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1. Introduction

Heat shrink tubing is a pervasive technology that is seen (or not) in almost every aspect of our daily lives and yet is poorly understood (if at all). Heat shrink products are used in almost all types of electrical products to seal, fit and retain wire connections, to provide electrical insulation by separating wires and also find a wide variety of uses as coverings for rollers and consumer goods.

This Plastics Topic looks at the basics of heat shrink products and shows that, despite their apparent simplicity and common use, they actually use some of the most advanced ideas and concepts in plastics processing. It is no accident that heat shrink products are still developing rapidly as the process and applications are extended and refined.

2. The basic technology

Heat shrinking fundamentally depends on the crystallinity of plastics. It might seem strange to think of polymer as having crystals when all the models of polymers tend to describe them as tangled loops of long chains. This traditional model describes polymers as being like cooked spaghetti with the long polymer chains all tangled up with one another. This is true for amorphous polymers and a representation of the chain orientation in shown below:



Amorphous polymer - Random molecular orientation in both the molten and the solid phase

Many common polymers are not fully amorphous and can be termed semi-crystalline and the structure of this type of polymer is shown below:



Semi-crystalline polymer - Random molecular orientation in the molten phase but densely packed crystallites in the solid phase (the red sections)

The division of polymers into amorphous and semi-crystalline types is actually one of the best ways of dividing up the large number of polymer types and provides a very basic guide to the properties of polymers – crystallinity is one of the fundamental concepts of polymers and their properties. The intricacies of crystallinity are dealt with in another Plastics Topic.

For now, it is sufficient to understand that the semi-crystalline polymers have small areas of "crystallites" when they are solid. These are not crystals like you would see in salt or other traditional crystals but are small areas of short-range order in the otherwise amorphous mass.

Heat shrinking also fundamentally depends on the process of cross-linking in polymers, again one of the fundamental divisions of the family of polymers. When in the molten state, the traditional

thermoplastics consist of a series of random chains that are essentially independent of one another apart from being tangled up with one another (the spaghetti model shown above). Some polymers have "cross links" between adjacent polymer chains. The cross links can be produced naturally in the polymer (these are known as thermosetting plastics) or by special methods for the traditional thermoplastics. In any polymer the cross links prevent further melting of the polymer and can be thought of as acting as small springs linking adjacent polymer chains. Cross-linking can be thought of as giving the polymer a "memory" of the shape it was in at the time of cross-linking.



Cross-linked semi-crystalline polymer showing cross-links between adjacent polymer chains (the green sections)

The process of producing heat shrink products is as follows:

- Form: The product is formed by one of the traditional plastics processing methods, i.e., extrusion or moulding.
- Cross-link: The material is cross-linked to form the essential cross-links or "springs" between the adjacent polymer chains.
- Stretch: The material is stretched to the expanded form and the cross-link "springs" are stretched under the load.
- Solidify: The material is cooled to a solid whilst still expanded and the crystallites form to lock the material in the expanded or stretched form.
- Remove stretching load: The stretching load is removed and the product is ready for delivery to the customer.



Producing heat shrink products

The process of using heat shrink products is then as follows:

- Heat: Heat is applied to melt the crystallites. The heat source can be a hot air gun, a gas flame or an oven (IR or conventional) when automated production lines are used.
- Shrink back: After the crystallites have melted the stretched springs in the cross-links are free to shrink back to their unstressed length and cause the material to shrink back to the original formed size.
- Cool: The material is cooled to allow crystallites to form again and to lock the material into place in the shrink fit condition.

It is important to realize that after cross-linking and shrinking into place the previously thermoplastic material is now a thermoset material and applying further heat will not melt the material but will lead to charring and eventual burning.



Applying heat shrink products

3. Cross-linking

The essential step in the production of heat shrink products is the cross-linking process and several methods are available to manufacturers to produce the essential cross links in the previously thermoplastic polymer.

Whichever type of cross-linking method is used the polymer after cross-linking generally has improved properties as a result of being changed into a thermosetting material. Improvements are seen in many areas such as general mechanical properties (modulus, strength, creep and impact), chemical resistance (general resistance to chemicals, stress cracking and swelling), thermal properties, abrasion resistance and many other properties.



The methods of producing cross-linked heat shrink products

Radiation cross-linking can use either beta radiation (an electron beam) or standard gamma radiation to create free radicals, break down some of the existing bonds and to promote carbon-carbon bonds to cross-link adjacent chains.

Peroxide cross-linking uses peroxide compounds mixed into the polymer as it is processed. The processed product is then subjected to higher temperatures to decompose the peroxides into free radicals that activate adjacent polymer chains to create the cross-links.

Moisture cross-linking uses silane groups (silicon compounds) that are grafted onto a polymer chain and included with the base polymer as it is processed. The silane groups are activated by moisture in the presence of a catalyst at raised temperatures (>80oC) to form cross-links between adjacent chains. In radiation and peroxides cross-linking the cross-link is a C-C bond but in moisture crosslinking the cross link itself is a -C-Si-O-Si-C- bond.

Radiation (e- beam or gamma) cross-linking		
Advantages	Disadvantages	
 Quick and economic after initial investment. 	 Uses costly radiation equipment and needs high investment in protection and maintenance. 	

Good for thin-walled products.	 Electron beams have limited penetration into thick-walled products. 	
Peroxide cross-linking		
Advantages	Disadvantages	
Good for thick-walled products.	Difficult to use for thin-walled products.	
 Investment required is moderate. 	• The peroxide reaction generates decomposition products such as methane and these can create voids in thick-walled articles.	
 Technology is well developed. 	 Cross-linking must take place at high pressure to prevent the formation of voids. 	
Moisture cross-linking		
Advantages	Disadvantages	
 Low initial investment and entry costs. 	 Can be more expensive for long runs of standard products. 	
 Good processing window for most polymers. 	Developing technology.	
 Products can be cooled quickly after processing. 		

4. Shrink ratio

The "shrink ratio" of a heat shrink product is the ratio of the pre-shrink dimensions to the after-shrink dimensions. The diagram below shows the shrink ratio for tubing products.

Shrink ratio = Pre-shrink diameter/After shrink diameter



Shrink ratio for tubing products

This is an important value for the selection of heat shrink products. In the case above, the pre-shrink diameter must be large enough to fit over any terminations or end connectors and the after-shrink diameter must be small enough to provide sealing and insulation of the cable or termination.

The shrink ratio varies with the material (some can withstand more expansion than others before plastic deformation occurs) and the type of cross-linking treatment used. The shrink ratio can vary from 1.2:1 to up to 6:1 for some specialist materials.

5. The materials

A wide range of materials can be processed to form heat shrink products and the selection of a material for a specific heat shrink application is similar to the selection of a material for any other application. The only significant difference is that the shrink ratio of materials varies widely and as with any other materials selection criteria, if a high shrink ratio is needed then the number of applicable materials decreases rapidly.

Some typical materials used for heat shrink products and their approximate heat shrink ratio are given in the diagram below:



The approximate heat shrink ratio for some of the materials used in heat shrink products

The selection criterion inevitably involves a combination of the maximum working temperature and the applicable shrink ratio and engineers often need to combine the two selection criteria to select the most appropriate material for the application.

Heat shrink products are covered by a wide range of specifications from organizations such as UL, AMS, VG, VDE, CSA, BS, NATO and SAE. Engineers intending to use heat shrink products should ensure that the selected product meets the relevant standard.

6. Formats

Tubing

The most common type of heat shrink product is simple single wall heat shrink tubing and this is available in a variety of diameters, wall thicknesses and materials to suit a variety of applications such as:

- Mechanical protection
- Cable binding and tying
- Cable marking
- Abrasion protection
- Cable termination covers
- Roller covers and component covering
- Corrosion protection
- Dust proofing
- Medical products (using sterilizable materials)

Single wall tubing is also available in lay-flat format for easy transport and application to products such as fluorescent light tubes and rollers.

Tubing can also be supplied in a dual wall format that combines an outer sheath of shrink tubing with an inner layer of hot melt adhesive or other low melting point polymer. The heating process to activate the tubing shrinkage also melts the adhesive/polymer and as the outer tubing shrinks the shrinkage pressure forces the adhesive/polymer around the cables or product. When the heat is removed the adhesive/polymer forms a watertight encapsulation around the product. These products are used for a variety of applications such as:

- Encapsulation
- Water proofing
- Dust proofing

A typical combination of polymers used in dual wall products is the combination of PTFE and FEP (as the inner lining) to provide encapsulation and sealing.

Moulded products

Heat shrink products are not limited to extruded formats and can include moulded products such as end caps, boots and junction covers. These products can be supplied in many of the formats of standard tubing, i.e., with hot melt adhesive linings to provide integral sealing, to provide integral protection and encapsulation.

Heat shrink tapes

Heat shrink tapes are a special type of heat shrink product where a fabric tape incorporates heat shrink fibres along the length of the tape. The tape can be wound around a joint and when heat is applied the fibres contract to tightly lock the tape around the joint. The tapes can also be supplied with an adhesive lining to encapsulate the joint formed by the tape.

Shrink sleeving

In this Plastics Topic, we have primarily considered heat shrink products as 'industrial' products but one of the largest uses of heat shrink products is as a decorative sleeving or covering for consumer goods, primarily for drinks and other containers. In this case, the printed and branded shrink sleeve/tube is shrunk into place over a generic bottle to brand the bottle where it is either not possible or uneconomic to brand the bottle itself - in this case the shrink tubing is acting as an easy method of applying a label. Shrink sleeve labels are generally manufactured from PVC, PET or OPS and can be decorated by gravure, Flexo or UV Flexo printing methods. It is also possible to use the printing to generate effects such as holographic effects, fluorescent effects and metallic finishes.

Shrink sleeving for bottles is generally shrunk into place by hot air or steam (or a combination) on an automated application line

Cold shrink tubing

Cold shrink tubing is a process where the shrink material, generally a rubber), does not have any crystalline regions and is held in the stretched state by a rigid former. Removal of the former allows the material to shrink back to the original dimensions and seal the wire, joint or fixing. This method has the advantage that no heat is used during the shrink process, a definite advantage in explosive atmospheres, but so far has far less market penetration than conventional heat shrink products.

7. Summary

Heat shrink products are a technology that meets a well-defined market need and as a result the products and applications have developed rapidly to become both an accepted and an indispensable technology. The applications of heat shrink products in industry are well developed but are still growing rapidly in consumer products where their convenience and value-adding capabilities are still being fully explored.