AN EXPERIMENTAL INVESTIGATION OF PEX-b EXTRUSION

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ABSTRACT

This paper will review the various methods of producing crosslinked polyethylene pipe (PEX) and will look at the processing characteristics of producing moisture-cured silane PEX by the one-step method. The one-step process, where liquid trimethoxysilane is grafted onto the polyethylene backbone during the pipe extrusion process, will be investigated. Based on the experimental data collected from a highly instrumented 88.9 mm extruder, two different screw geometries, and information from production PEX pipe systems the most robust screw design will be suggested.

INTRODUCTION

The crosslinking of polyethylene is a useful way to improve the mechanical properties of polyethylene. These improved properties include, but are not limited to; thermal stability, chemical resistance, melt flow, processability and surface properties (1). The process of crosslinking the polymer involves chemically bonding different polymer chains to form a three dimensional matrix network (2). For polyethylene pipe production there are currently three commercially accepted ways to crosslink polyethylene. These are peroxide, moisture-cured silane, and beta irradiation commonly referred to PEX-a, PEX-b, and PEX-c respectively (3).

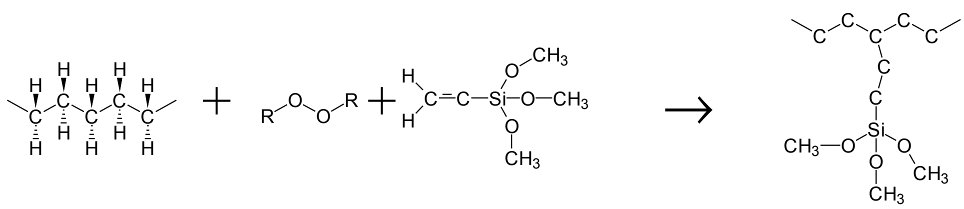
In PEX-a and PEX-c processes, the crosslinking is accomplished with the use of radicals. In peroxide crosslinking, heat is used to activate the peroxide to create the free radicals. These free radicals then cause molecules to crosslink and from the matrix. “In irradiation, high energy is transferred to the electrons orbiting the atomic nuclei of the target these electrons are either released from the atom, yielding a positively charged ions and free electrons, or moved to a higher-energy atomic orbital, yielding an excited atom or molecule known as a free radical” (4). The result of irradiation it the creation of free radicals which will generate both crosslinks and limited chain scission.

In PEX-b the crosslinked network is generated by linking chains of polyethylene via silane bridges. This is accomplished in two steps. The first step is to graft silane molecules to the backbone of the polyethylene. The second step is to react adjacent silane branches in the presence of moisture. This is done after the final product is formed. In PEX-b there are three ways in which the materials can be processed. The first is the Sioplas process (5). In this process the silane is grafted to the backbone of the polyethylene via reactive extrusion, typically done on a twin-screw extruder. The material is then blended with a catalyst masterbatch and a process aid masterbatch and processed on an extruder to form the product. The second process is the Monisil process (6) where polyethylene, a catalyst masterbatch, silane, and a free radical generator (typically peroxide) are all added to the extruder at the same time. The grafting reaction and extrusion of the pipe is performed in one step. The final method is Dry Silane (7), which is similar to the Monisil process except the liquid silane and free radical generator are absorbed into a carrier prior to introduction to the extruder. This is then extruded with polyethylene and a catalyst masterbatch to create the grafted material and end product.

There are advantages and disadvantages to the different methods of crosslinking the polyethylene that this paper will not discuss. In the moisture cure systems there are processing differences between the three basic systems. The Sioplast process is the oldest of the systems and is the most costly, primarily due to requiring two extrusion steps. The second disadvantage is the two heat histories that are required to produce the PEX pipe, which may adversely affect the polymer. Another disadvantage with the grafted material is the limited shelf life before moisture reacts with the silane graft, which will prevent the material from crosslinking, after the pipe is extruded. The main advantage is on the secondary extrusion of the pipe. Since there is no free silane there is very little build up on the screw and die components as compared to the single extrusion processes. This means that the extruder can be run for a significantly longer period of time before the system needs to be broken down and cleaned. The Monisil and Dry Silane processes have similar problems; primarily build up on the screw and die. Since both of these processes involve reactive extrusion there are free radicals and charged molecules that have an affinity for the metal surfaces. These will have a tendency to build up on the screw and die and form a shellac like coating. This periodically breaks off and is extruded as a defect in the pipe. In addition, the build up will change the geometry of the screw and tooling, eventually causing the pipe to fall outside acceptable tolerances.

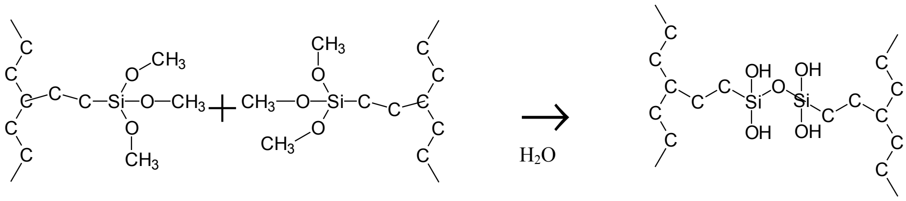
PEX-b CHEMISTRY

The chemistry behind the one step PEX-b process requires that a liquid silane blend is mixed together with polyethylene and a catalyst masterbatch just prior to entering the extruder. Once inside the extruder the peroxide creates free radicals due to the heat. The free radicals allow the trimethoxysilane to graft onto the backbone of the polyethylene. See Reaction #1. After forming the final product a second reaction to crosslink the polyethylene needs to take place. This is achieved by introducing water to the plastic, either in a sauna or by passing heated water through the pipe. Water causes the silane branches of adjoining chains to react which crosslinks the polyethylene. This reaction will evolve methanol as a byproduct. See Reaction #2.



Polyethylene　Peroxide　Vinyl Silane　Grafted PE

Reaction #1



Grafted PE Grafted PE XLPE

Reaction #2

EXPERIMENTAL
The materials that were tested in this work were based on the Constab "One-Step" process. This process is composed of two parts, first is the materials and second is the blending/dosing station. There are four components that are used in this process to produce PEX pipe. The main material is a bare foot polyethylene, which contains minimal antioxidants. The second material is a liquid silane blend that contains trimethoxysilane and peroxide. The third is Spherisil processing aid, which is a porous polyethylene granule that will adsorb the silane blend. The last material is a masterbatch pellet that contains the catalyst that is required to cross-link the grafted polyethylene chains in the presence of water.

The second component that is critical in producing PEX is the gravimetric blending/dosing station. In order to ensure that the correct percentages of each component is introduced gravimetric loss in weight hoppers are used. The liquid silane is metered from a loss in weight hopper into a mixing chamber via a gear pump. This chamber is positioned right above the feed opening of the extruder. The silane is adsorbed into the porous pellet, which is uniformly blended with the other two components. The materials that were evaluated in this work are described in Table #1.

There were two different single-screw extruders used in this paper. The first is an 88.9 mm 30:1 L/D smooth bore machine with pressure ports every 4.5 L/D down the barrel, and, the second was a 75 mm 32:1 L/D with a 1.5 L/D grooved liner and was part of a production PEX pipe line. The same tooling was used on both extruders and was a simple spider die with a pin and bushing designed to produce 0.5" diameter PEX pipe per ASTM F876. In the case of the 88.9 mm extruder a total of seven pressure transducers were installed along the barrel. In addition, there is an eighth pressure transducer located in the 0.5" tooling. The pressure from each transducer was recorded by a high speed data acquisition system with a sampling rate of 50Hz. These pressure traces will give insight as to how the material feeds, melts and pumps inside the extruder along with the process stability.

Two different screw geometries were evaluated in this work. A double mixing screw on the 88.9 mm diameter and a DSB-V barrier screw on the 75 mm extruder. The double mixing screw has a 3:1 compression ratio with two 4 L/D barrier mixing sections located in the metering zone. Figure #1 shows the layout of this design.

The second screw geometry was a DSB-V barrier design of moderate intensity. The initial portion of the barrier section is identical to a standard barrier screw in which a secondary flight is introduced over the transition section of the screw, which separates the screw channel into two channels known as the solid or primary channel and the melt or secondary channel. Further down the channel, a tertiary flight is introduced into the solid channel and subsequently forms two channels. Periodic depth changes are made in each of these channels. The crests of the periodic depth changes are out of phase between the two channels and the height of the tertiary flight tapers along the crests of the depth changes. The actual design is described in prior work by Christiano et al. (8). Figure #2 shows a drawing of the screw.

OBSERVATIONS AND DISCUSSION

The 88.9 mm extruder was run at screw speeds of 20, 40 60 and 80 RPM and this data is presented in Table #2. In addition, the data was scaled to the 75 mm diameter extruder production line and is presented in Table #3. The production line was run at a screw speed of 68 RPM and produced pipe at 100 kg/hr, which corresponded to 21.6 m/min. As the data shows, the barrier screw ran at a slightly higher specific output rate as compared to the double mixing screw. The total pressure variation in the tooling was measured to be approximately 1.0%. The total melt temperature variation, which was measured with an exposed junction melt thermocouple, was measured to be 0.3°C. This is an indication that the barrier screw was ran with very good stability and mixing.

The double mixing screw showed signs of instability at the first pressure transducer and screw speeds above 40 RPM. Figure #3 shows the high speed pressure traces for one minute at a screw speed of 60 RPM. This condition would be a typical operating condition for production on an 88.9 mm pipe line. The instability is an indication of solid bed breakup (9) and results in a total pressure variation of 3.8%. Although the variation is greater than that of the barrier screw it is still low enough to be able to produce pipe in accordance to the tolerance specifications outlined in ASTM F876.

In addition to the laboratory work, field observations on the performance of the two different screw geometries have been reported. With the "One-Step" process there are some limitations, which include the acceptable run time of the extruder. Due to the liquid silane and charged molecules there is a tendency for the material to build up on the screw creating a "shellac". Over time this will have a tendency to break off and be extruded into the final pipe causing a defect in the pipe along with changing the polymer flow through the die. When this happens the entire system has to be broken down and cleaned. It has been reported that longevity of the double mixing screw is greater than that of the barrier design.

CONCLUSIONS

The double mixing design appears to be a better choice for processing PEX-b by means of a one step process. Although the process stability and specific output rate are not as good as the barrier design, there are other factors that influence the optimum design for this process. In this case one of the drawbacks is the time between cleaning the screw. Therefore, sacrificing process stability for a more robust operating window is the better choice. It is possible that because the barrier geometry is designed to melt the material over a much longer portion of the screw that there is a greater tendency to build up throughout the barrier and metering sections. Meanwhile the solid bed break-up that has been documented does increase to total pressure variation, it may also add some benefit. When the solid bed ruptures, all the unmelted material is encapsulated by melt. It is possible that this action also prevents the ungrafted silane from plating out on the screw root in the early portion of the screw. The result is a longer processing window between shutdowns.

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ILLUSTRATIONS AND TABLES

Table #1 – Monisil Formulation

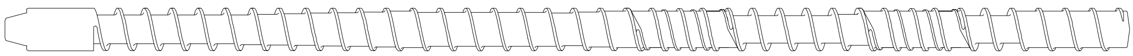
Material	% of Formulation
Solvay 4040A HDPE	73.6%
Constab PA0861HD Spherisil Porous Pellet	20.0%
Constab TA2124HD Catalyst Masterbatch	5.0%
Silmix 59 D-2 Silane Liquid Blend	1.6%

Table #2 – Operating Conditions 88.9 mm Double Mixing Screw

Screw Speed	Output Rate	Melt Temperature	Power Consumption
20 RPM	40.0 kg/hr	207°C	3.5 Kw
40 RPM	82.3 kg/hr	223°C	10.8 Kw
60 RPM	128.6 kg/hr	236°C	20.0 Kw
80 RPM	163.2 kg/hr	240°C	30.5 Kw

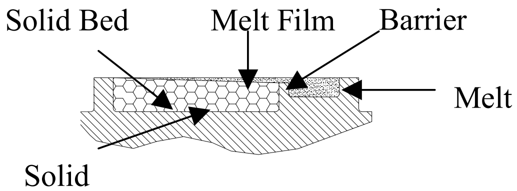
Table #3 – 88.9 mm Data Scaled to 75 mm

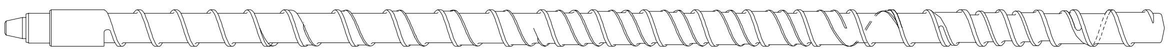
Screw Speed	Output Rate
22.7 RPM	28.5 kg/hr
45.4 RPM	58.6 kg/hr
68.1 RPM	91.5 kg/hr
90.9 RPM	116.2 kg/hr



Feed	Transition	Meter / Mixing
5 L/D	7 L/D	18 L/D
16 mm		5.3 mm

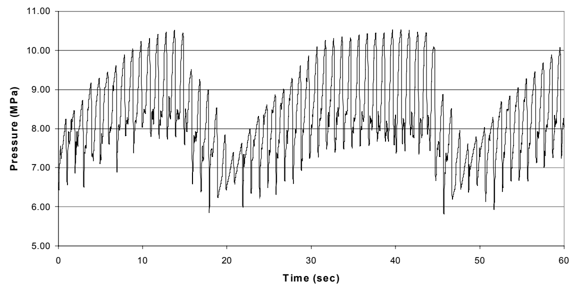
Figure #1 – 88.9 mm 30:1 L/D Double Mixing Screw



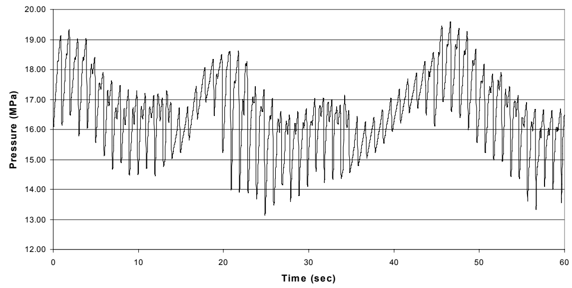


Feed	Barrier	Meter / Mixing
5 L/D	14 L/D	13 L/D
14 mm		5.6 mm

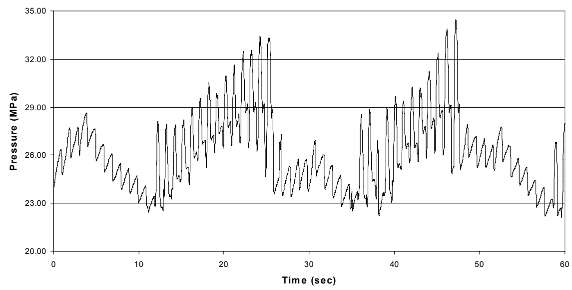
Figure #2 – 75 mm 32:1 L/D DSB-V Barrier Screw



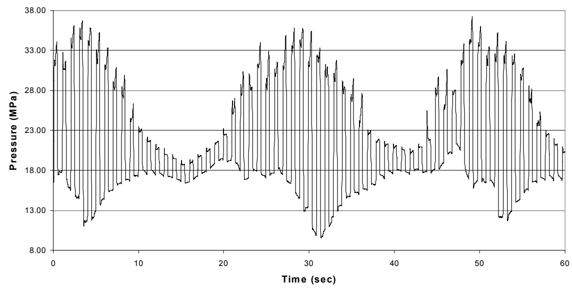
Pressure Transducer #1 @ 4.5 L/D



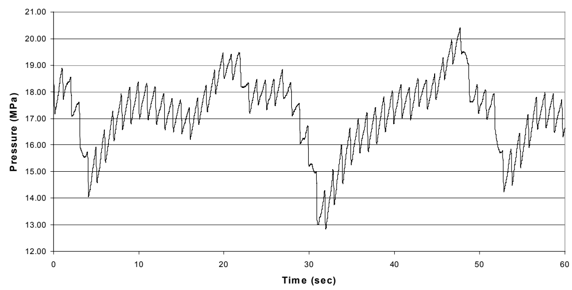
Pressure Transducer #2 @ 9 L/D



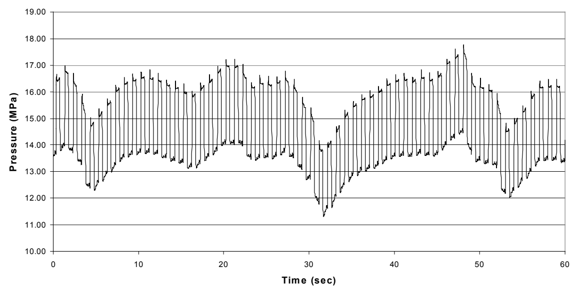
Pressure Transducer #3 @ 13.5 L/D



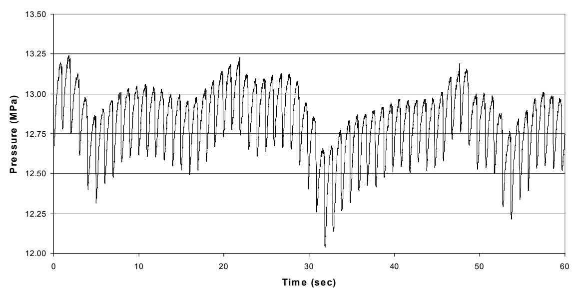
Pressure Transducer #4 @ 18 L/D



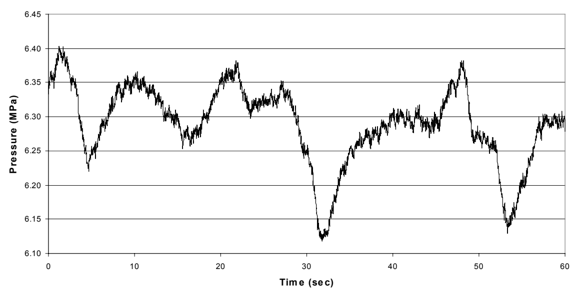
Pressure Transducer #5 @ 22.5 L/D



Pressure Transducer #6 @ 27 L/D



Pressure Transducer #7 – Breaker Plate



Pressure Transducer #8 – In Tooling

Figure #3 – High Speed Pressure Traces