

# pH and How It Affects Flooring Adhesive

Applying Alkaline Hydrolysis & Polymer Erosion Theory to Adhesive Failure

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## Short History on Polymers

Despite significant advances in synthesis and characterization of polymers, a correct understanding of polymer molecular structure did not emerge until the 1920s. Before that, scientists believed that polymers were clusters of small molecules (called colloids), without definite molecular weights, held together by an unknown force, a concept known as association theory. In 1922, Hermann Staudinger proposed that polymers consisted of long chains of atoms held together by covalent bonds, an idea which did not gain wide acceptance for over a decade and for which Staudinger was ultimately awarded the Nobel Prize.

Synthetic polymers today find application in nearly every industry and area of life. Polymers are widely used as adhesives and lubricants, as well as structural components for products ranging from children's toys to aircraft. They have been employed in a variety of biomedical applications ranging from implantable devices to controlled drug delivery.

## Structural Properties Overview

The structural properties of a polymer relate to the physical arrangement of monomer residues along the backbone of the chain. Structure has a strong influence on the performance properties of a polymer. For example, a linear chain polymer may be soluble or insoluble in water depending on whether it is composed of polar monomers (such as ethylene oxide) or nonpolar monomers (such as styrene). On the other hand, two samples of natural rubber may exhibit different durability (even though their molecules comprise the same monomers) based on their degree of side chain branching and resulting film density.

The attractive forces between polymer units will also affect performance. Because polymer chains are so long, these interchain forces are amplified far beyond the attractions between conventional molecules. Different side groups on the polymer can lend the polymer to ionic bonding or hydrogen bonding between its own chains. These attractive forces typically result in higher tensile strength and melting points.

Types of polymer properties can be broadly divided into several categories based upon scale. At the nano-micro scale there are properties that directly describe the chain itself, and can be thought of as polymer structure. At an intermediate mesoscopic level there are properties that describe the morphology of the polymer matrix in space. At the macroscopic level properties describe the bulk behavior of the polymer and its formulation when incorporated into an adhesive. The bulk properties of a polymer are those most often of end-use interest. These are the properties that dictate how the polymer actually behaves.

## Glass Transition Temperature (T<sub>g</sub>)

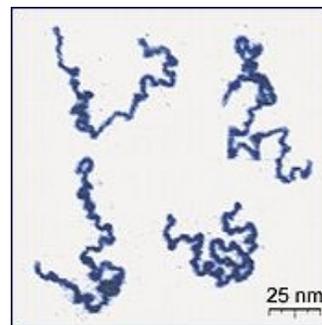
A parameter of particular interest in synthetic polymer manufacturing is the glass transition temperature (T<sub>g</sub>), which describes the temperature at which amorphous polymers undergo a second-order phase. The glass transition temperature, T<sub>g</sub>, is the temperature at which an amorphous solid, such as glass or a polymer, becomes brittle on cooling. The glass transition temperature may be engineered by altering the degree of branching or crosslinking in the polymer or by the addition of plasticizer. Inclusion of plasticizers tends to lower T<sub>g</sub> and increase polymer flexibility. Plasticizers are generally small molecules that are chemically similar to the polymer and create gaps between polymer chains for greater mobility and reduced interchain interactions. A good example of the action of plasticizers is related to polyvinylchlorides or PVCs. A uPVC, or unplasticized polyvinylchloride, is used for things such as sprinkler pipe. Plastic pipe has no plasticizers in it, because it needs to remain strong and heat-resistant. However, plasticized PVC can be made so flexible it can be used in clothing.

## Branching

The degree of branching of polymer chains can also affect the bulk properties of polymers. Long chain branches may increase polymer strength, toughness, and T<sub>g</sub> due to an increase in the number of entanglements per chain. Random length and/or random substituted or atactic short chains, on the other hand, may reduce polymer strength due to disruption of organization. Short side chains may likewise reduce crystallinity due to disruption of the crystal structure. Reduced crystallinity may also be associated with increased transparency due to light scattering by small crystalline regions (glass is an amorphous solid without crystal structure). A good example demonstrating crystalline density is related to the range of physical attributes of polyethylene. High-density polyethylene (HDPE) has a very low degree of branching, is quite stiff, opaque and is used in applications such as milk jugs. Low-density polyethylene (LDPE), on the other hand, has significant numbers of short branches, is quite flexible, clear and is used in applications such as plastic films. Low density polyethylene has a loose crystalline structure.

## Chemical Crosslinking

Crosslinking tends to increase  $T_g$  and increase strength and toughness. Crosslinking consists of the formation of chemical bonds between chains resulting in increased film density. Among other applications, crosslinking is used to strengthen rubbers in a process known as vulcanization, which is catalyzed by sulphur. Rubber used for car tires, for example, is highly crosslinked in order to reduce the leaking of air out of the tire and to provide durability. Concrete sealers are highly crosslinked to prevent topical penetration of chemicals. Liquid moisture vapor retarders applied to a concrete surface have an increased film density due to crosslinking that reduces the emission of water vapor. Eraser rubber, on the other hand, is not crosslinked in order to allow flaking of the rubber, preventing damage to writing paper.



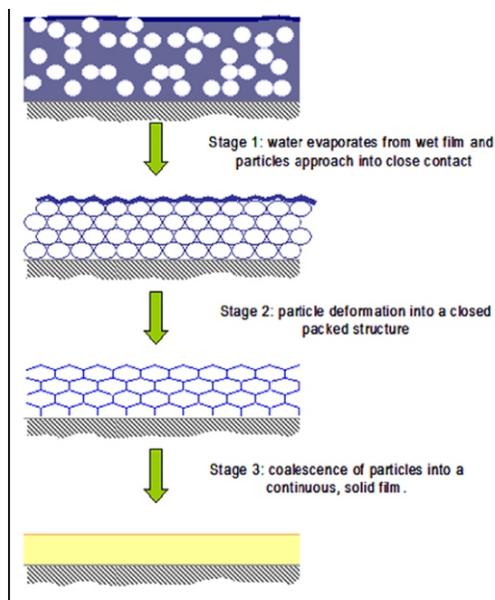
Appearance of real linear polymer chains as recorded using an atomic force microscope on surface under liquid medium. Chain contour length for this polymer is  $\sim 204\text{nm}$ ; thickness is  $\sim 0.4\text{nm}$ .

## Polymer Film Formation

The process by which polymer solutions turn into solid continuous films can be simplified as a series of events occurring during three main stages, as shown in the figure. During the first stage, water evaporates from the film while particles come into close contact. The second stage is characterized by deformation of particles into a closed packed structure. In the third stage, individual entities are no longer defined due to sintering of particles into a solid, continuous film strengthened by inter-diffusion of chain segments.

In many commercial formulations of thermoplastic and thermosetting latexes (a common term for aqueous polymers referring to their resemblance to natural liquid rubber) the most common functional groups introduced are carboxylic acids and hydroxyl groups. Carboxylic acid groups are usually incorporated in the polymer backbone via co-polymerization of Acrylic or Methacrylic Acids. Carboxyl groups usually improve mechanical and shear stability, film hardness and adhesion to substrates. Cross-linking is possible ionically and/or covalently.

When an adhesive is formulated, the base polymer is supplied in an aqueous emulsion at around 50% solids. The emulsion is created in a reactor under a chemical synthesis referred to as emulsion polymerization. Modern acrylic resin polymers and their copolymer adjuncts are carboxylated to enable ionic/covalent cross-links to form upon drying. As the formulated adhesive dries water is evaporated and the carboxylation reaction propagates, enabling cross-link formation. This chemical reaction is not in equilibria or is reversible only through degradation. The polymer crosslinks result in a multiplier effect on the molecular weight or mass, developing a crosslink lattice that decreases the volume of the adhesive product and increases the polymer/film (crystalline) density. Upon cure the dried adhesive material has reduce water solubility and when formulated correctly can exhibit water resistant properties. It becomes obvious then that incorporating materials such as inorganic clays, plasticizer, crushed marble or heavy surfactant loads to an adhesive formulation will increase the hygroscopic character, facilitate the diffusivity of water inside the matrix and can lead to the eventual failure of the adhesive film.



## Factors Contributing to pH Resistance

1. Length of side chain. The longer the better providing for more interpolymer interaction.
2. Hygroscopic constituent content of formulation. High surfactant and inorganic clay loads increase the diffusivity of water/pH into the film.
3. Amount of nonpolar monomer content. Styrene monomer addition leads to pH resistance of finished polymer due to its hydrophobic character.
4. Crosslink density of polymer film matrix. Higher degree of carboxylation initiates more crosslinks and increases film density. Crosslink density and crystalline structure can be viewed proportionately.
5. Reduced levels of non-polymeric constituents in adhesive film. Plasticizer will soften and disrupt crystalline structure. The resulting loss of cohesive film properties leads to film porosity or a loose crystalline lattice.

## Factors That Accelerate Polymer Degradation

1. More hydrophilic polymer backbone.
2. More hydrophilic polymer end groups.
3. More pH sensitive or hydrolytically labile polymer segments.

4. Less crystallinity or ability to form cohesive films. Also relates to porosity of film.

### General Stages of Adhesive Failure from Hydrolysis

1. Starts when water penetrates deeply into the interior regions of adhesive film.
2. The pH labile functionalities in the polymer chains hydrolyze. Inorganic salts react within the polymer film resulting in cleavage of covalent chemical bonds and crosslinks.
3. Polymer is broken down to oligomers and monomers (transported from the polymer bulk controlled by diffusion)  
The release of degradation products leads to mass loss and bulk erosion.
4. Observational viscosity loss and blushing due to water penetration typically mis-characterized as “re-emulsification”.

### Theory of Polymer Erosion

A theoretical model describing the erosion mechanism of water insoluble biodegradable polymer matrices or films. The erosion of a polymer describes a physical loss in mass and macroscopic properties. The two common erosion mechanisms are surface and bulk erosion.

### Polymer film may have differing modes of erosion:

**Surface erosion** degradation from exterior only with little/no water penetration of the film

**Bulk erosion** water penetrates entire structure and degrades entire device simultaneously

Polyanhydrides are surface eroding polymers. Surface eroding polymers do not allow water to penetrate into the film matrix. They erode layer by layer, like a lollipop. By manipulating the polymer composition we can affect the rate of this surface erosion. The hydrophobic backbone can be altered with hydrolytically labile (pH sensitive) anhydride linkages allowing hydrolytic degradation to be controlled.

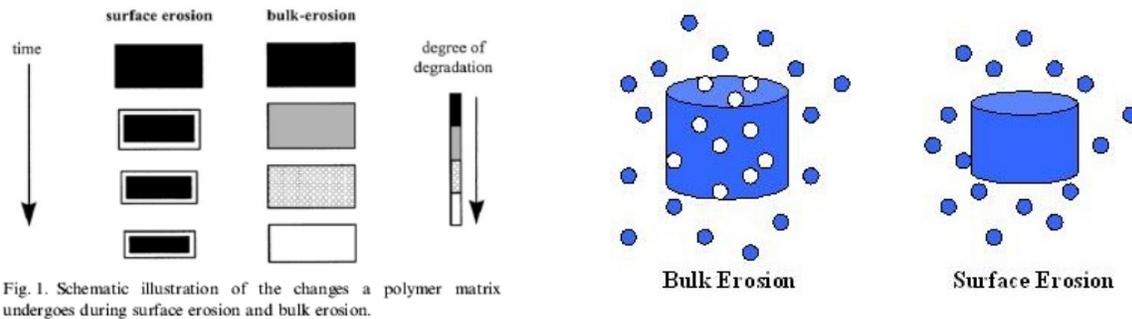


Fig. 1. Schematic illustration of the changes a polymer matrix undergoes during surface erosion and bulk erosion.

Polyanhydride copolymers with hydrophilic groups exhibit bulk eroding characteristics. Bulk eroding polymers take in water like a sponge (throughout the material) and erode inside and on the surface of the polymer. This description best describes the loss of an adhesive to elevated MVER and pH. Conventional adhesives contain hygroscopic materials that draw additional moisture into the adhesive film. With this diffusive event dissolved alkaline salts migrate initiating hydrolytic degradation. Poor choice of polymer such as an acrylic modified with a high vinyl acetate content exacerbates the situation with pH labile linkages.

Polymer degradation is a change in mesoscopic (intermediate scale) properties—tensile strength, color, shape, etc.—of a polymer or polymer device (adhesive, sealant, paint) under the influence of one or more environmental factors, such as heat, light or pH. Polymer degradation occurs due to the hydrolysis of the bonds connecting the polymer chain, which in turn leads to a decrease in the molecular mass of the polymer. These changes may be undesirable, such as flooring adhesive failure due to water penetration of the adhesive bond layer and subsequent hydrolysis from elevated pH. Polymer degradation can also be desirable, as in biodegradation, a strategy used to deliver polymer encased drugs that erode as a function of time.

The degradation of polymers to form smaller molecules may proceed by random scission or specific scission. The degradation of polyethylene occurs by random scission—a random breakage of the linkages (bonds) that hold the atoms of the polymer together. When heated above 450°C it degrades to form a mixture of hydrocarbons. Other polymers like polyalphanmethylstyrene undergo specific chain scission with breakage occurring only at the ends. They literally unzip or depolymerize to become the constituent monomer.

The model shows that all degradable polymers can undergo surface erosion or bulk erosion. Which way a polymer matrix erodes depends on the mechanism of diffusivity of water inside the matrix, the degradation rate of the polymer's functional groups and the matrix dimensions.

### Chemical Erosion

Heller describes three general chemical mechanisms that cause polymer erosion.

Mechanism I - describes the degradation of water-soluble macromolecules that are crosslinked to form a three-dimensional network. As long as crosslinks remain intact, the network is intact and is insoluble. Degradation in these systems can occur either at crosslinks to form soluble backbone polymeric chains (A) or at the main chain to form water-soluble fragments (B). Generally, degradation of polymers (A) provide high molecular weight, water-soluble fragments, while degradation of type (B) polymers provide low molecular weight, water soluble oligomers and monomers.

Mechanism II - describes the dissolution of water-insoluble macromolecules with side groups that are converted to water-soluble polymers as a result of ionization, protonation or hydrolysis. With this mechanism the polymer does not degrade and its molecular weight remains essentially unchanged. Instead these polymers become soluble through ionization of their crosslinking functionalities.

Mechanism III - describes the degradation of insoluble polymers with labile bonds. Hydrolysis of labile bonds causes scission of the polymer backbone, thereby forming low molecular weight, water-soluble molecules. Polymers undergoing type III erosion include poly (lactic acid), poly (glycolic acid) and their copolymers. The three mechanisms described are not mutually exclusive; combinations of them can occur.

### Physical Erosion

The physical erosion mechanisms are characterized as surface or bulk. In surface erosion, the polymer erodes only at the surface, and maintains its physical integrity as it degrades. Crystalline regions within the polymer exclude water and remain hydrophobic, resistant to the effects of pH (hydrolysis) initiated by water penetration. Highly crystalline polymers tend to undergo surface erosion and are the best choice for flooring adhesive formulation. Few polymers exhibit this type of erosion and the ones that do are expensive and difficult to formulate. Most polymers undergo bulk erosion, the pH initiated hydrolysis and degradation occurs at even rate throughout the polymeric matrix or lattice. Generally these polymers tend to be more hydrophilic than those exhibiting surface erosion. As a result, water penetrates the polymeric matrix and increases the rate of diffusion. In bulk erosion there is a complete loss of integrity of the entire polymer matrix.

### Summary

#### Loss of Adhesion and Secondary Emissions Due to pH Hydrolysis

The observational result of white soft adhesive found under resilient tile in flooring applications is more accurately described as a re-wetting process. The dried adhesive has regained a measure of liquid water content due to the diffusivity of water and/or water vapor from the concrete slab into the polymer matrix. The loss in viscosity is due to hydrolytic degradation of the polymer and/or polymer crosslinks.

Hydrolysis of adhesive polymers can result in secondary emission products that negatively contribute to indoor air quality. Volatile degradation products are not only emitted to the air. A substantial amount of volatile degradation products are also absorbed into the pore system of the concrete and will release long after the damaged adhesive is removed. Some individuals suffer non-specific complaints such as headache, nausea, cough or skin problems after exposure to certain indoor environments. This is generally described as "Sick-building syndrome". Although it is difficult to link health related complaints to specific indoor air quality issues, both primary and secondary emissions are likely suspects.

**A Caveat:** Re-emulsification is a valid descriptive for the process in which the penetration of water to a water soluble salt or mixture containing hygroscopic materials such as surfactant or clay causes liquification and suspension.

- Gopferich, A. Mechanisms of polymer degradation and erosion. *Biomaterials* 17, 103-14 (1996).
- von Burkersroda, F., Schedl, L. & Gopferich, A. Why degradable polymers undergo surface erosion or bulk erosion. *Biomaterials* 23, 4221-31 (2002).
- Brandrup, J.; Immergut, E.H.; Grulke, E.A.; eds *Polymer Handbook* 4th Ed. New York: Wiley-Interscience, 1999.
- Surface chemistry of biodegradable polymers for drug delivery systems. *Chem. Rev.* 2005, 105, 4205-4232.
- Kotwal VB, Saifee M, Inamdar N, Bhise K. Biodegradable polymers: Which, when and why?. *Indian J Pharm Sci* 2007;69:616-25
- Heller J. Controlled release of biologically active compounds from bioerodible polymers. *Biomaterials* 1980;1:51-7.