The ABC of Radiant Heating reads PEX

Why PEX?

Previous articles in this series have described the success story of Radiant Panel Heating with PEX tubing. Why is PEX the only alternative, and are there different kinds of PEX tubing? This article will look at the history behind today's situation, and review some differences between the materials used.

The PP era (in Europe)

Radiant floor heating started to revive in the late 60's in central Europe. The typical installation included a few hundred feet of tubing per loop installed in the concrete slab. A minimum of one foot of tubing per square foot is required so each project typically consists of thousands of feet of tube. Installing stiff pipes would require a lot of labor to connect and fit into the floor. Additionally, fittings or couplings are considered to be weak points; the potential for leaks is thought to be larger there, and codes often require all fittings to be accessible.

In order to install the tubing in an efficient and practical way, the tubing had to be flexible. This requirement considerably reduced the number of polymer candidates. The material selected in the late 60's was Polypropylene. Since “pure” Polypropylene (this is called a Homopolymer, PP) is comparatively stiff, it was somewhat cumbersome to install and it was easily kinked. Installation instructions soon included recommendations to warm the tubing before installing it, or even to fill it with hot water. While these recommendations were acceptable to users - it was another issue that became critical.

Trade magazines reported an increasing number of failures of the tubing in the early to mid 70's These happened typically in the bends of the concrete embedded tubing. The additional stresses caused by bending the comparatively stiff tubes initiated cracks that propagated through the tubing wall. Suppliers then developed Polypropylene copolymers (PPC) that included some Polyethylene groups in the material (that’s why it’s called copolymer) to make it more flexible and more resistant to stress cracking. Although these improvements were made, the market had become suspicious of the material, and it never regained its early popularity. PPC is still successfully used for radiant panel heating in several markets, but the market share remains small. There is virtually no PP tubing available on the North American market. Since the material Polybuthylene was developed here during the late 60's and early 70's, raw material manufacturers did not see a large potential in PP tubing, so standards were not developed, and it was not promoted. The situation remains the same today.

PB Made Inroads - For a While.

Polybuthylene (PB) tubing was introduced to the US market in the early 70's and a few years later in Europe. It was flexible and more stress-cracking resistant than PP, so it worked well for radiant floor applications and later for plumbing. In Europe, the standards for pressure rating are strict and the tubing wall was made comparatively thick. This, combined with a relatively high material price made the tubing somewhat expensive. As a result, the market share in Europe has remained limited, around 5% with swings 2-3% up or down over the years.

In North America, PB became virtually the only alternative for radiant floors until the mid 80's, when PEX was introduced. The material price was lower than in Europe, and the US rating system allowed a smaller wall thickness. But radiant floors were not well promoted and the market penetration was slow during the years between 1971 and 1985. Also, the public remained somewhat skeptical of PB, because there were major failures of regular cold water lines. (The reason was that batches without antioxidants in them were mistakenly released. Those pipes had begun to degrade already during extrusion). The next development was fitting systems for PB tubing made out of acetal plastics intended to make plumbing systems more affordable. This material degrades when it comes in contact with water at increased temperatures (so called hydrolysis) and it turned out to be another disaster for PB. Class action law suits came as a result and PB was withdrawn from the US marketplace.

The success of PEX

Crosslinked Polyethylene (PEX) tubing was introduced during the early 70's in the European marketplace. The material was flexible and installed easily, it was stress-cracking resistant, and could hold up to high temperatures. There were no failures and the market began to trust PEX tubing. Rather than selling only plastic tubing and fittings, complete systems were developed. These included manifolds, controls, tools, accessories, and design methods. Contractors could concentrate on installing systems instead of figuring out what components to use and how to build the systems. The design of radiant floor heating systems is somewhat complicated, making the manufacturers’ system approach a major success factor. Market penetration was rapid and the volume increase approached 100% per year over several years during the late 70's and early 80's In the early 80's there was a debate regarding oxygen diffusion through the plastic tubing (see the article: “The Oxygen Diffusion Debate - Defused”) which slowed down the increase. The issue was resolved with a barrier layer applied to PEX tubing, and the increase rate has since remained at about 20% per year in Europe with the beginning sign of a market saturation.
In the US, PEX sales for radiant panel heating systems started in the early 80's, but the real expansion and penetration began after an ASTM standard was published (1984) and European-inspired complete systems were introduced in the mid and late 80's. PEX tubing with a barrier for oxygen took increasing market shares.

Since then, the market has continued growing steadily by around 30% per year, and with an increasing number of competitors present, price pressure resulted.

During the 90's, composite tubing consisting of aluminum between two layers of PEX (PEX-Al-PEX) was introduced, but is mainly used for other heating and plumbing applications, rather than for radiant panel heating. During the late 80's until recently, increasing volumes of reinforced rubber hoses were used for radiant floors. Several of those suppliers have now disappeared from the market, and after major hose failures in the 90's, sales of radiant rubber hose is rapidly decreasing.

Are all PEX the same, or are they different?

In the US, virtually all tubing used for radiant floors is now PEX tubing. It has proven to be a winner and a reliable alternative. There are several commercially utilized crosslinking methods, and they can produce different kind of crosslinks, crosslinking density, and crosslinking distribution leading to significant variations in properties. Let's look closer at the different PEX processes to better understand the differences.

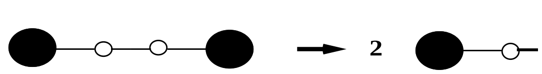
The commercially important crosslinking methods are the chemical methods using Peroxides (PEX -a) or Silanes (PEX-b) and Beta radiation (PEX-c).

Peroxide Crosslinking

Polyethylene is mixed with an organic peroxide (plus Antioxidants and possible other additives). The compound is poured into an extruder that heats the material until it melts and then extruded as pipe. The X-link reaction takes place either inside the extruder (Engel) or immediately after the extruder for other peroxide crosslinking methods. The reaction temperature/extrusion temperature is dependent on what peroxide is utilized. After crosslinking, the pipes are pulled through calibration tools into a cooling water bath.

The chemistry of the peroxide crosslinking reaction is easy to understand:

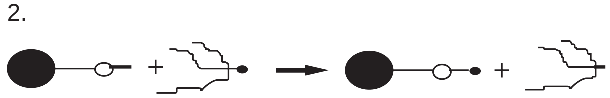
Step 1.



R - O - O - R + heat -> 2 R - O°

A peroxide is affected by heat so it splits up into two aggressive radicals.

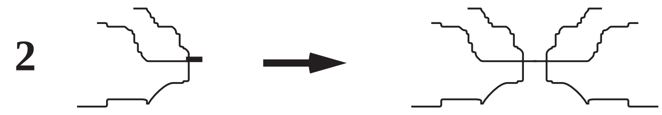
Step 2.



R - O° + P - H + heat -> R - O - H + P°

Each radical reacts with a Hydrogen in the Polyethylene (PE) making the peroxide radical stable while the PE turns into a Polymer radical.

Step 3.



2 P° -> P - P

Two polymer radicals react with each other, forming stable Crosslinked PE.

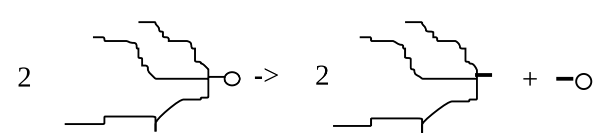
Beta Radiation Crosslinking

First, a suitable PE raw material blend is selected, with stabilizers and possible colorants/other additives included. It is then extruded into tubing onto large spools, perhaps 30,000 ft. on each. This tubing is then run under an electron beam many times. It is twisted and turned by large wheels and is "tanned" from every angle.

Electron beams, or beta radiation, are fast moving electrons from an electron accelerator. In a TV tube, high electrical potentials - 10,000 volts or more - are used to guide and speed up electrons until they hit the screen generating the picture. For crosslinking of PE, potentials of millions of volts are necessary to penetrate the material and generate crosslinks.

The energy of these electrons is selected so it corresponds to the bonding energy of Hydrogen atoms to the PE molecular chain. Hydrogen atoms are shot loose, forming pairs to become Hydrogen gas that is vented away. The PE chains now have open ends (known as radicals), but as these meet their “twins” they are bond together into a three dimensional network. The dose - the number of electron shots - will determine the degree of crosslinking.

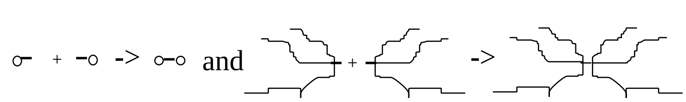
Step 1.



2 P - H + energy -> 2 P° + 2 H°

Radiation splits up 2 polymer molecules into polymer radicals and hydrogen atoms.

Step 2.



2 P° + 2 H° -> P - P + H_2

Two Hydrogen atoms form a Hydrogen molecule and the two polymer radicals merge together (they crosslink).

The ABC of Radiant Heating reads PEX (continued)

As we can see, both above methods result into the same kind of crosslink bond, a strong carbon-to-carbon bond between the original polymer molecules. This is not the case with the following method.

Silane “Crosslinking”

The Silane process includes several steps. The PE raw material must first be grafted in a separate extrusion process before the pipes are extruded. Raw material manufacturers often make this. Alternately, special extruders can allow injection of chemicals during the extrusion, eliminating the need for two extrusion steps. Generally, this is called the “Monosil Process” although there are a number of variations utilized in the systems.

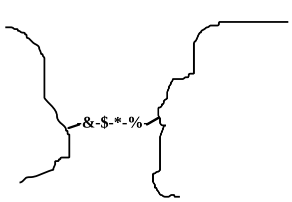
After pipes are extruded, the degree of “crosslinking” is very low, most of the bridges between the polymer molecules are formed afterwards when the material is exposed to humidity. When storing the pipes at room temperature and normal humidity, it could take months before final crosslinking is reached. This may be decreased to hours by storage at high temperatures and high humidity (“Sauna treatment”), or by circulating hot water inside the tubing. For larger wall thickness, many hours of hot water exposure may be required.

There are many variations to the chemicals that are called Silanes. They have somewhat different properties, and several different types can be utilized for building bridges between molecules. The example below is representative since the principal is similar to other Silanes. The chemistry is somewhat complex and not as easy to display as those above.

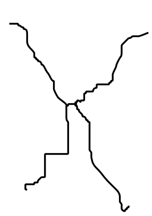
(CH2)n + RO° + CH2=CH-Si(OCH3)3 ->(CH2)n-CH2-CH2-Si(OCH3)3 + RO°
Vinyltrimethoxysilane is first grafted to PE with help of a peroxide.
Then, by treatment with hot water (add H2O to above), methanol is split off:
-> (CH2)n-CH2-CH2-Si(OCH3)2-OH + CH3OH (Methanol !!)

Two of these merge to form the crosslink, giving off water. The bridge between the two Polymer chains in the Silane “crosslink” looks like this:

-CH2-CH2-Si(OCH3)2-O-Si(OCH3)2-CH2-CH2-



Silane, a bridge



"real" PEX - a crosslink

Some people (including myself) think that the Silane reaction should be called a vulcanization rather than a crosslinking since there is a bridge between the polymer chains - not a Carbon to Carbon crosslink.
The saying is: "The strength of a chain is equal to its weakest link"; the Silane bridge includes many different kinds of bonds between chemicals connecting the polymer chains. Each kind of bond has its unique bonding energy level and can be accordingly affected...

The last step in the crosslinking reaction described above is the step when water is released and the link is formed. This reaction can be reversible when moisture is available and the temperature is comparatively high. For each grade of Silane vulcanization the possible effects of hot water to the vulcanization bridge should be studied.

The health effects of Silanes, and/or their reaction by-products, and/or solvents used should be studied for each Silane composition when used for potable water. There are currently no Vinylsilanes in the list of chemicals in materials approved for contact with food and water in the “Official Journal of the European Communities # L 61/26 EN (European Norm) of March 12, 1996”.

The ABC of PEX

In the short overview of the three kinds of PEX tubing materials commercially available, we saw that Chemical Crosslinking (or Engel) with the acronym PEX-a and Radiation Crosslinking, PEX-c, have the same kind of crosslinking bonds while Silane Crosslinking, PEX-b, has a different bond. We can see corresponding differences in the materials, for example when heated up to release the thermal memory of the materials. There are other differences between them, and I may revisit this in future article(s). However, the most important property is the long-term strengths of the materials. They must be able to withstand the exposures in their intended applications. Long term testing has been ongoing since 1961 for radiation crosslinking and since 1972 for chemical crosslinking, and I must believe that long-term test results are being developed also for Silane crosslinking.

From the history (in the first part of this article) we have learned that some hot water plastic tubing materials have come and gone. Those disappearing did not meet the requirements. They survived for many years but finally they failed to provide what was expected or demanded. PEX tubing has proven to sustain in all its' applications and the growth continues all over the world. We must hope and rely that all PEX manufacturers continue to maintain the PEX history of success.