

PEXIDAN TECHNICAL BULLETIN



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What is Cross-linked Polyethylene?

To understand what cross-linked polyethylene is, or PEX and XLPE as it is sometimes called, it is useful to know a few general concepts about polymers. The chemical structure of a polymer is a series of molecular “chains” of various lengths and may even have a branched geometry. These chains are usually “tangled” up in each other to some extent depending upon the temperature and applied stress. When the polymer is heated towards its’ melting point these chains begin to move and slip between each other. This is the phenomena that allows a polymer to flow during processing such as extrusion or injection molding.

A *thermoplastic* is a polymer that can be melted and re-melted over and over again. A *thermoset* polymer is one that cannot be re-melted once it has been set. In the context of the above discussion a thermoset polymer is one that has an infinite molecular weight and the structure is that of a “network”. There are chemical bonds that are formed between the polymer chains and these effectively reduce the mobility, which in turn prevent the material from flowing. This is a rather simplified explanation but it serves the purpose of this document.

Cross-linked polyethylene is a thermoset that is produced by creating an infinite molecular weight polymer of polyethylene.

Why Cross-link Polyethylene?

Cross-linking polyethylene improves some of the physical properties of the polymer as compared to the thermoplastic version. The most significant change is the performance at elevated temperatures. Properties such as tensile strength, elongation, permanent set and deformation are improved at temperatures where a thermoplastic PE would melt. This makes cross-link PE suitable for applications such as wire insulation, hot water pressure pipe and shrink tubing.

Other properties that are improved by cross-linking are stress crack, abrasion and chemical resistance. It is also important to mention that the elevated temperature performance is achieved without sacrificing the low temperature performance. The cross-linking simply expands the service temperature range of the polyethylene.

Methods of Cross-linking Polyethylene

There are three common methods for producing cross-linked polyethylene; peroxide, moisture and irradiation. Each method is slightly different, has advantages and disadvantages but they all end up with essentially the same product; a *thermoset* polyethylene. It is useful to discuss each method and some of the advantages/disadvantages of them.

1) Peroxide

This method is the oldest and most well established. An organic peroxide is used to initiate a free radical chemical reaction in the polymer. These free radicals abstract a hydrogen ion from a polymer chain, which enables it to combine with another chain. This reaction is repeated and the result is the infinite molecular weight polymer discussed above.

The peroxide is melt compounded into the polyethylene at temperatures below its’ decomposition point. The final product is then formed and the temperature is increased to initiate the reaction. In wire extrusion this is achieved by the use of a high-pressure steam tube downstream from the extruder. As the wire exits the die it goes into the tube, which is usually several hundred feet long, and the steam supplies the heat required. This process is referred to continuous vulcanization or CV.

In pipe extrusion the method used is called the Engel method. Again the peroxide is melt compounded cold into the PE, but the material is “rammed” through a high pressure/high temperature head and exits as a cross-linked pipe. The table in Appendix 1 lists the advantages and disadvantages of the peroxide method as compared to the other two.

2) Irradiation

The irradiation method uses a high-energy electron accelerator to cross-link the polyethylene. The finished product is made and then cured off-line by exposing it to the electron beam. The chemistry is similar to that of the peroxide process in that it is a free radical reaction, but instead of peroxide to initiate the reaction it is the electron beam that is used.

To better describe this process consider the manufacture of cross-link pipe or wire. The polyethylene is extruded using regular thermoplastic equipment and can be processed at high speeds. The resin may contain special additives to accelerate the cross-linking process but it is not absolutely necessary. The next step would be to take the large coil/reel of pipe or wire and re-wind it through the electron beam unit. These units are usually quite large with thick walls and cost in the order of three to five million dollars. The rate of curing is dependent upon wall thickness and it may even be necessary to run the product through the unit twice to ensure uniform curing.

It is worth mentioning that there are companies who specialize in irradiation “toll curing”. One can send large reels of the product to these facilities and they will cure the product with their electron beam units. Obviously this eliminates the need to buy the unit but there is a cost and there are logistical issues with doing this.

3) Moisture Cure

The moisture cure method has several variations on a theme and it is useful to understand what they are, but the chemistry is the same. A copolymer of ethylene and vinyl silane will undergo a reaction with water, in the presence of a catalyst, to form the infinite molecular weight polymer. These methods are described as either one or two step processes.

Similar to the irradiation method the product is made on thermoplastic processing equipment and then cured off-line by exposing it to moisture. The cure rate is dependent upon moisture level, temperature and wall thickness. The curing can be accelerated by use of a low-pressure steam environment or hot water but it is possible to cross-link under “ambient” conditions.

i. Reactor Copolymers

The copolymer of ethylene and vinyl silane is made in a reactor via the high pressure free radical process. This resin is then mixed with a catalyst masterbatch just prior to processing, hence the terminology “two step”. At this time the technology is limited to the manufacture of a low density polyethylene. The catalyst masterbatch usually will contain other additives such as antioxidants, stabilizers, process aids and flame retardants. The use level will depend upon the application but can vary from 5-50%.

ii. Reactive Extrusion (Sioplas)

The so-called Sioplas method, patented by Dow Corning in the late ‘60s, utilizes the reactive extrusion to graft vinyl silane onto the backbone of the polyethylene. As with the reactor copolymer, this graft resin is then mixed with a catalyst masterbatch just prior to processing, so it is also a two-step product. The catalyst masterbatch will contain many of the same additives as described above.

While both methods produce an ethylene-vinyl silane copolymer, there are some differences between the graft and reactor products that should be understood. In the reactor product the vinyl silane is part of the main polymer chain as compared to the Sioplas product where the vinyl silane is grafted onto the chain. It is believed that this accounts for the difference in curing time/shelf life between the two products. The grafted product cures faster than the reactor copolymer which is a definite advantage because it has an

effect on finished goods inventory and energy consumption. Conversely, the faster cure time means that the product has a shorter shelf life. Moisture cure will start to cross-link even without the catalyst but it is very slow. Nevertheless the graft product does have a finite shelf life if precautions are not taken, some of which will be discussed in more detail in the "Processing" section of this bulletin.

The second significant difference between the two products is the range of polymers that can be made. As mentioned the reactor process is limited to a low density resin, where the Sioplas process can utilize almost any polymer that contains ethylene in the backbone. This means that one can start with any density PE, EVA, EPR, CPE, EMA and many others, allowing one to tailor the product for the specific application. This flexibility allows the graft product to potentially be used in applications beyond the cable and pipe markets.

iii. Monosil

The Monosil process, which is based on the Sioplas technology, was developed in the mid '70s by a cable manufacturer. It is referred to as the one step process because the grafting, mixing and finished product extrusion is done simultaneously. The polyethylene resin is fed into the extruder and a solution of silane, initiator and catalyst is injected into the barrel. The grafting reaction occurs during the extrusion and the material is put onto wire as it exits the die. The example here is wire but theoretically this could also be done for pipe extrusion.

One of the big disadvantages of this process is that it requires a longer extruder than one would normally use for thermoplastic processing and also a special screw design. It also requires the processor to handle potentially hazardous liquid chemicals that he would not usually have. Another problem is the limitation of additives that can be used. Certain stabilizers, antioxidants and flame retardants will interfere with the grafting reaction so it is difficult or impossible to use them in a Monosil process. On the positive side this process does offer good economics on the raw material side but this needs to be weighed against the capital investment, scrap rates and intangibles such as material handling issues.

iv. Dry-Sil

The last variation of moisture cure products is a relatively new one. It is very similar to Monosil except that instead of using liquid additives, the silane, initiator and catalyst are absorbed into a porous polyethylene resin. This "sponge-like" resin can reportedly hold up to 40% liquid and is used as a masterbatch. It is mixed with a suitable polyethylene resin, by the processor, just prior to extrusion. After that it behaves much like Monosil and has the same advantages/disadvantages. It should be noted that it is a new technology and at this time still unproven.

PROCESSING PEXIDAN

Materials Handling

Pexidan is always a multi-component system consisting of the graft or base resin (A-XXXX) and a catalyst masterbatch (CAT-XXX). The base resin is the product that has a shelf life so it is good practice not to open the package until ready to use. Once the package is open it should be used or re-sealed if possible. It is also strongly recommended to have first-in, first-out (FIFO) inventory procedures in place. The Pexidan lot number contains the date of manufacture and one should always use the oldest material before moving on to the new lot.

For best results it is recommended that the catalyst masterbatch be dried to remove any residual moisture, which could cause processing problems such as gels or fish-eyes. It should be dried for at least four (4) hours at 150°F (60°C) in a desiccant dryer with a -40° dewpoint. Again, this is only the catalyst that should be dried and *not* the base resin. If color concentrates are used it is also recommended that these be dried under the same conditions.

Once the materials have been pre-dried it is important to mix them in the correct proportions. Gravimetric mixing systems are preferred, as the accuracy is much better than volumetric. Error for the latter type can be as high as 4% depending upon the type of materials being handled. It is important to note that Pexidan systems are always given as a weight percent.

Extrusion

A good guiding principle for extruding Pexidan is to get it through the extruder as quickly as possible. If the material is exposed to heat for too long a time, "scorching" can occur, which is actually very localized cross-linking. For the same reason it is important the extrusion line be streamlined so that there are no dead spots where the material can "hang-up". If this occurs there will eventually be lumps on the finished product. The head and tooling are usually where this occurs the most and it will be discussed in the next sections.

There are several different types of screw designs that can be used to extrude Pexidan but they must all be polyethylene screws. Barrier-Maddock screws can be used but the temperature profile should be about 20°F colder than for a non-barrier screw. Chromed screws are good as the material has less of a tendency to stick. The screw should have a short transition zone and the Maddock section should be two diameters from the end. Screws with mixing pins or multiple stages are not recommended. These details are summarized in Appendix 2.

Tooling

This is perhaps the most critical part of the extrusion line because it is here that the material does have a tendency to stick. The tooling should be streamlined to avoid dead spots and again chroming is preferred.

a) Pipe

For best results it is recommended that slightly oversize tooling be used. A drawdown ratio of 25% will give improved surface finish, less die build-up and lower head pressures. It is possible that some experimentation will be required to find the ideal drawdown for different pipe sizes. Shorter die lands are suggested to give optimum surface finish.

b) Wire and Cable

A pressure set-up is recommended for wire extrusion as opposed to tubing. Drawing down can be done but care must be taken not orient the polymer too much and adversely affect the tensile properties. Orientation can also cause an increase in “shrink-back” which may be a problem for small size solid conductors. On a positive note drawdown will reduce the amount of die build-up.

Low volume heads are recommended because they are more streamlined and there is less chance of material hanging up and scorching. Tooling should be on size and the land length should be the same as the wall thickness of the cable.

Curing

The fastest method of cross-linking Pexidan products is to force cure, which can be achieved by exposing them to elevated levels of humidity and temperatures. The most practical way to do this is to use a low pressure steam chamber. Consisting of four walls, a steam inlet and a drain, it is easy and economical to build. The steam chamber can easily attain a temperature of 160°F and 90% relative humidity, which is sufficient to cure most products within 2-24 hours depending on the thickness.

Hot water is another method of induced curing but it can be more difficult. Re-circulating hot water through a pipe or total immersion of the product(s) in a hot water bath are two examples of this method. The latter method can be a problem if one is dealing with very large products such as a 48-inch reel of wire.

The third method of curing is so called “ambient curing”, where the product is left to cure with the moisture levels in the air. This method works well for products with low wall thickness and in geographical areas that are humid and hot. Nevertheless this method does require longer times than an induced cure. Instead of hours the time scale is in days or even weeks so there is a negative with regards to inventory. If this is manageable then ambient curing is feasible for some products and obviously has the advantage of being cleaner and inexpensive.

Padanaplast USA can help you with questions regarding the curing of Pexidan products and even tailor make compounds with different cure rates. Catalyst types and levels have an effect on the rate and we can probably provide one to meet your needs. However, it should be mentioned that there are compromises required, as a faster catalyst system could be more difficult to process.

APPENDIX 1

COMPARISON OF CROSS-LINKING METHODS

METHOD	ADVANTAGES	DISADVANTAGES
Peroxide	<ul style="list-style-type: none">➤ High levels of cross-link density (gel) are attainable➤ Lower raw material costs	<ul style="list-style-type: none">➤ High capital investment➤ Slow production rates➤ Energy intensive➤ High scrap rates
Irradiation	<ul style="list-style-type: none">➤ Clean (pipe) because there are fewer additives➤ High production rates➤ Lower raw material costs	<ul style="list-style-type: none">➤ Cross-link density can vary➤ High capital investment or logistical problems to cure➤ Post extrusion step required
Moisture	<ul style="list-style-type: none">➤ Low capital investment➤ High production rates➤ Low scrap	<ul style="list-style-type: none">➤ Post extrusion step required➤ Slightly higher raw material costs

APPENDIX 2

COMPARISON OF MOISTURE CURE TECHNOLOGIES

TECHNOLOGY	ADVANTAGES	DISADVANTAGES
Reactor Copolymer	<ul style="list-style-type: none"> ➤ Long shelf-life ➤ Low capital investment 	<ul style="list-style-type: none"> ➤ Slow curing ➤ Low density product only ➤ Higher raw material costs
Graft Copolymer (Sioplas)	<ul style="list-style-type: none"> ➤ Fast curing ➤ Versatility of base resins (i.e. LDPE, EVA, EPR, CPE, etc) ➤ Low capital investment 	<ul style="list-style-type: none"> ➤ Limited shelf-life ➤ Higher raw material costs
Monosil	<ul style="list-style-type: none"> ➤ Low raw material costs ➤ Versatility of base resins ➤ Fast curing ➤ Shelf-life not an issue 	<ul style="list-style-type: none"> ➤ Use of additives such as flame retardants and stabilizers, limited or impossible ➤ Handling of hazardous liquid chemicals ➤ High scrap rates ➤ High capital investment
Dry-Sil	<ul style="list-style-type: none"> ➤ Potential low material costs ➤ Versatility of base resins ➤ Fast curing 	<ul style="list-style-type: none"> ➤ Use of additives limited or impossible ➤ High scrap rates ➤ Moderate capital investment ➤ Limited shelf-life

APPENDIX 3

CHARACTERISTICS OF EXTRUSION LINE FOR PEXIDAN

- 24:1 L/D minimum extruder
- Maddock or Barrier-Maddock screw design with a 3:1 compression ratio; short transition zone
- No screw cooling
- Chroming screw and tooling is advantageous
- Pressure regulating devices such as gear pumps are not recommended
- Mixing equipment either on top or adjacent to extruder
- Desiccant dryer capable of -40° dewpoint for drying the catalyst and color concentrates is recommended

PIPE EXTRUSION

- Temperature profile of 320-360°F along barrel; head and die zones may be slightly higher for better surface finish
- Drawdown of approximately 25%
- No screen packs
- Pre-conditioning of extruder with a process aid concentrate is recommended

WIRE AND CABLE EXTRUSION

- Conductor preheat of 180-200°F for small sizes to improve adhesion and physical properties
- Pressure tooling is best; short lands improve surface
- On-size tooling
- Low volume head
- Screen pack 20/60/20
- Water temperature in first trough should be 120-140°F for optimum tensile properties and surface finish
- Temperature profile of 310-340°F along barrel; head and die may be higher for better surface finish; melt temperature of approximately 365-380°F
- Small flame on die to prevent die drool and improve surface finish

APPENDIX 4

Troubleshooting Guide

<u>Problem</u>	<u>Possible Cause</u>	<u>Suggested Remedy</u>
Poor Surface Finish	Moisture in catalyst masterbatch Drooling Temperature too low Poor die design	Dry catalyst Place flame at die tip Raise temperature profile Decrease die land/increase drawdown
Gel formation	Moisture in catalyst masterbatch High melt temperature Old product Excessive residence time Scorched material	Dry catalyst Verify/reduce temperature profile Verify production date - have product checked if more than 3 months old Increase screw RPM/check for bridging in feed section Inspect/clean tooling and extruder
Low Output	Bridging Low melt temperature High back pressure	Decrease temperature in feed section Increase temperature profile Change screens/increase gum space
High Melt Temperature	Incorrect temperature profile Die Design Screens clogged Screen pack too fine	Reduce temperature profile Decrease die land Change screens/determine source of clogging Use coarser screens or reduce number
Creasing	Too much vacuum Die too small	Decrease vacuum Use larger die

<u>Problem</u>	<u>Possible Cause</u>	<u>Suggested Remedy</u>
Voids/skipping	Too rapid cooling	Use hot water in cooling trough as per recommendations
Poor Adhesion /Shrinkback on Conductor	Conductor too cold Too rapid cooling	Preheat conductor Use hot water in cooling trough as per recommendations
Insufficient Crosslinking	Insufficient cure time Insufficient or no catalyst masterbatch Poor catalyst masterbatch dispersion	Verify cure time and temperature Verify/correct blend ratio per recommendations Review/revise blending procedures
Poor Flame Retardancy	Low masterbatch level Low cure level	Check S.G. and blender operation Wait additional time to retest or force cure before testing
Low Tensile Strength	Moisture in masterbatches Rapid cooling Test problem	Increase drying time Use gradient cooling Verify sample condition and crosshead speed