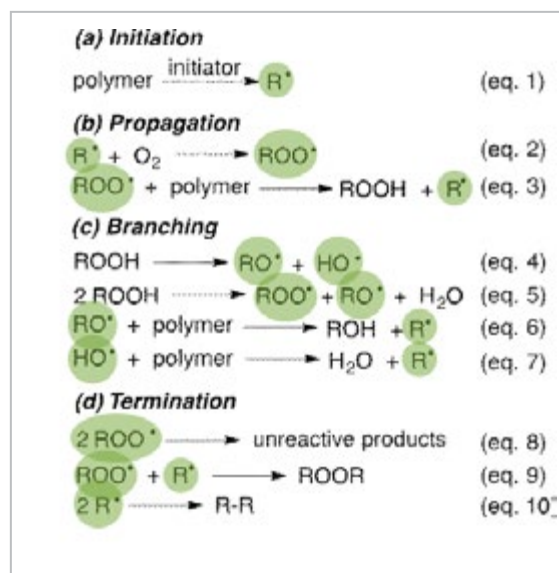


Source: Adapted from Ebnesajjad, 2016

Oxidation

Oxidation reactions involve the loss of electrons, stolen by more electronegative oxidizers like oxygen or chlorine. This electron loss can result in the formation of free radicals, which are unstable molecules looking for any opportunity to further react. These reactions may lead to chain scission, where the actual backbone is degraded, to the breaking of side group bonds, or to crosslinking between adjacent chains. Figure 10 shows a generalized reaction scheme for polymer oxidation. The exact reactions will vary based on the participating reactants.

Figure 10: General Mechanism for Polymer Oxidation, Where Free Radicals are Highlighted

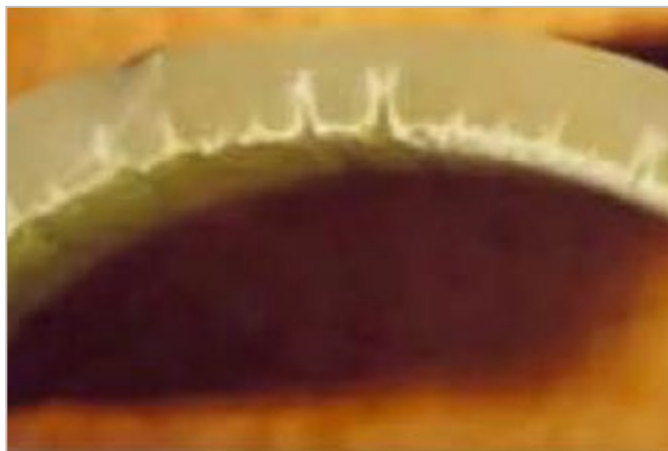


Source: Gervasoni, B. et al, 2015

Oxidation reactions lead to a kind of snowball effect – unstable chemical species are formed and will react with surrounding molecules, forming even more unstable species. The reactions do not terminate until all free radicals are converted into more stable products. These reactions can induce a number of effects in polymers, including embrittlement, strength reduction, and toughness reduction [8].

Polyethylene can be oxidized by chlorine-containing compounds. PEX piping, composed of HDPE, often comes into contact with chlorinated water while in service. The molecular chains can be degraded over time, and microcrack formation is eventually observed. Cracks may propagate through the pipe wall as seen in Figure 11. The risk of catastrophic bursting and failure is increased with property loss. This effect is accelerated with increasing temperatures or chlorine concentrations and leads to a drastic decrease in material life [15].

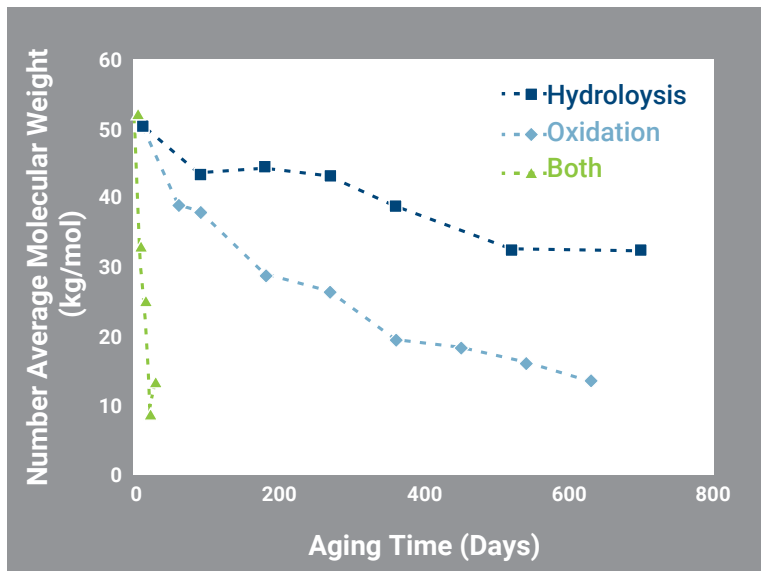
Figure 11: Cross Section of PEX Piping After Chlorine Attack



Source: Adapted from Samarth, 2021

Different chemical attack mechanisms may work simultaneously to damage materials. Nylon for example can experience both hydrolysis and oxidation when in contact with water containing an oxidant. Material degradation is significantly accelerated, compared to the individual effects from each mechanism, as shown in Figure 12 [2].

Figure 12: PA6 Molecular Weight Degradation with Chemical Attack in Accelerated Aging Tests at 100°C



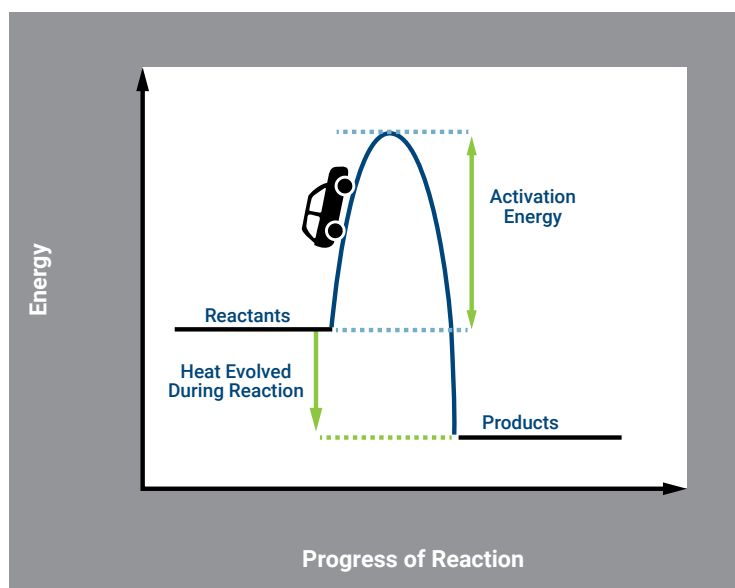
Source: Brette et al, 2023

CONSIDERATIONS FOR TEMPERATURE, CONCENTRATION, AND EXPOSURE TIME

The extent of damage caused by chemical attack can be influenced by certain factors. Typically, polymer resistance increases with increasing bond stability, degree of crystallinity, and molecular weight. Chemical attack is not limited to the material surface, so the amount a chemical is able to diffuse into the polymer matrix can also influence the amount of damage. More damage is seen with increasing contact between the chemical and polymer molecules.

Contact is also the key to understanding how factors like chemical concentration and temperature influence attack. Collision theory states that for any given reaction to occur, the reactants must collide with the proper orientation and sufficient energy to break and form chemical bonds. Every chemical reaction has an associated activation energy that it is required to overcome. This energy barrier is the hill seen in Figure 13. Imagine this figure represents a road, and you want to drive from point A (the reactants) to point B (the products). The higher the hill, the more difficult it will be to drive over. If two reactants collide with insufficient energy, then no reaction will occur. This is similar to the ideas covered for breaking secondary bonds in diffusion, but note that we are now referring to primary chemical bonds.

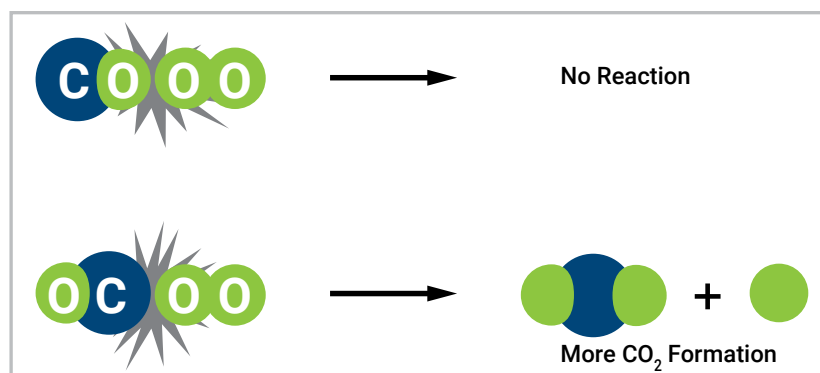
Figure 13: General Activation Energy Curve for an Exothermic Reaction



Source: Adapted from Clark, 2023

Some reactions will only occur if the reacting species collide with a certain orientation, often seen in asymmetrical molecules. If reactants collide with improper orientation, they will bounce off each other and, even with sufficient energy, no reaction will occur (see Figure 14). The required activation energy and molecular orientation will vary by reaction.

Figure 14: Potential Outcomes of Two Collisions with Different Orientations Occurring Between Carbon Monoxide and Oxygen Molecules



Source: OpenStax, 2022

As temperature increases, molecules have greater kinetic energy. They move more and with greater speed. This has two major impacts:

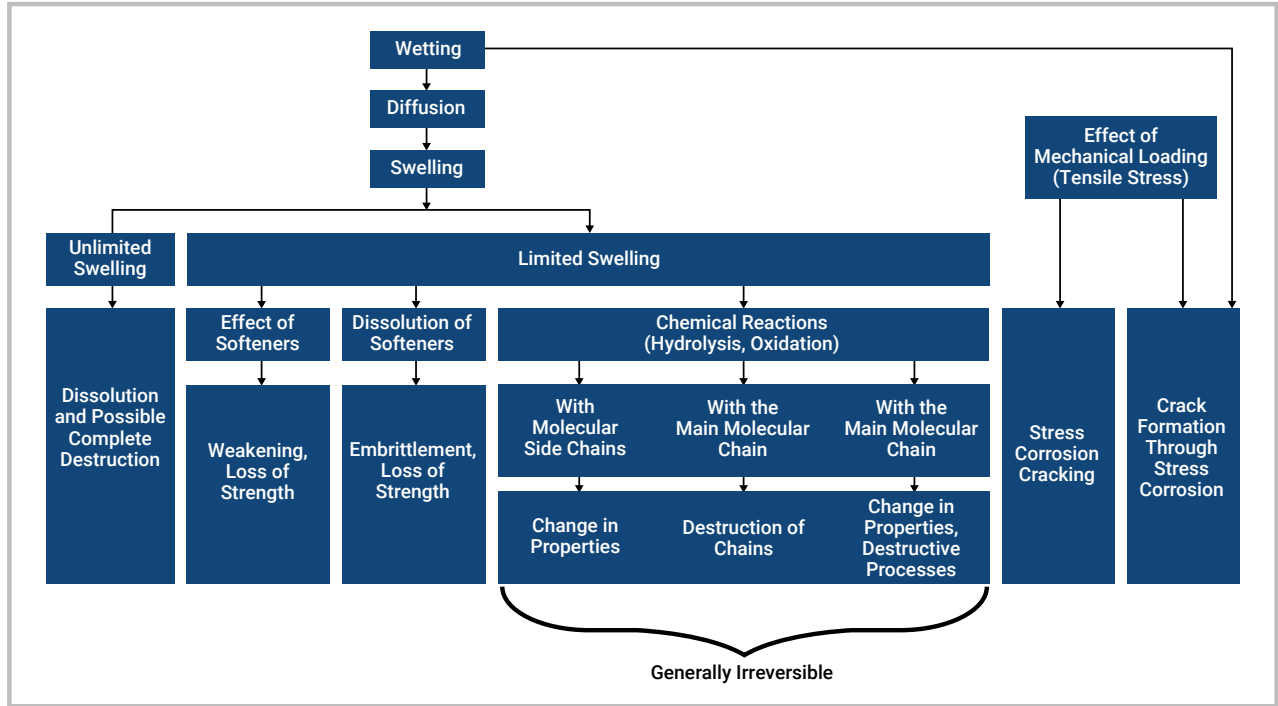
1. More collisions are able to occur, so the chances of a successful collision increase.
2. The reactants tend to collide with more energy making it more likely for the activation energy to be overcome.

Reactions are typically able to proceed more rapidly and more aggressively with increasing temperature [4, 14]. Since reactions are a series of collisions, rather than an instantaneous event, increasing the time of exposure will also increase the extent of attack. A similar impact is seen with increasing chemical concentrations. If there are more molecules present to participate in a reaction, then more collisions can happen.

There is existing chemical compatibility data for many polymers exposed to pure chemicals and diluted solutions. Mixtures of two or more substances create a unique challenge, as the properties may differ from the individual components. For instance, many commercial cleaners are mixtures, with multiple ingredients in differing concentrations. To make matters worse, there is often a lack of resistance data for these products. Data on the most abundant ingredients or similar products may provide an idea of compatibility, however testing is the only way to verify compatibility for chemical mixtures.

Figure 15 below summarizes the complex physical and chemical effects influencing the chemical compatibility of polymers.

Figure 15: Overview of the Mechanisms and Damage Seen in Chemically Incompatible Polymers



Source: Adapted from Grote & Antonsson, 2009

ENVIRONMENTAL STRESS CRACKING

One last factor that is important in chemical resistance is the presence of mechanical stresses or loads. Environmental stress cracking (ESC) is a common mode of failure for polymers exposed to a combination of stress and chemicals (known as environmental stress cracking agents). Failure may occur even well below the normal yield stresses of the material.

The mechanisms behind ESC are thought to vary on a case by case basis. Stress, in combination with factors like chemical exposure and temperature, promotes the disentanglement of polymer chains. Less tangled chains have weaker intermolecular forces, and are more susceptible to crack propagation. Crack initiation sites tend to occur in areas directly contacting an ESC agent. These sites can also correspond to areas of high localized stress, like defects or voids. Visible cracks or crazing may be seen on the affected material, while increasing brittleness, decreasing strength, and decreasing toughness are often observed as well.

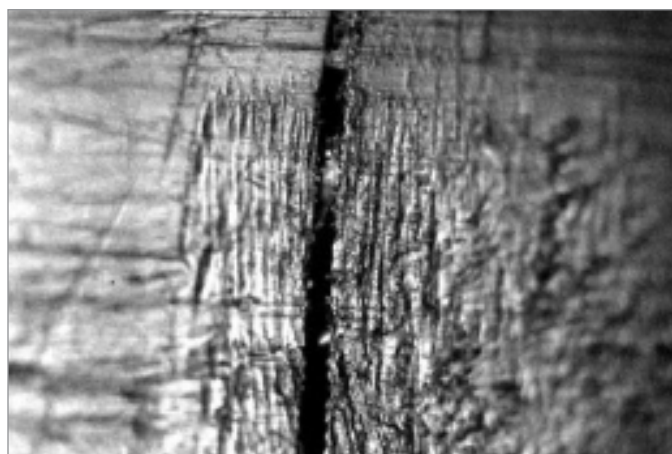
The degree that a chemical absorbs into a polymer can have implications for ESC, as the molecules need to penetrate the polymer matrix to disrupt intermolecular bonding. Polyethylene for example, is a polymer that is resistant to many chemicals, but susceptible to ESC. Benzene and toluene are two known nonpolar ESC agents, that are able to readily absorb into amorphous regions or defects to cause cracking. However, common polar chemicals can also act as ESC agents in polyethylene, including many soaps, alcohols, surfactants, and silicone oils. These substances do not absorb into the matrix to cause swelling or internal bond disruption. Rather, they are able to weaken the material surface and cause crack propagation from preexisting surface flaws [5]. Figure 16 shows the surface topology of an HDPE sample undergoing a constant bending force, before and after exposure to an ionic surfactant.

Figure 16: HDPE Surface (a) Prior to Exposure and (b) After Exposure to a Surfactant Under Constant Stress



(a)

Source: Ghanbari-Siahkali et al, 2005



(b)

ESC behavior is highly unpredictable and the underlying mechanisms are not fully understood. It can be accelerated by increasing stress-cracking agent concentration, temperature, exposure time, and the level of applied strain. The resistance of a material to ESC tends to increase with increasing molecular mass, but the effects of crystallinity can vary. While some materials like fluoropolymers are known to not commonly exhibit ESC, the complex and unpredictable nature of this phenomena creates a challenging obstacle in chemical compatibility determination [5]. Material testing in the expected application conditions is of great importance to rule out the risk of ESC.

CHEMICALLY RESISTANT PLASTICS

After exploring the details of what chemical resistance truly means, chemically resistant plastics take on a new meaning. No polymer is resistant to all chemicals, in all concentrations, at all temperatures or stress levels. However, there are some plastics that show excellent resistance in a wide range of conditions.

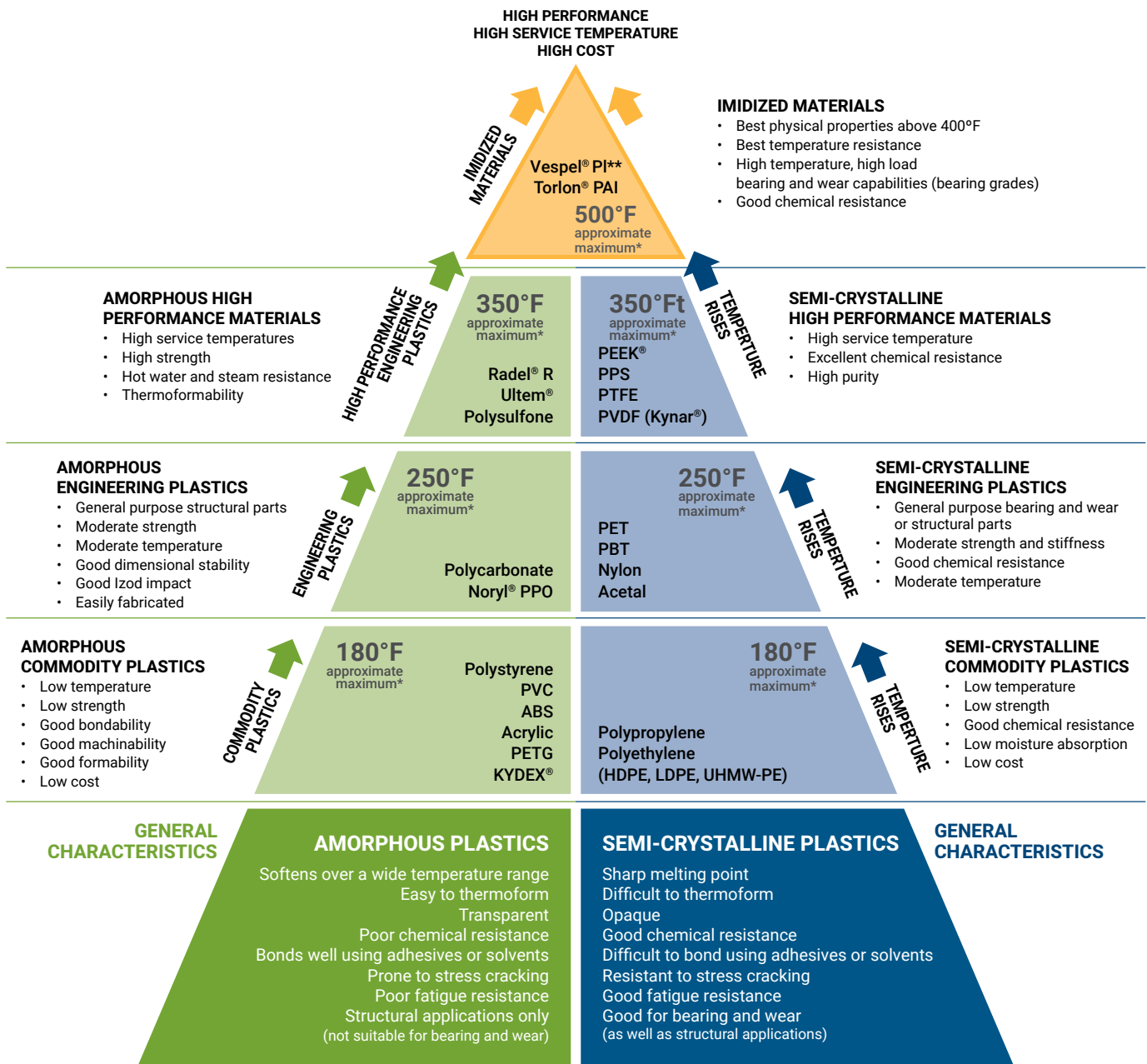
Polyolefins like HDPE for example, tend to resist many polar substances due to their largely nonpolar and non-reactive structures. Nonpolar solvents, strong oxidizers, and strong acids can be cause for concern at high temperatures or concentrations. Polyolefins are especially sensitive to increasing temperatures, as they show less thermal stability compared to other plastics.

Polymers containing aromatic rings within their backbone, like PEEK, can form highly stable structures. The strong bonds and semi-crystalline nature of PEEK contribute to its high degree of compatibility with many chemicals. Note however that PEEK can be susceptible to certain strong acids or strong oxidizers, especially when concentrations or temperatures are high.

Fluoropolymers like PTFE contain halogens within their structures. These polymers have outstanding resistance due to the strength of these carbon – halogen bonds. Although even in fluoropolymers, chemical attack is possible from some strong oxidizers at high temperatures and concentrations.

The thermoplastics triangle seen in Figure 17 provides trends for material behavior. Chemical resistance generally increases with increasing crystallinity, molecular weight, and bond strength. We see commodity plastics with good chemical resistance, like HDPE, on the bottom right-hand side of the triangle. Moving up on this side, we see high performance plastics with excellent chemical resistance like PEEK or PTFE towards the top.

Figure 17: The Thermoplastic Triangle



*Materials should be considered for applications up to approximate maximum temperature. Selecting a plastic material for use in a high temperature environment requires careful review of material properties data. This chart is for comparison purposes only.

**Vespel® is a thermoset.

While this is a helpful material selection tool, please note that it does not provide sufficient details to determine chemical resistance. For example, PVC resists many chemicals even though it is located on the amorphous side of the triangle. PEEK and PTFE have excellent chemical resistance, but they can still be attacked in certain conditions. Recall the claim made at the beginning of this paper that defining a plastic as simply having 'good' or 'poor' chemical resistance is problematic.

Plastics may also contain a number of different fillers, reinforcements, or other additives. Many formulations are proprietary – there is no way of knowing exactly what compounds may be present, or in what proportions. This can be another complicating factor in chemical resistance evaluation. Resistance data pertaining to the material brand and grade being considered, when available, can provide good insights into material performance. Data pertaining to the base resin or to similar brands often provides sufficient information (but note the small degree of uncertainty that comes with this).

CONCLUSION

This paper provides a summary of the factors that determine the chemical resistance of plastic materials, including:

- Mechanisms of physical attack
- Mechanisms of chemical attack
- Influences on the extent of attack
- Environmental stress cracking
- Examples of chemically resistant plastics

Chemical resistance in plastics is a complex topic, compatibility can be difficult or impossible to predict with certainty. Whenever data are not available or otherwise in doubt, testing a material candidate in the expected application conditions will be the best indication of performance.

For more information on chemical resistance, readers can find general data for select material-chemical pairs on Curbell Plastics' website at <https://www.curbellplastics.com/resource-library/material-selection-tools/chemical-resistance-of-plastics/>. For application-specific questions, inquiries are always welcomed via Curbell's Ask a Plastics Expert link on the website (www.curbellplastics.com) or call 1-888-287-2355.

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TECHNICAL EXPERTISE

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