

Slide 1

MICROPOL

WHAT IS CROSSLINKED POLYETHYLENE AND WHY DO WE USE IT?

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This slide features a red background with a white envelope-shaped logo in the top right corner containing the word 'MICROPOL'. The main title is centered in bold black text. Below the title, a bulleted list identifies the speaker as M J Rogerson B.Sc, Technical Director at Micropol Ltd.

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PE MOLECULAR STRUCTURE

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POLYETHYLENE MOLECULAR STRUCTURE.

This slide has a red border and a light pink background. At the top, the title 'PE MOLECULAR STRUCTURE' is underlined. Below the title is a diagram showing several long, black, wavy lines representing polymer chains that are intertwined and cross-linked. In the top right corner of the diagram area is the 'MICROPOL' logo. Below the diagram, the text 'POLYETHYLENE MOLECULAR STRUCTURE.' is written in a smaller font.

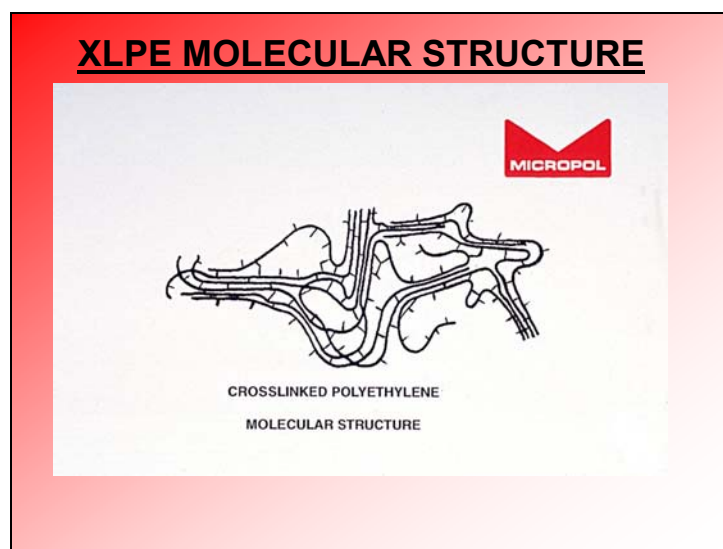
1.1 STRUCTURE [Slide 2]

To understand this topic we need to know a little about the basic structure of the polyethylene polymer. Polyethylene in its various forms is essentially a long chain carbon-based polymer. The chains are not linked directly to each other, but the basic structure is held together by entanglement of the long chains and, in the more crystalline areas, by weak intermolecular forces. Application of heat to this polymer allows the molecules to move relatively easily with respect to each other. The material is thus easily processed and its basic structure gives a tough, flexible material with excellent tensile and impact properties.

For example, high density grades of polyethylene having medium to high molecular weight and only short chain branches can be extruded into pipes which exhibit excellent pressure resistance and low creep characteristics at room temperatures.

However, at higher temperatures a major weakness of polyethylene is that the material starts to become softer and more elastic due to the polymer chains separating and moving and the material has less resistance to tensile and creep forces. Improvements in polyethylene's pressure performance can be made by adopting as near as possible a linear, i.e. an un-branched structure, and having as high a molecular weight as possible, but the basic property of lack of resistance to heat still applies.

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1.2 CROSSLINKED POLYETHYLENE [Slide 3]

The creation of direct links or bonds between the carbon backbones of individual polyethylene chains forms the crosslinked polyethylene structure. The result of this linkage is to restrict movement of the polyethylene chains relative to each other, so that when heat or other forms of energy are applied the basic network structure cannot deform and the excellent properties that polyethylene has at room temperature are retained at higher temperatures. The crosslinking of the molecules also has the effect of enhancing room temperature properties. Sioplas consists of chemically modified polyethylenes which are capable of being crosslinked.

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WHAT USEFUL PROPERTIES DOES CROSSLINKING POLYETHYLENE GIVE? *[Slide 4]*

2.1 TEMPERATURE RESISTANCE

Crosslinking polyethylene changes the polymer from a thermoplastic to a thermoelastic polymer. Once it is fully crosslinked, polyethylene tends not to melt but merely to become more flexible at higher temperatures.

Low density polyethylene film grades which have been designed for medical applications, for example, have been autoclaved at 130°C without losing their properties. Low density grades for cable, foam and foam tube applications have been thermally aged at 150°C, again without loss of properties. Medium and high density pipe samples have been thermally aged at 190°C without losing their shape and size.

The influence of crosslinking on polyethylene can be seen by the fact that non-crosslinked polyethylene grades melt at temperatures between 100 and 130°C.

2.2 PRESSURE RESISTANCE (STRESS RUPTURE RESISTANCE)

Crosslinking improves this property at room temperature, reducing tendency to creep. At high temperatures the improvement comes by reducing relative molecular movement. At elevated temperatures crosslinking allows the properties of the original base polyethylene to be preserved. Thus crosslinked high density polyethylene, which has closer packing of the chains and an intrinsically higher pressure resistance, is used for higher pressure applications than crosslinked low density polyethylene. So for flexible underfloor heating pipes a minimum density of 0.935 to 0.940 is necessary to meet relevant pressure regulations and for hot sanitary water pipes, which have to meet more stringent requirements, a minimum density of 0.945 to 0.950 is required. Crosslinkable polyethylene for hot sanitary applications will meet the standard DIN 16892 test, which has a pressure requirement of 8000 hours at 110°C at 2.8 mega pascals hoop stress.

2.3 ENVIRONMENTAL STRESS CRACK RESISTANCE (ESC)

Crosslinking polyethylene dramatically improves this property at room and elevated temperatures. High density homopolymers grades of polyethylene which fail dramatically under the influence of applied stress and known cracking agents can, in their crosslinked form, outperform high molecular weight polyethylene copolymers.

2.4 RESISTANCE TO UV LIGHT

There is some evidence that crosslinking improves performance in UV light. The theory behind this is that there are more bonds to break before embrittlement occurs.

2.5 CHEMICAL RESISTANCE

The basic crosslinked structure physically inhibits the diffusion of aggressive chemicals. The material is thus rendered more resistant to permeation and softening by these chemicals.

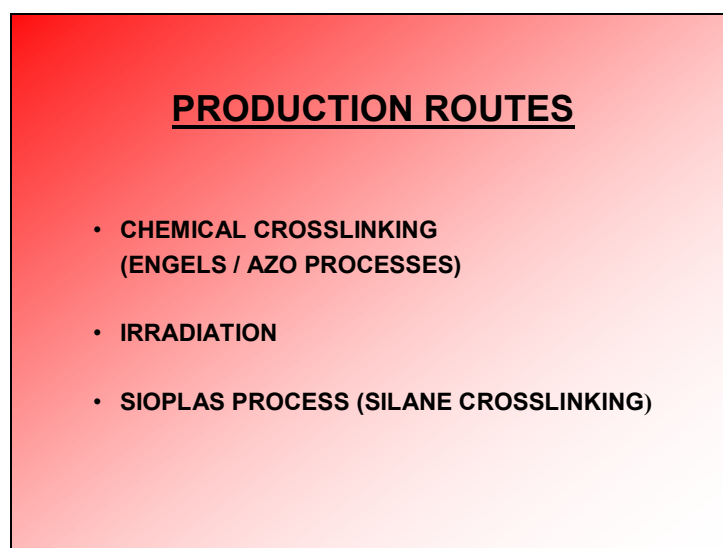
2.6 OXIDATION RESISTANCE

DSC and DTA measurements have shown that the oxidation resistance of crosslinked polyethylene is improved against the un-crosslinked version.

2.7 ROOM TEMPERATURE AND LOW TEMPERATURE PROPERTIES

Crosslinked polyethylenes historically have found their major applications in the cable and pipe industries at elevated temperatures. However, recent interest in the gas, oil and water distribution industries has led to a re-evaluation of XLPE's room and low temperature properties, particularly of impact and creep. Initial data suggests useful improvements over polyethylene in this area.

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PRODUCTION ROUTES

- **CHEMICAL CROSSLINKING
(ENGELS / AZO PROCESSES)**
- **IRRADIATION**
- **SIOPLAS PROCESS (SILANE CROSSLINKING)**

3 METHODS OF CROSSLINKING POLYETHYLENE [Slide 5]

These fall into three main types:

1. Chemical Crosslinking (Engels / Azo Process)
2. Irradiation
3. Silane Grafting and Hydrolysis (Sioplas Process)

3.1 CHEMICAL CROSSLINKING

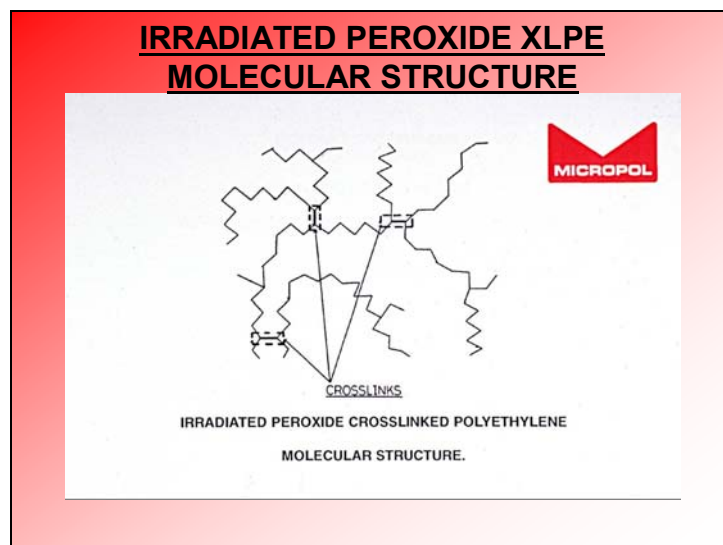
The Engels process uses polyethylene containing a high concentration of organic peroxide. The polyethylene is extruded and held at elevated temperatures for a period of time after extrusion inside long pressure tubes. During this time the peroxide decomposes to free radicals which react with the polymer to form carbon-carbon bonds between the polyethylene chains.

The high capital cost of the extrusion equipment necessary for this process has mitigated against its widespread introduction since the 1950's and 60's when it was the first crosslinked polyethylene to be commercially exploited.

The crosslinked structure created (direct carbon to carbon crosslinks between PE. chains) is two-dimensional / planar in character and not as ultimately effective as the Silane grafted structure. It is also restricted to extrusion processes. **[Slide 6]**

The Azo process is similar in nature to the Engels process, using an Azo compound rather than a peroxide. The Azo compound decomposes at very high temperatures, normally in downstream catenary tubes, once again to form free radicals to crosslink the polyethylene chains together.

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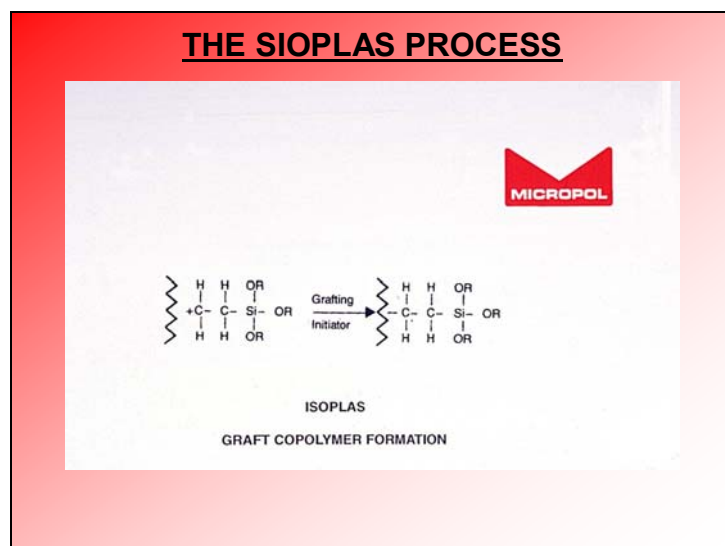


3.2 IRRADIATION

Moulded polyethylene articles or extrusions are passed through an accelerated electron beam (Beta or Gamma radiation) which forms free radicals in the polymer and links directly polyethylene chain to chain. The structure created is planar as in the peroxide (chemical) crosslinking system. The polyethylene used should ideally contain “co-agents”, which adds to the raw material costs.

For pipe production, higher energy beams of up to 10 MeV have to be used to crosslink thicker walled tubes and large coils (several kilometres long) have to be produced, passed through the irradiation chamber, then rewound into smaller coils for sale. The purchase of an irradiation chamber deters all except the largest pipe extrusion companies. Time rental is the usual route for this process.

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3.3 THE SIOPLAS PROCESS [Slide 7]

In this process crosslinkable graft copolymer is formed by grafting short side chains of organosilanes on to the main polyethylene structure. The resulting polymer is still thermoplastic. The grafting process is normally carried out in a high shear extruder. This is normally carried out on a Ko Kneader or twin co-rotating screw extruder, using the extruder as a chemical reactor. The moulder or extruder then blends this graft copolymer with a catalyst masterbatch and extrudes the still thermoplastic material to form the finished product. **[Slide 8, 9]**

At this stage, e.g. pipe extrusion, injection moulding, only a very low level of crosslinking occurs. The bulk of the crosslinking is achieved later by reacting the pipes with moisture, either from hot water baths or a steam chamber. **[Slide 10]**

The water molecules diffuse into the polyethylene and a chemical reaction takes place between water and the end groups of the organosilane side chains. This reaction forms siloxane crosslinks which directly join the polyethylene chains. **[Slide 11]**. The catalyst present merely accelerates the rate of crosslinking and enables economically viable crosslinking times to be achieved. Importantly, the end of any silane side chain is capable of forming crosslinks with three different adjacent silane side chains. This gives a bunch-like crosslink structure having a three dimensional trellis type form. This final crosslink network can be shown to be more resistant to heat and pressure changes than the planar type structures given by the peroxide of irradiation routes. **[Slide 12]**

Silane grafted polyethylenes are increasingly being exploited for a range of reasons.

- a) They can be processed on any equipment capable of handling polyethylene.
- b) The process separates the fabrication and the crosslinking steps. Each can be achieved at optimum conditions.
- c) The capital cost is low. No process equipment modifications are required, merely the addition of a hot water tank or steam chamber for the actual crosslinking process.
- d) The large range of polyethylenes available to be grafted and the nature of the grafting process allow Sioplas graft copolymers to be “engineered” or tailor-made to suit particular processing or product applications. Specific gravity, molecular weight distribution, viscosity, melt stability, crosslinking rate of finished product, can all be adjusted by choice of base polymer and formulation

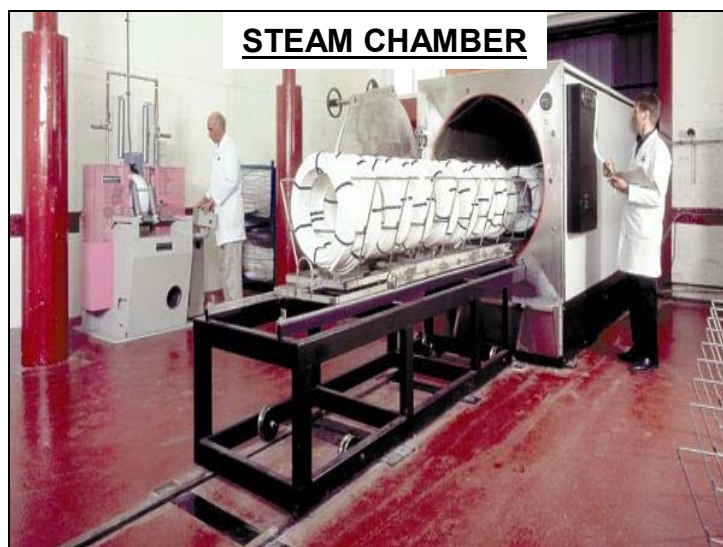
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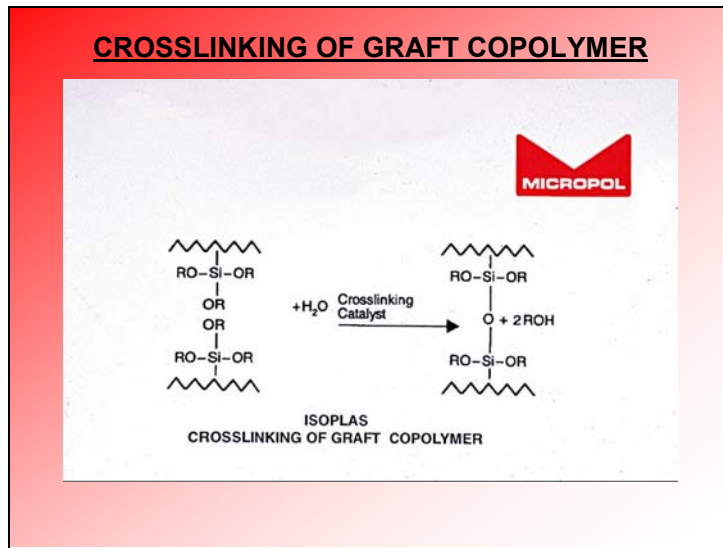
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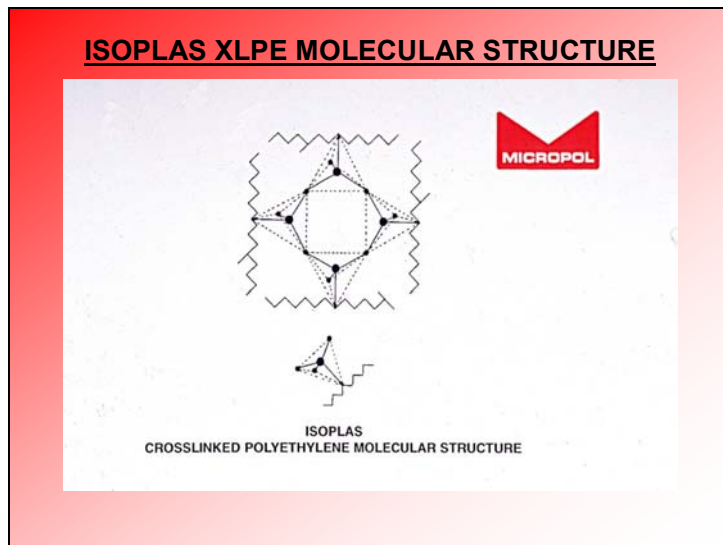
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Slide 11



Slide 12



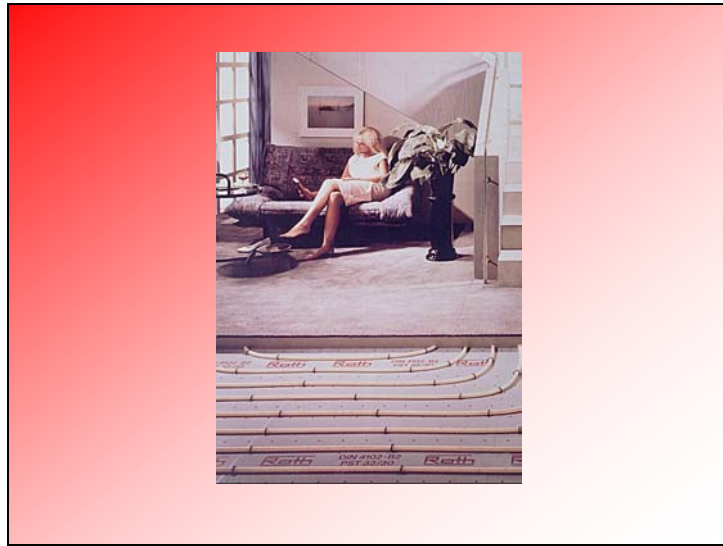
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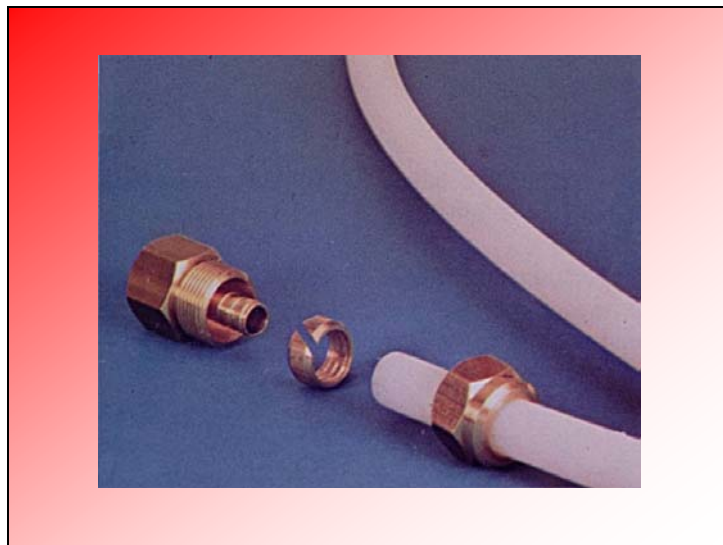
4. APPLICATIONS

4.1 **[Slides 13-19]** Since their introduction in the late sixties, silane grafted polyethylenes have largely been used in the production of power cables, where their use has enabled larger currents to be used without thermal breakdown or softening of the insulation. Together with the other forms of crosslinked polyethylenes, Silane grafted HDPE has achieved big penetration into the market for copper and mild steel replacement in domestic hot water systems. Traditionally the main markets have been in Scandinavia and Continental Europe, but now in the USA, Australasia and Japan XLPE is becoming the material of choice in new buildings and replacement systems. The main advantage over copper and steel is in the speed of installation with push fittings replacing brazed or mechanical joints. The material's insulation properties as well as its resistance to freeze bursts are also important.

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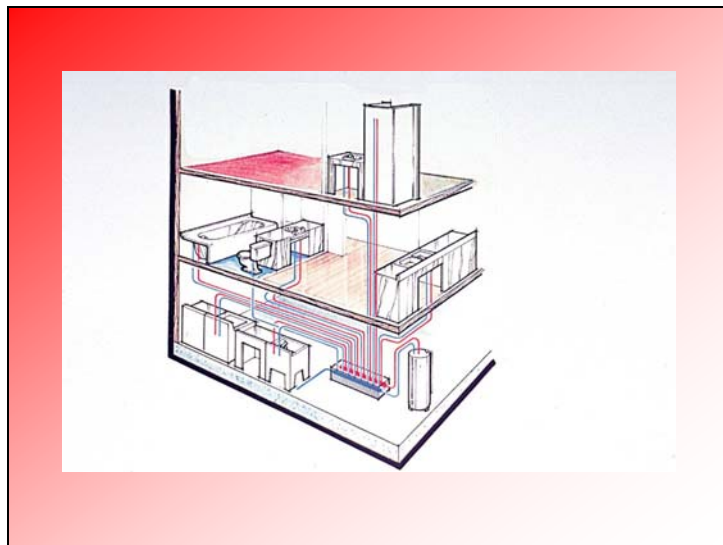
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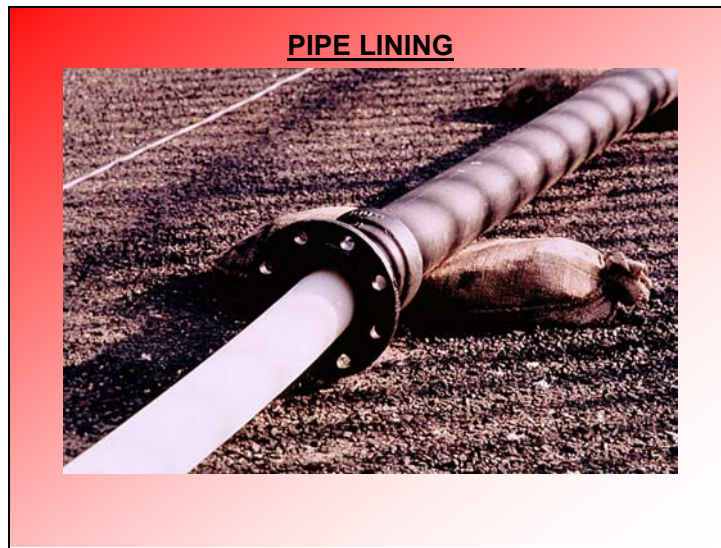
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4.2 In the late nineties newer applications have begun to appear. **[Slide 20, 21]** The SPEX system first presented at the Plastic Pipes X conference in Gothenburg exploits the fact that, uniquely, uncrosslinked Silane grafted HDPE pipes can be produced at diameters of up to 1000mm. These can be welded together and then inserted into existing larger diameter metal pipe systems which have been corroded, damaged, etc., and are no longer serviceable. Once in place the Silane grafted pipe can then be expanded with hot or cold water under pressure to line and repair the pipeline. The crosslink network structure is formed during the expansion process and prevents the necking that would occur in expanding conventional HDPE liners. This system will be applied to the rehabilitation market for gas, oil and water pipes and also to produce new mild steel, XLPE-lined pipes to replace duplex stainless steel pipes in the offshore market. Once in place the XLPE liner will give temperature, chemical and environmental stress crack resistance.

4.3 Silane crosslinked liners are now being used to protect nylon tubes from ESC attack by hot water / ethylene glycol mixtures in underbonnet applications.

4.4 Silane crosslinked injection moulding grades are now being used in pipe fittings. Here they are replacing acetal, polysulphone and polybutylene. Once again any component welding is carried out on the uncrosslinked moulding and the full assembly is then crosslinked.

4.5 The room temperature creep properties of XLPE can be exploited in PE gas pipes, which will withstand a higher pressure than conventional HDPE pipes and thus enable greater volume gas transmission rates to be achieved.

4.6 Coloured, fully crosslinked powders have been used as non-melting decorative particles in EVA and Surlyn Ionomer floor coverings.

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5 SIOPLAS - FUTURE DEVELOPMENTS

The Silane grafting technique has allowed polyethylene to be “engineered” into a copolymer with a much wider envelope of useful properties and applications. Technically the same process could be used to broaden the scope of other commodity polymers. These engineered grafts would bridge the gap in properties and price between conventional thermoplastics and ultra-expensive high performance “engineering” resins. Already EVA, EBA and EPDM have shown promise. A patent exists for crosslinking polypropylene. Other polyolefin structures could well be worth looking at. The reactive nature of the Silane side chains may also be of use in bonding Silane graft copolymers to other polymers in composite structures or in the melt phase of alloys and blends.