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# HEAT SHRINK TECHNOLOGY AND APPLICATONS: AN OVERVIEW

KEVIN J. BIGHAM, PhD.

## INTRODUCTION

Heat shrink materials have been known and commercially available for nearly 60 years. Most of us are familiar with “shrink wrap”, and many of us may have even used heat shrinkable tubing for repairs around our home or on our car. Stemming from the observation of the peculiar effects of radiation upon plastics, the heat shrink materials industry has grown to a world-wide enterprise whose value is in the billions of dollars (US) today [1]. Heat shrinks are used for applications ranging from form-fitting wire insulation to food wrapping, sensor and connector encapsulation, sterilization protection and packaging, to medical device and aerospace industries. Aside from their copious uses, heat shrink materials opened new avenues of discovery in both material behavior and radiation effects. Indeed, continued study has revealed key insights that continue to be carried forward for today’s and the next generation’s advanced materials.

## ORIGIN AND INVENTION

Heat shrink technology as it is known today can be traced back to the early post-World War II era. As nuclear energy programs sprang up in the United States and elsewhere during this time, scientists began to take notice of the effect of radiation on a variety of materials, including polymers. In the 1950s, among these scientists was Paul Cook working out of Stanford University. In particular, he was interested in the effects of ionizing radiation upon plastics. Cook and others discovered that some plastics took on a heat shrinkable quality after being exposed to radiation [2, 3]. Cook soon commercialized his discovery starting his own company (later to become Raychem). While Cook is largely given credit for bringing heat shrinkable materials to a commercial market, other researchers soon followed his invention. By the early 1960s, heat shrinkable tubings and wrapping were available to the public. Multiple innovations and variations on heat shrinkable products have led to continuous growth in this industry ever since.

## TECHNOLOGY BEGINNINGS

Heat shrinkable materials are part of a larger group of materials that display *shape memory*. These materials have the ability to transition from a permanent (original) shape to a temporary (deformed) shape and back to their permanent shape to varying degrees following the application of some stimulus [4, 5]. This feature is termed the *shape memory effect* (SME), and materials with this ability are known collectively as *shape memory materials* (SMMs). Such materials were first described as early as the 1930s in metal alloys (later termed *shape memory alloys* – SMAs) [6]. Later in the 1940s, shape memory was discovered in polymers [7]. Interest in these *shape memory polymers* (SMPs) grew quickly in large part because of the easier processing of plastics and polymer-based materials compared to metals and the overall lower cost SMPs [8].

Interest in SMPs has thus surpassed that of SMAs leading to the vast commercial enterprise surrounding SMPs.

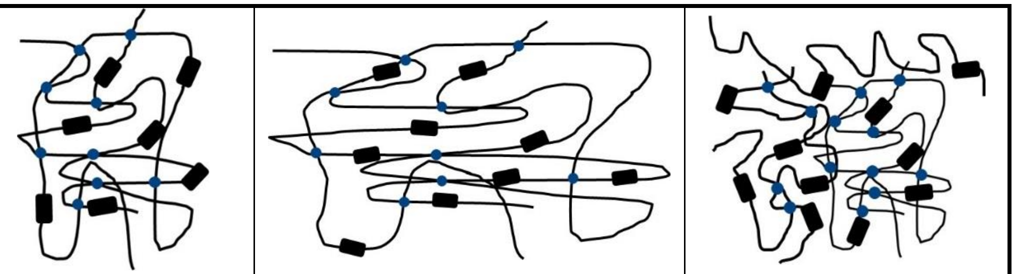
## MORE ON THE SHAPE MEMORY EFFECT

Shape memory materials have the ability to regain their original shape after being deformed and after a particular stimulus is applied to the material. The stimulus can be of a variety of types including acid-base change (pH), light (such as infrared or UV), or chemical exposure (such as water or other liquid) [9-13]. In the case of heat shrink tubing – a highly common shape memory application – the obvious stimulus is heat [4, 14, 15]. SMPs can also be designed to respond to more than a single stimulus [16]. In this way, SMPs provide an adept means to affect localized and acute stimulus to direct re-formation of the original shape.

### General Mechanism

The mechanisms involved in heat shrinkable materials and SME are complex, but some commonalities can be described. For heat shrink polymers (HSPs), solid phase polymers possess crystalline and amorphous regions. To enhance their heat shrinkabilty, HSPs are also almost always crosslinked. With regard to SME and HSPs, these materials can be modeled as a two component system. The amorphous polymer chains represent an elastic component (because they are not constrained as those in the crystalline phase), and the crystalline regions represent a reversible transition component (**Fig. 1**) [17]. Without elastic and rigid (transition) components, the material will not possess heat shrink qualities [18].

Using naive heat shrinkable polymer tubing as an example, after extrusion, the tubing is exposed to a crosslinking agent such as an electron beam (e-beam) to crosslink individual polymer chains **(Fig. 1A**). The tubing is next heated to just above its melting temperature and mechanically expanded (*deformed*, radially) **(Fig. 1B)**. Expanding the tubing also produces some crystallite and amorphous chain alignment from being drawn radially. The tubing is held in its expanded state and quickly cooled to room temperature. As cooling takes place, the transition component – as crystallites – reforms. The elastic component – the amorphous chains – are stretched in the expanded state, and the quick cooling leads to limited or confined amorphous chain mobility. The rapid cooling locks the tubing in its expanded state and gives it its ability to change shape [19]. This fixing of a new temporary shape of the tubing is referred to as the *programming* step. With subsequent heating to just above the melt temperature, crystallites melt along with the amorphous regions. Melting allows the elastic component – stretched and strained amorphous chains – to relax and return to, or *recover*, their original shape **(Fig. 1C)**. The amorphous and crystalline regions become more compact and are less oriented than in the expanded state [19]. Transition element crystallites form more efficiently with the slower cooling further locking the shrunken or *recovered* tubing back in its original shape. (As a note, SME can also be triggered by the glass transition temperature, but this is not the mode for heat shrink materials.) The temperature at which the tubing begins to return to its original shape is thus termed its *recovery temperature*, and the reheating of the expanded heat shrink is called the *recovery* step. Together, the programming and recovery steps constitute the *shape memory cycle*.



**A**
Original

**B**
Expanded: Programming

**C**
Recovery

**Figure 1: Transition and elastic components of HSPs.** Using heat shrinkable tubing as an example, amorphous polymer chains (black lines) provide the elastic component for the expanded tubing. Elastic component energy is supported by crosslinking of polymer chains (blue dots). Crystallites (black rectangles) form the reversible transition component. **(A)** Unexpanded tubing shows only crosslinking. **(B)** *Programming*: The tubing is heated to just above its melt temperature and expanded. Held in its expanded shape, the tubing is then quickly cooled to lock the stretched polymer chains in place storing elastic energy. **(C)** *Recovery*: With the application of heat to the cooled and expanded tubing, the stretched amorphous chains are freed by melting and recover their original (unexpanded) permanent shape. In the recovered state, the polymer chains are more disordered and compact.

## CROSSLINKING

A principal factor that SMMs share is that they require a driving force to return them to their permanent shape from the deformed temporary shape. The transition from a temporary to a permanent shape can be viewed as an energy barrier which must be overcome to affect the transition [20]. In this respect, heat shrink materials are similar to rubbers and elastics. For heat shrinks, which undergo a temporary-to-permanent transition, this energy barrier is high; for rubbers and more elastic-like materials, the energy barrier is low [20]. For SMMs, and in particular heat shrinkable materials, the driving force to return the deformed shape back to its permanent shape stems from the stretched amorphous chains – but with a variation. Heat shrink materials such as heat shrink tubing or wrap feature their polymer chains crosslinked – adjacent chains connected to each other at the molecular level. Crosslinking provides greater elastic recovery force.

Crosslinking can be accomplished by a number of ways. Very long chain polymers can experience entanglement from polymer chains crossing over one another resulting in a kind of physical crosslinking **(Fig. 2A)**. Secondly, there is chemical crosslinking **(Fig. 2B)**. Historically, addition of chemical linkers or additives was required to crosslink polymer chains in this way. However, exposing polymers (plastics) to ionizing radiation also induces crosslinks in the chains; this was the observation made by scientists (ca. 1940s) as nuclear facilities became more available to public and research interests. The creation of crosslinked polymers and formation of covalent bonds in bulk material without a chemical additive was quite surprising to researchers at the time [21].

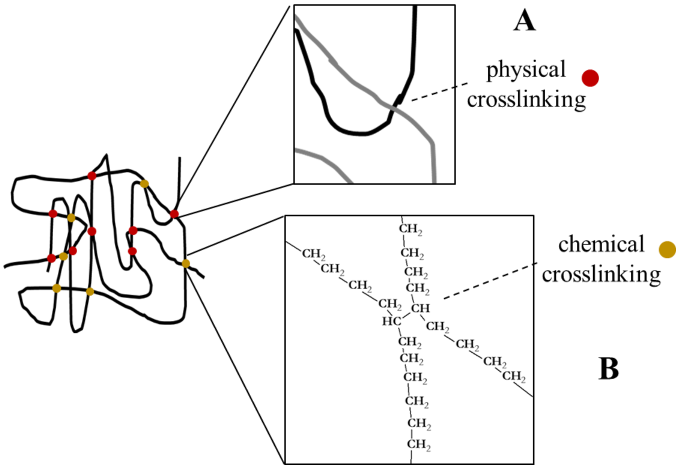


**Figure 2: Crosslinking of HSP chains.** Crosslinking provides the elastic recovery force for heat shrinkable materials such as tubing. Crosslinking may be either physical crosslinking (**A** and *red dots*) from overlapping polymer chains and entanglement or chemical crosslinking (**B** and *gold dots*) via a direct chemical bond between adjacent polymer chains. (Example shown: polyethylene).

Crosslinking of HSPs is vital to impart heat shrinkability and provides several benefits to the material. Crosslinking forms a denser polymer chain network increasing the potential to store elastic energy. Crosslinking also prevents long range chain slippage when under strain. Restricting chain slippage helps to ensure that any shape change is the result of entropy change, which is recoverable [18]. The greater the extent that chain slippage can be prevented (within the elastic range of the elastic component), the greater the HSP recovery potential. Crosslinked materials also typically exhibit improved resistance to impact and stress cracking and may even show increased chemical resistance [22].

For heat shrink materials in particular, the most common method of crosslinking is via radiation such as from an e-beam. Irradiating polymers induces the formation of radicals (unpaired valence electrons) leading to the formation of covalent bonds between adjacent polymer chains **(Fig. 3)**. This form of radiation crosslinking is typically performed under vacuum or in an inert atmosphere and has proven to be quite useful. (Irradiating in air or in the presence of oxygen can lead to unwanted oxidative degradation.) E-beam crosslinking is both rapid and uniform and is comparatively less expensive than using chemical additives [23]. Radiation crosslinked polymers generally possess greater strength and preferred properties at higher temperatures than their non-crosslinked versions [22]. Importantly, effects upon polymers can be controlled by radiation intensity, dose rate, and exposure time allowing some tailoring of the crosslinked material properties.

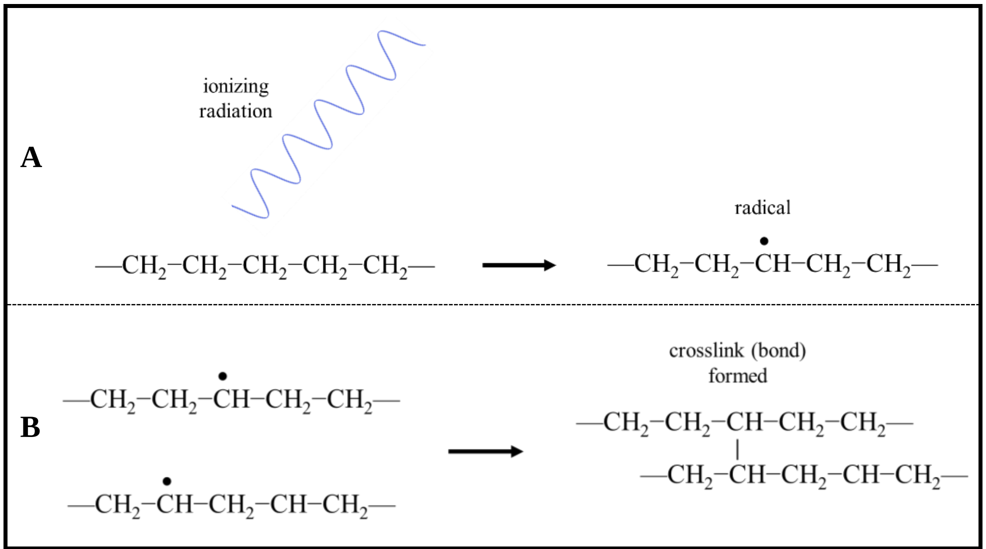


**Figure 3: Radiation crosslinking of polymer chains. (A)** Ionizing radiation induces the formation of radicals (unpaired valence electrons) in the polymer chains. **(B)** Radical electrons pair and form covalent bonds between neighboring polymer chains creating crosslinking. (Example shown: polyethylene).

Irradiating polymers can also have the opposite effect of crosslinking: chain scissioning. For heat shrink materials, crosslinking is necessary. For other applications, chain scission is the goal and has been used to significant advantage in the creation of materials with unusual or improved properties [22]. Some polymers are more prone to crosslinking while others tend towards chain scission, and reference materials exist describing these. (Branching may also occur for polymers with double bonds.) It is not uncommon, however, for scissioning, crosslinking, and oxidation to occur simultaneously during irradiation [24]. Experimental and environmental factors, thus, can be used to influence the preferred outcome of the irradiation [22].

## PRACTICAL CONSIDERATIONS

With a basic understanding of heat shrink materials, there are a number of practical aspects that bear consideration before use. At the outset, for heat shrink tubing, the user should be well-versed in the application intent. A thorough understanding of the potential hazards that the heat shrink must endure is vital for successful application and long usage. Chemical hazards, including moisture, figure prominently in the choice of heat shrink material. Electrical aspects, temperature tolerance, and toughness of the material are also important. These and more should be carefully explored to select a heat shrink that is most appropriate for the application.

### *Component Shape and Heat Shrink Ratio*

A primary consideration for a heat shrink tubing is the shape of the part or component to be covered. Heat shrink ratio – the ratio of the expanded inside diameter (ID) of the tubing compared to its final recovered ID – becomes important here. Smooth, linear parts such as mandrels or wire splices can utilize smaller shrink ratios than parts with more angular and irregular geometries. While some heat shrinks can be produced with up to a 6:1 ratio, not all polymer materials are capable of a ratio this large. Thus, heat shrink ratio can be a limiting factor for the choice of heat shrink material and should be weighed against part shape.

### *Shrinkage*

Aside from the heat shrink ratio, users should anticipate the final dimensions of the heat shrink product. Although heat shrink tubing is expanded radially imparting some radial polymer alignment within the material, recovery culminates in the loss of much of this alignment. Thus, there will likely be some longitudinal shrinkage in addition to the circumferential shrinkage. Secondarily, shrinkage will affect wall thickness of the tubing. If wall thickness is not properly taken into account and an inappropriately thin walled heat shrink tubing is used, shrinkage may result in a recovered wall thickness approaching nil as the material stretches over the covered component.

### *Electrical Considerations*

A large segment of the heat shrink tubing market is devoted to wiring and electrical applications. Users prefer heat shrink tubing that not only protects or secures wiring connectors and splicing but also provides some level of insulating capability. For applications where insulation is required, there will be regulatory provisions that must be met. These requirements also may be unrelated to insulation *per se* such as UL 94 flammability requirements when used over wires. As an example, some polymer heat shrinks with the preferred electrical properties may be disallowed under certain regulatory guidelines. Thus, electrical considerations for heat shrinks may extend beyond just their dielectric properties.

### *Application Environment*

Perhaps the most important consideration for heat shrink materials is the environment where they will be deployed. Obvious elements such as temperature and chemical environment are paramount but should not overshadow other factors. For example, the applied heat shrink may be subjected to physical trauma such as scraping, abrasion, or vibration. Repeated deployments of the heat shrink covered components and rough handling may also pose problems for the wear and tear on the heat shrink. Whether the working environment is dark or brightly lit or whether color coding or transparency is required can also be significant concerns. Also important is whether the heat shrink will be exposed to radiation. These factors and more highlight the importance of a thorough understanding of the environment before proceeding with the selection of a best heat shrink material.

### *Optimizing Recovery*

An often underappreciated matter for heat shrinkable material is the importance of achieving optimal recovery. Uniform heating is vital in this regard. Heating methods vary and have particular advantages and disadvantages. Ovens, for example, provide even heating but are convenient only for discrete lengths and are not portable. Heat guns, on the other hand, can be used in the field but can be difficult to achieve uniform heating. Users frequently modify heat sources such as heat guns with attachments to address uneven heating with varying degrees of success. Heat rings provide uniform heating but are limited by their diameter and require stable positioning of the parts to be covered and the heat ring. Traversing heat sources provide steady and even heating but are also limited in portability. Any heat shrink application should begin with a series of optimization trials to address these concerns. Allowance for waste should be incorporated during the optimization phase. Adopting these first steps will significantly shorten the time to devise an optimum heat shrink recovery technique for the application.

### *Cost*

The cost of heat shrink applications can also be a deciding concern. For some applications, it may be feasible to sacrifice certain heat shrink performance attributes in exchange for a less expensive material. Conversely, it may be more beneficial in the long run to opt for a more expensive heat shrink to attain better performance. Factors such as frequency of use, usage life, and the ability to redeem used heat shrink material through a recycler can sway overall costs of a heat shrink application. Furthermore, disposal costs may also factor into the choice of heat shrink. As plastic waste continues to accumulate worldwide, steps that can mitigate this trend will pay dividends in the short and long term. These factors can have significant impact on attaining a heat shrink that excels in the application at an optimal cost.

## SUMMARY

Heat shrinkable products have proven to be a boon not only economically but also to numerous innovative industries that have found new and creative ways to use them. The discovery of radiation-crosslinked polymers broke new ground for the study of SMMs and HSPs. In very short order highly practical applications such as heat shrinkable tubing and wrap were commercially available. With their easier processing requirements over SMAs, HSPs and products proliferated allowing accelerated study into the structural rearrangement occurring during the heat shrink recovery process. The essential nature of crosslinking helped to focus a mechanistic understanding of SME as well as the heat shrink recovery process. HSPs can be described principally as a two component system possessing an elastic component and a reversible transition component. Irradiation of polymers is now commonplace not only to produce heat shrink materials but also for enhancing material properties for applications unrelated to heat shrinks. With the plethora of heat shrinks now available, it is incumbent upon end users to understand their application intent, working environment, and how best to recover the heat shrink. Appropriate preparation in the beginning will go a long way towards maximizing the benefits of a heat shrink application.

## Abbreviations And Terms

**HSP** – Heat Shrink Polymer

**SMA** – Shape Memory Alloy

**SME** – Shape Memory Effect

**SMM** – Shape Memory Material

**SMP** – Shape Memory Polymer

**Shape Memory** – The property of a material to change from a permanent (original) shape to a temporary shape and back to its original shape upon exposure to a particular stimulus.

**Recovery** – The process whereby a shape memory material regains or returns to its original shape following a stimulus.

**Recovery Temperature** – The temperature at which a heat shrinkable material begins to recover its original shape.

**Programming** – The process whereby a heat shrinkable material (or other shape memory material) is deformed in some manner and held or retained in the deformed shape until the shape becomes fixed.

**Shape Memory Cycle** – The process of deforming (fixing) a temporary shape into a shape memory material (such as a heat shrink) followed by the application of an appropriate stimulus such that the material recovers its original shape.

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Zeus Industrial Products, Inc.
3737 Industrial Blvd.
Orangeburg, SC 29118
USA

**Zeus Ireland** - Tel +353-(0)74-9109700
**Zeus China** - 电话 +(86)20-38791260

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