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Heat sensing Thermoplastic Elastomer Based on Polyolefins for Encapsulation Applications

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/61691>

Abstract

Use of Thermoplastic Elastomers (TPEs) has become a unique pathway to meet the daily requirements of various applications. The ease of using TPEs lies in the fact that they provide both the character of the individual properties as they are constructional polymers, which are physically crosslinked materials made up of a thermoplastic and an elastomer. There are several TPE's in market and individual have several outstanding performances. Out of several researches, our aim in this article is to focus on the influence of Polyolefin based TPE's. This paper focusses on the different aspects of TPO's their physical, chemical, mechanical, and electrical characteristics, advantages and uses of these materials along with a particular focus on their use in encapsulation application. Factors that could affect the end use are also explained here in details. Heat shrinkability test, cure time, and SEM are some of the characterisations used to demonstrate the exact criteria of polyolefin based TPE's for encapsulation application.

Keywords: Thermoplastic elastomer (TPE), Thermoplastic polyolefins (TPO's), Shrinkability, Encapsulation application

1. Introduction

Elastomers are polymers which have viscoelasticity and weak intra-molecular forces. They can be generally explained by their mechanical response rather than their chemical structure. One of the most versatile and immensely used materials in today's world is the engineered Thermoplastic elastomers (TPE's). The TPE's are a class of polymer which consists materials having both thermoplastic and elastomeric properties. They are novel constructional polymers, which are physically cross linked materials made up of a thermoplastic and an elastomer. The unique properties of both materials exist because TPE materials are created only by physical mixing of a thermoplastic and an elastomer and no chemical or covalent bonding

exists between the two [1]. TPEs are generally low modulus, flexible materials that can be stretched repeatedly to at least twice their original length at room temperature with an ability to return to their approximate original length when stress is released. TPE's offer a wide range of performance attributes including: heat and oil resistance, improved adhesion, tear resistance, surface appearance and low permeability. In addition, TPE's are colorable and can be specified in a variety of hardness grades. They can be processed with the efficiency and economy of thermoplastics and can be molded with other olefin based materials, such as polypropylene, polyethylene without the use of adhesives. Various mechanical designs were implanted within the parts to ensure tight fit in case of other substrates like polyamides, acrylonitrile butadiene styrene and so on. Rubbery materials have high degree of flexibility in their elongated polymeric chains which binds them into an ordered network structure [1]. Due to this mobility and flexibility the long chains when subjected to external pressure or stress change their configuration. Thus chain allied to a structure gives a solid feature preventing them to flow under pressure. Due this fact, this type of materials may be stretched or pulled up to several times of its original length. Withdrawing external forces, it rapidly restore its nearly original dimensions, with essentially no residual or nonrecoverable strain. TPEs serve a wide range of markets:

- Agriculture & Off Road Appliance
- Automotive & Transportation · Consumer
- Electrical & Industrial Controls · Food & Beverage
- Hydraulics & Pneumatics · Marine
- Medical & Safety Plumbing & Irrigation

One of the major usages of TPE is in encapsulations. By encapsulation we mean covering of an object with some material to protect and to insulate it. Polymeric materials are used extensively as encapsulants for coils, motor windings and micro electronics packaging industry. Use of TPEs speed manufacturing with low cost compared with any other material and technology. TPE gives both the characteristics like thermosets along with the process and design flexibility same as plastics thereby enhancing wide design alternatives and cost reduction facility. TPE's can be processed faster more easily and more efficiently. Apart from these advantages TPE's possess many other additional characteristics like lightweight, elastic recovery properties within a specific temperature range, metal replacement, noise reduction by self lubrication, very good electrical insulation properties, heat resistance with in a specific temperature range, oil resistance, improved adhesion, tear resistant surface, low permeability and colorability [2]. TPE's which have contribution in encapsulation application are Polystyrene, Polyolefin and Polyurethanes. In this chapter we will concern our focus on Polyolefins.

1.1. Compounding of TPE's

The basic characteristics of thermoplastic elastomer greatly depend on polymers used in their manufacturing process based on their application. These properties can be modified, however, through the appropriate addition of compounding ingredients. Some are added to accelerate

cross-linking in order to impart the exact cure time required some improve processability, while others improve the properties of the finished product.

Some ingredients are added to deliver the highest levels of performance in the end product. In some applications, compounding is required to reduce cost, diluents and extenders are sometimes added to minimize the ratio of high valued components within the system. By this, certain compromises in the mechanical and other properties are obtained, but for some specific high end applications it is worthwhile. Some other factors that influence the quality of the resulting material includes the quality of the neat materials, the equipment's used and the quality control in mixing techniques [3]. Processing of the compounded material can also influence the end product properties. The major ingredient that affect the properties of the finished product and which have its own importance while making an end product are classified as:

1.1.1. Matrix

The neat or raw polymer, is the fundamental or main ingredient in determining the properties of the compound or the end product. It is selected in such a way so as to optimize service life and processing requirements with cost effectiveness as one of the main parameter taken into account. Polymers with high molecular weight can give very tough material as the final product. Again this criterion sometimes becomes a disadvantage for some specific product. So depending on the end use application selection of polymer is yet challenging.

1.2. Filler

The most important part of filler is to provide better reinforcement and secondly to reduce the cost of the end product. Generally we have two basic types of fillers. One is the reinforcing type which can reinforce the system according to need and the other is the diluent type which are generally used for calibrating the physical properties of the system. Carbon Black or Nano silica's basically come under reinforcing fillers and are categorized by their respective particle sizes. They become more reinforcing as the particle size decreases [4]. As mentioned above fillers with high reinforcing character can make a compound very hard and rigid which in turn can result in poor flow behavior. Carbon blacks are generally alkaline in nature and tend to accelerate cure time. Other non-black fillers may be acidic and can retard cure as well as absorb moisture, which can result in blistering problems during the processing stage. Several nano-fillers like super-fine clays have a high surface area as compared to their volume and can induce better mechanical behavior. They are more expensive than general fillers, the same weight of material goes further because the particles are so much finer.

1.2.1. Accelerators

These speed up the cure mechanism of the system. Accelerators increase the rate of cross-linking and therefore decrease both production time and cost. Accelerators can help to control the cure speed and cure time and also other material properties. They can be incorporated within the system at any amount and sometimes may be more than one accelerators are used

in a single formulation. Some important accelerators include peroxides for curing which plays dual character in the network. They can act like an accelerator as well as a modifier for the physical properties of the system.

1.2.2. Flame retardants

These are compounds added to materials to suppress or delay the flames and prevent fire spreading. Most of the TPEs promote combustion and thus the end by-products can be extremely hazardous and dangerous. Due to this fact manufacturers induce flame retardants to improve their flame resistance. There are several flame retardants that can be added to the compound, either inorganic or organic. These include antimony trioxide, zinc borate, aluminum hydroxide and chlorinated paraffins and so on.

1.2.3. Curatives

Curatives are very crucial for compounding of elastomers. They are the crosslinking agents generally used to connect separate neat polymers. The type of curative used varies upon the elastomer selected. Like in sulfur-cured, sulfur donors give better heat stability as they tend to give single sulfur crosslinks. Peroxide cures promotes good thermal stability due to the short length of the cross-links between the polymer chains. Fluorocarbons, along with some other polymer types, can have their own specialized cure systems.

1.2.4. Plasticizers

Plasticizers help to reduce the hardness with given filler loading and also gives better filler addition and dispersion. They should be compatible with the matrix polymer. Special types of plasticizers can improve the low temperature flexibility of some rubber. Process aids can also assist with filler dispersion, although they are normally added to improve processability.

2. General characteristics of elastomers

2.1. Cure characteristics

The cure characteristic is one of the major properties of an elastomer to study before its application to different areas. As the compound cures within the hot platens it gradually becomes stiffer. This is measured via a strain gauge connected to an oscillating rotor in contact with the elastomer. The resistance to torque or the stiffness of the material is plotted on a graph against time, known as a rheograph. This information shows the behavior of the moulding characteristics, since the rheograph shows the time available to load the press, the time of cure and the final state of cure. The ultimate state of cure is not always a straight line but can also be a slope [5]. For some elastomers the cure continues in a different way which could be explained as the heat is actually breaking the polymer chain rather than the crosslinks formed during the curing stage.

2.2. Abrasion resistance

Abrasion resistance is important where friction, rough surface, industrial use is a key factor. Hard TPOs have good abrasion resistance. Abrasion damage can occur when there is dynamic motion against an abrasive surface. Standard abrasion tests depend on producing relative motion between a rubber sample and an abrasive surface, pressed together by a fixed force. These tests do not correlate particularly well with application experience. It is sometimes believed that tensile strength is related to abrasion resistance, higher the tensile strength higher is the abrasion resistant property while a high tensile strength compound can have good abrasion resistance. Abrasion resistance is mainly related more to the polymer taken and the nature of compounding ingredient used [6]. Abrasion resistant elastomers must therefore be specifically developed. Polyolefin based TPEs show good abrasion resistant character.

2.3. Tear strength

Tear strength is a measure of the resistance of an elastomer to tearing. It is measured using a tensile test machine operating at a constant rate of traverse until the test piece breaks. Various types of test pieces can be used, and depending on the method employed the maximum or median force achieved is used to calculate the tear strength.

2.4. Adhesion and bondability

Parameters affecting the adhesion and bond ability: The application of elastomers at high temperature is generally determined by their chemical structure and stability and varies depending on the elastomers being used. In course of developing high temperature product, these elastomers can be attacked by several chemical species like hydrogen, oxygen, and other groups which results in some chemical reaction and as a result the effectiveness or power increases at high temperature. Another parameter responsible for affecting the adhesion and bond ability is the degradative chemical reactions. It may hamper the product in two specific ways. 1. Breaking the molecular chains or cross-links, thus softening the rubber because they weaken the network. 2. Additional cross-linking, hardening the rubber, often characterized by a hard, cracked and degraded skin occurring on the elastomer component [7]. One more important criterion responsible for adhesion and bond ability is the perfect selection of the materials based on the end product needed. For example elastomers significantly weaken at high temperatures so in the case of seals, can result in a significant reduction in extrusion resistance. For applications involving elevated temperatures, especially at high pressures, anti-extrusion elements may also need to be used, either incorporated into the seal design or added as an additional component when manufacturing the seal.

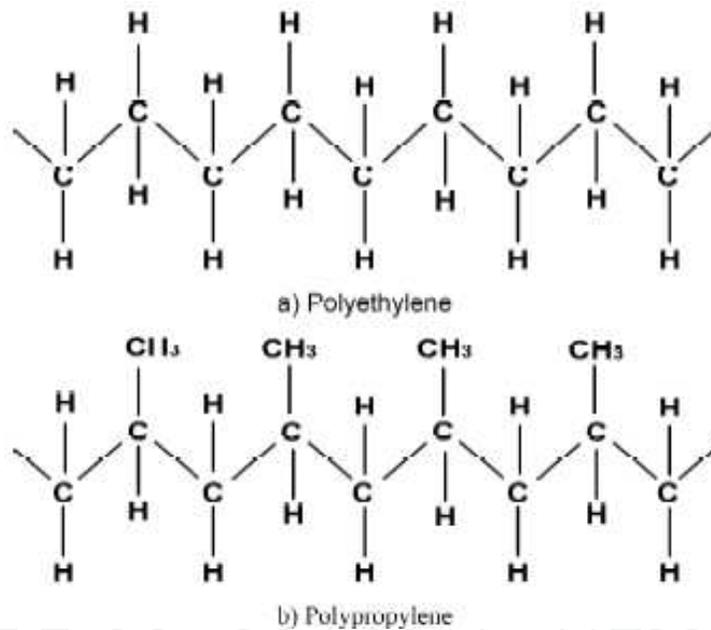
2.5. Low temperature applications

Elastomers when cooled to sufficiently low temperatures show the characteristics of glass, including hardness, stiffness and brittleness, and do not behave in the readily deformable manner usually associated with elastomers. As the temperatures rises, the segments of the polymer chain gain sufficient energy to rotate and vibrate. At high temperatures full segmental

rotation is possible and the material behaves in the rubbery way. The usefulness of an elastomer at low temperatures is dependent on whether the material is above its glass transition temperature (T_g), where it will still behave elastically, or below its T_g , where the material will be hard and relatively brittle.

3. Polyolefins (POEs)

Polyolefins also named as poly alkenes are simple long chain hydrocarbon. They are prepared by the reaction of an alkene as a monomer with general formula C_nH_{2n} . The most commonly used Polyolefins are low and high density polyethylene copolymer, polypropylene copolymer and polymethyl pentene. Polyethylene and polypropylene are produced by long chain polymerization of olefins ethylene and propylene respectively

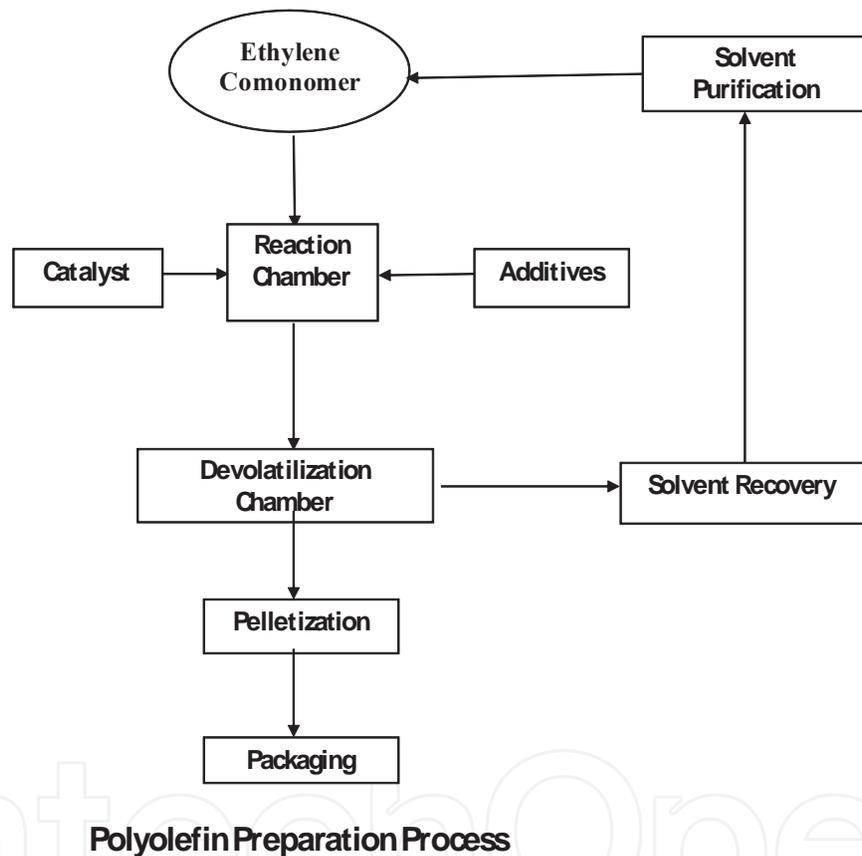


Scheme 1. Structure of Polyolefins

3.1. Chemistry and manufacturing process

The metallocene catalyst helps to instigate polymerization of the ethylene and co-monomer sequences and while further increasing the co-monomer content will produce polymers with higher elasticity due to the fact that the co-monomer incorporation disrupts the polyethylene crystallinity. The molecular weight of the copolymer will help determine its processing characteristics and end-use performance properties. Higher in molecular weights higher is the polymer toughness. Hence depending on the end use application one can choose the appropriate copolymer with molecular weight according to the requirement. POEs are produced using refined metallocene catalyst. These catalysts have a constrained transition metal such as

Ti, Zr, sandwiched between one or more cyclopentadienyl ring structures to form a sterically hindered polymerization site. The catalyst is usually first mixed with an activator or co-catalyst, which can significantly enhance the polymerization efficiency rate to beyond a million units of polymer per unit of catalyst [8-9]. The molecular weight build-up with the polymerization of ethylene and comonomer at the catalyst site until restricted by catalyst deactivation or chain termination with hydrogen introduction to the reactor. The polymerization process is exothermic in nature and requires efficient heat removal from the transport media of gas or solvent. Post-reactor processes involve additives addition and isolation of the polymer from the transporting media. The final product is then packaged as per manufacturer demand or end-user need.



Scheme 2. Polyolefin Preparation Process

4. Thermoplastic Polyolefins (TPOs) blends

These are a class of plastic used in a wide range of markets and applications – mainly in transportation sector, including automotive exterior and interior parts. TPOs are generally produced by the blending of polypropylene (PP) with elastic ethylene copolymers (polyolefin elastomers or POEs), and the addition of other fillers and additives. Thermoplastic olefin (TPO)

elastomers are obtainable in several grades in the market, having room-temperature hardness starting from 60 Shore A to 60 Shore D. These polyolefin elastomers have the lowest specific gravities of all thermoplastic elastomers available in the market. They are uncured or have low levels of crosslinking. These elastomers are flexible at around -60°F and are not brittle at -90°F . They can be used at service life at temperatures as high as 275°F in air. The TPOs have good resistance to some acids, most bases, butyl alcohol, many organic materials, formaldehyde, ethyl acetate and nitrobenzene. They are affected by chlorinated hydrocarbon solvents [10]. The specific blending amounts are dependent upon the properties needed to meet the desired end product application. TPO system generally include:

- Polymer., (provides rigidity and temperature stability to the body)
- Elastomers, which gives movability and impact strength to the system
- Filler (like minerals or talc), imparts higher stiffness and dimensional stability of the body
- Other additives (plasticizers, antioxidants, and additives for ignition resistance, scratch resistance) for improving end-use performance and shelf life.

Rigid TPOs are normally made up of polypropylene or polyethylene component in majority, with other component to attain an overall balance of properties. Efficient rigid TPO development starts by optimizing an appropriate polymer, and adjusting the optimum modifier level to achieve acceptable ductility, while maintaining rigidity as high as possible. In contrast, flexible TPOs contain a majority phase of elastomer with polymer added for improved temperature stability.

TPO's as one of the fastest growing synthetic polymers can be substituted for a number of generic polymers including ethylene styrene-block copolymers (SBCs), propylene rubbers (EPR or EPDM), ethylene vinyl acetate (EVA), and poly vinyl chloride (PVC). TPO's are well-matched with most of the olefinic materials, are an excellent impact modifier for plastics, and offer unique performance application for compounded products [11]. These compounds are easily colored, possess soft-touch molding and extrusion applications. They are generally resistant to acids and bases and are available in UV-resistant grades for outdoor applications. The main advantages are excellent abrasion resistance, high heat stability, wide use temperature, low-temperature flexibility and so on. Recently, TPO's has established itself as a leading material for automotive exterior and interior applications like extruded and molded goods, wire and cable, film applications, medical goods, adhesives, footwear, and foams. The advantage of using Polyolefins with other materials is that they have wide hardness range, excellent flex fatigue and impact resistance, good retention of properties etc. They are solvent resistant. The typical glass transition temperature can exceed 140°C . They are also used to make lenses for cameras, projectors and copiers, LCD monitors, contact lenses for eye and reinforced tubes or pipes for medical use. TPO's provide an economical alternative to traditional thermoset rubbers and more costly thermoplastic elastomers [12]. Thermoplastic polyolefin elastomers provide an excellent balance of performance and price. Their service temperature range is from -60 to 275°F (-50 to 135°C); hardness ranges from 35 Shore A to 50 Shore D. TPO ingredients generally have a polymer (homopolymer, copolymer) which provides the rigidity and thermal stability, along with elastomers which gives the flexibility. It also includes mineral

fillers which gives dimensional stability to the system. Other additive includes additives (antioxidants, plasticizers, and so on) depending on the application of the end use.



Scheme 3. Car Bumper made out of TPO material, (Source Google)

4.1. Heat sensing property of TPO's based materials

When a polymeric materials is subjected to stretch either at room temperature or at elevated temperature, the molecules of the materials are oriented towards the stretching direction and the material freezes in its elongated or extended form. Stretching decreases the entropy of the system. If we heat the stretched sample without applying mechanical force the material shrinks. Such heat shrinkable polymers are recently getting tremendous application in the packaging industry, cable industry and heat shrinkable tube production. As a flexible material elastomers do not provide the same level of tolerance as rigid materials do. Shrinkage is highly dependent on tolerance which again varies with the type of elastomers and other factors like hardness, stiffness and so on. Soft elastomers generally shrink more than harder elastomers. Shrinkage is also affected by other parameters like cure time, pressure, temperature, post-cure time, etc[13]. Most materials like metals, plastics or fabric have their own percentage tolerances. However, when designing inserts for moulding to elastomers, other factors need to be considered such as, the location of the inserts with respect to other shapes, fit in the mould cavities, proper spacing to match with mould pins, and the fact that inserts at room temperature should fit into a heated mould.

4.2. Electrical property of TPO's

With increasing demand for insulating materials researchers have paid attention towards materials that can provide the best according to the requirement. Various factors depend on to which materials can suit the best. Among them the most important criteria of a material as electrical insulation is determined by its dielectric breakdown strength. This in turn depends on some other properties like voltage applied, frequency, temperature, partial discharges, impurities in that material, dielectric constant, thickness and layers of insulation, and volume resistivity[14-15]. A material should fulfill some of the criteria to become useful in electrical insulation application. These properties include low specific weight, good mechanical,

chemical and thermal strength, and good surface leakage resistance, ability to maintain good surface hydrophobicity, easy processing and production [4]. TPO gives a package of these combinations of properties and thus makes it most suitable to use in encapsulation applications. These materials are recently used widely for medium to high voltage cable encapsulations. They are also used in encapsulation of coils.

5. Experimental

5.1. Heat shrinkability test

- a. Shrinkage was measured at 150°C for above materials.
- b. Above materials were given stretching at ambient and at 150°C and then the shrinkage of the stretched samples was measured at the same temperature.
- c. Above materials were stretched at 150°C and cured under stretching conditions and then shrinkage was measured also at 150°C.

For R-T stretched samples the samples were stretched at room temperature at a stretching rate of 50 mm/min. Samples were allowed to shrink at 80 °C for 10 min in a hot air oven. The percentage shrinkability was measured by the following equation..

$$S_h = (L_{str} - L_{shr}) / L_{str} \times 100$$

where S_h is the percentage of shrinkability, L_{str} is the length of the sample after stretching, and L_{shr} is the length of the shrunk sample.

Uncoiling of the polymer chains occurs when a polymer sample is stretched above the glass transition temperature, which in turn is frozen into the structure when the samples are cooled down. Although sufficient drop of entropy is witnessed during the uncoiling process the obtained stretched polymers are stabilized by a cohesive force received from the semicrystalline region of the polymers. Stretching also has some properties of its own. It causes unrecoverable viscous flow, which gradually increases with the increased stretching temperature and are not recoverable in any circumstances. Crosslinked points also known as permanent point strongly contribute in the shrinkage process. The molecules in the flexible amorphous phase shrink easily due to their mobility as compared to those in the crystalline zone. The observed shrinkability is a composite effect of the above mentioned factors. All samples were stretched at room temperature. The viscous flow is same in all cases.

5.2. Effect of cure time on heat sensing property of TPO

Some experiments were performed with different types of TPO's to study the heat sensing property. The parameter on which the heat sensing character depends gives a vast knowledge to the industries as well as other fields which deals especially with this parameter of TPO's.

Polymers taken are LLDE, LDPE, HPDE and the curing agents are mostly CSM, DCP, sulfur etc. The formulations are given in Table 1 and 2.

i	ii	iii
LLDPE/CSM/Sb ₂ O ₃	LDPE/CSM/ Sb ₂ O ₃	HDPE/CSM/ Sb ₂ O ₃
40/60/1	40/60/1	40/60/1

Table 1. Formulation of TPO with curing agents

i	ii	iii	iv	v	vi
HDPE/BB/Sulfur	LDPE/BB/Sulfur	LLDPE/BB/Sulfur	HDPE/BB/DCP	LDPE/BB/DCP	LLDPE/BB/DCP
40/60/1	40/60/1	40/60/1	40/60/1	40/60/1	40/60/1

Table 2. Formulation of TPO with curing agents

Figure 1. elaborates that with increasing the cure time the shrinkability of the blends increases for all the systems. From the graph it could be observed that the LLDPE/CSM blends show the highest shrinkability degree both for Room Temperature and High Temperature stretched sample as compared to LDPE/CSM and HDPE CSM blends. H-T stretching is accompanied by high shrinkage rather than R-T stretched samples. Increase in cure time accelerates the shrinkability. This may be due to more crosslinking of the elastomeric phase. In case of Figure 2. we notice the same trend as above. Shrinkability of all blends increases with increase in cure time. Here two types of curing agent were applied a) DCM b) sulfur. From both the figures it is apparent that rate of increase in shrinkability is much higher in case of DCP than sulfur as curing agent.

LLDPE/BB blends show the highest degree of shrinkability with increase with cure time for both the systems either with sulfur or DCP as the curing agent. But the extent of increase in shrinkability is even sharper in case of DCP as curing agent. This may be due to the fact that DCP attacks both polymer chains to generate active sites leading to more efficient crosslinking which results in higher degree of shrinkability whereas the sulfur only gives a bridging agent between the elastomers. Higher shrinkability of H-T stretched samples than the R-T stretched samples may be due to more crosslinking of elastomeric phase at elevated temperature to deposit curatives to crosslink further strongly which is not possible in case of room temperature stretched samples. Increase in cure time allows the elastomer phase to crosslink for longer duration resulting in sufficient crosslinking thereby increasing the shrinkability of the system.

5.3. Effect of flame retardant on shrinkability

Flame retardant plays an important role in shrinkability. It can be observed that with incorporation of some amount of flame retardants the shrinkability of the system is changed to some extent. For blends having high elastomer ratio the reduction in shrinkage occurs to a very small

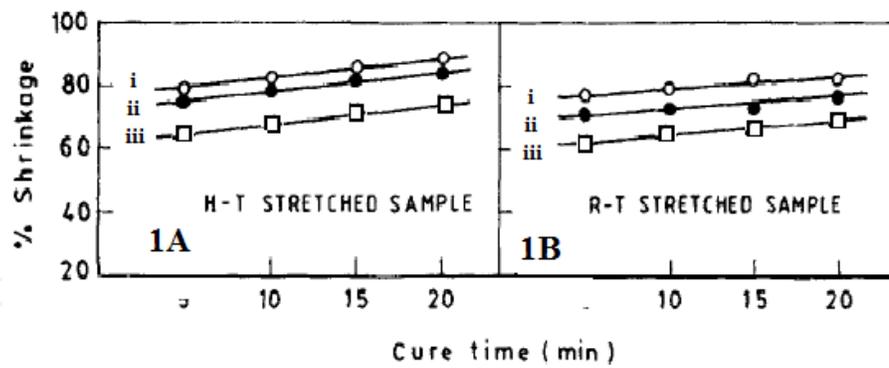


Figure 1. Study of shrinkability over cure time i) LLDPE/CSM, ii) LDPE/CSM, iii) HDPE/CSM

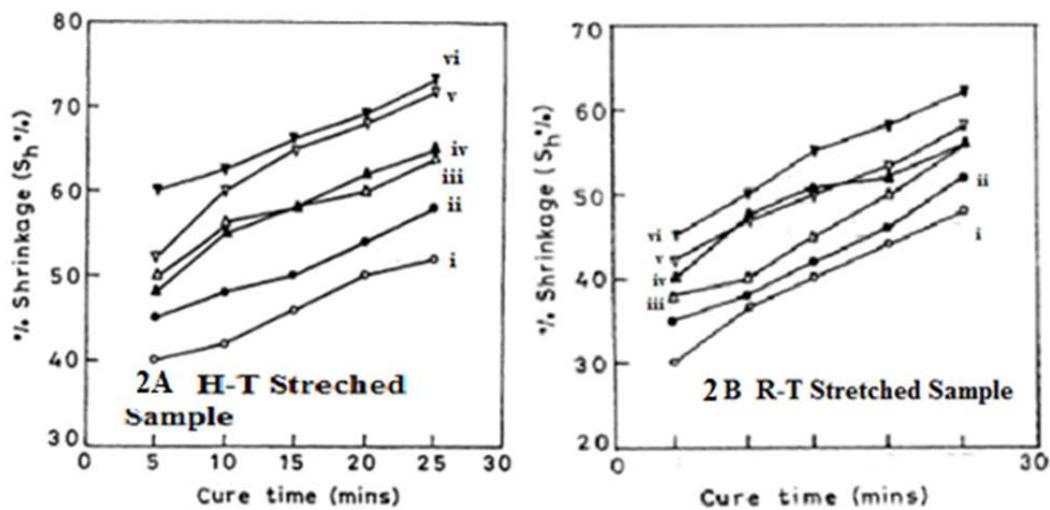


Figure 2. Study of shrinkability over cure time 2A) H-T stretched samples and 2B) R-T stretched samples of the blends of HDPE, LDPE, LLDPE with sulfur and DCP as curing agents.

extent in case of H-T stretched samples but for the low elastomer ratio the shrinkability value is sacrificed to larger extent. The stretch ability of the H-T stretched blends again decreases to some extent with the addition of flame retardants. This may be the result of lower compatibility of flame retardants in the polyolefin phase at its higher level, suggesting the efficiency of flame retardants. The observed flame retardancy may be due to the fact that formation of some groups; entrap the flame propagating radicals like H, OH, O etc. and does not allow the flame to propagate. One more reason may be due to the fact that polymer structure after addition of flame retardants, is modified in such a way that char formation is facilitated thereby resisting the flame.

6. Encapsulation applications

Thermoplastic elastomeric encapsulation is used in many applications that require some special manufacturing techniques and materials of encapsulation. These include solenoids,

sensors, self-supporting coils, transformers, motors, and electronic components of various types.

Various heat recoverable materials, which possess sufficient rigidity to hold out the elastomeric layer, may be used for the heat recoverable layer. Thermoplastic polymers are generally suitable heat recoverable materials either being crosslinked, or possessing the property of heat recoverability. Examples of such desirable TPEs that are crosslinked or which inherently possess the property of heat recoverability are polyolefins, such as ethylene-vinyl acetate copolymer, polyethylene, ethylene-ethyl acrylate copolymer or other ethylene copolymers, polyvinyl chloride, polyvinylidene difluoride, etc. Apart from that, other flexible polymers possessing necessary crystallinity such as trans-polybutadiene, ethylene-propylene-diene terpolymers, and trans-polyisoprene may also be used [16-18]. In addition, various commercially available elastomer-thermoplastic blends such as nitrile rubber-PVC and nitrile rubber-ABS may be taken into consideration. The only necessary property of the said thermoplastic material, used in place of the heat-recoverable material, should have sufficient rigidity at storage temperatures to seize the elastomeric sleeve. Such a material could be bonded to the elastomeric sleeve on either sides, by molding it in place or by placing concentric sleeves of thermoplastic material and relaxed elastomeric material in contact with each other and bonding them together at the interface.

In case of the elastomeric layer, any chosen material possessing elastomeric properties may be used. Suitable elastomers include rubber or rubber-like material such as natural rubber, styrene-butadiene rubber (SBR), cis-polyisoprene, cis-polybutadiene, butadieneacrylonitrile rubber, Neoprene Rubber, butyl rubber, (BB), silicone rubber, polysulfide, urethane rubber, polyacrylate, propylene oxide rubber, fluorosilicone rubber, chlorosulfonated polyethylene, chlorinated polyethylene, fluorohydrocarbon rubber, and so on.

It is generally desirable that the two layers be bonded to each other. If the inner layer is the heat recoverable layer the external rubber layer may stick or adhere tightly enough to it by virtue of its tendency to contract down onto the heat recoverable layer. In cases for some other applications where the elastomeric material is the inner layer, a stronger bond may be desired. A bond can be developed by several means. Any suitable adhesive can be used to bond the heat recoverable and elastomeric layers together. Examples of such adhesives are laminating adhesives, such as polyesters, polyurethanes. Peroxides, either organic or silyl, which form crosslinks between the two layers; structural adhesives such as epoxies, nitrile rubber, phenolics,, hot melt adhesives of suitable bond strength and softening temperatures, such as polyamides and various rubber-based adhesives such as those based on silicone nitrile and neoprene [19].It may be desired to bond or weld both the layers together without using an adhesive. Such bonding may be achieved simply by heating the layers to a high enough temperature at their interface so that they become soft and flow able and then applying sufficient pressure to achieve a bonding or welding of the layers [20-22].

General applications of heat-shrinkable items are caps, sleeves, pipes, tubes, multi-way cable breakouts etc. In order to achieve the best quality the materials need to undergo certain specifications during the manufacturing process and application stages. Therefore there is also a great requirement to develop new materials tailored or manufactured exactly to specific

applications. But developing such tailored products requires overcoming certain challenges like dispersibility, processability, exact mechanical properties (expandability, shrink ratio and temperature, flexibility, tensile properties, hardness), continuous operating temperature, chemical resistance, flame retardancy, electrical and dielectrical properties, and crack resistance. These are some of the criteria's that should be taken into consideration during the process of development of new materials for heat-shrinkable items [23]. As a result the process need several materials some times more than 10 ingredients and there is the possibility of unwanted interactions between them [24]. The aim of this paper was to focus on some selected topics of technological importance, related with the research and development of work dedicated to modern materials for production of heat-shrinkable items.

6.1. Application of encapsulated TPO's

- TPO heat shrink tubing is used to protect wires, for better abrasion resistance as well as environmental protection for solid wire conductors, connections, joints and terminals used in several industrial and domestic fields. It also has application to modify or repair the insulation on wires or to bundle them together, to protect wires or small parts from minor abrasion, offering environmental sealing protection. The tubing provides good electrical insulation protection from dust, solvents and other foreign materials, and is mechanically held in place by its tight fit [25-27].



Scheme 4. TPO heat shrinkage tube

Some types of heat shrink tube contain a layer of thermoplastic adhesive on the inside to help provide a good seal and better adhesion, while others rely on friction between the closely conforming materials.

The manufacturing process of these types of tubes generally follows certain simple steps. The raw material is chosen based on its properties and end use application. The material are always manufactured along with many additives like certain stabilizers, colorants based on the application concerned. It can be briefly discussed for better understanding. At first the tube is

extruded from the raw or neat material. Then the tube is subjected to a separate process where it is cross-linked. The material is often cross-linked through the use of electron beams, peroxides, or moisture. The main objective for cross-linking is to create a memory in the tube so that it is able to shrink back to its original extruded dimensions upon heating. Then the tube is heated just above the polymer's crystalline melting point and expanded in diameter, often by placing it in a vacuum chamber [28-29]. After this step, in its expanded form a rapid cooling is applied. Later, when heated (above the crystalline melting point of the material), the tubing shrinks back to its original extruded size. For external use, heat shrink tubing often has a UV stabilizer added.

- PO tubes, are the most widely and commonly used tubes in some major field in military, aerospace industries. It has maximum continuous-use temperatures from -55 to 135 °C. The main advantage of using PO tubes are their flexibility and fast-shrinking property, and they are manufactured in a wide range of colors (including clear), which can be used for color-coding wires also. Black color PO tubes tend to have lower resistance to ultraviolet light; accordingly, and are only recommended for outdoor applications. A common shrink ratio is 2:1, but high-grade polyolefin heat shrink is also available with a 3:1 ratio [30].

There are several other materials that offers resistance to diesel and aviation fuels, and also some woven fabric, providing increased abrasion resistance in harsh environments.

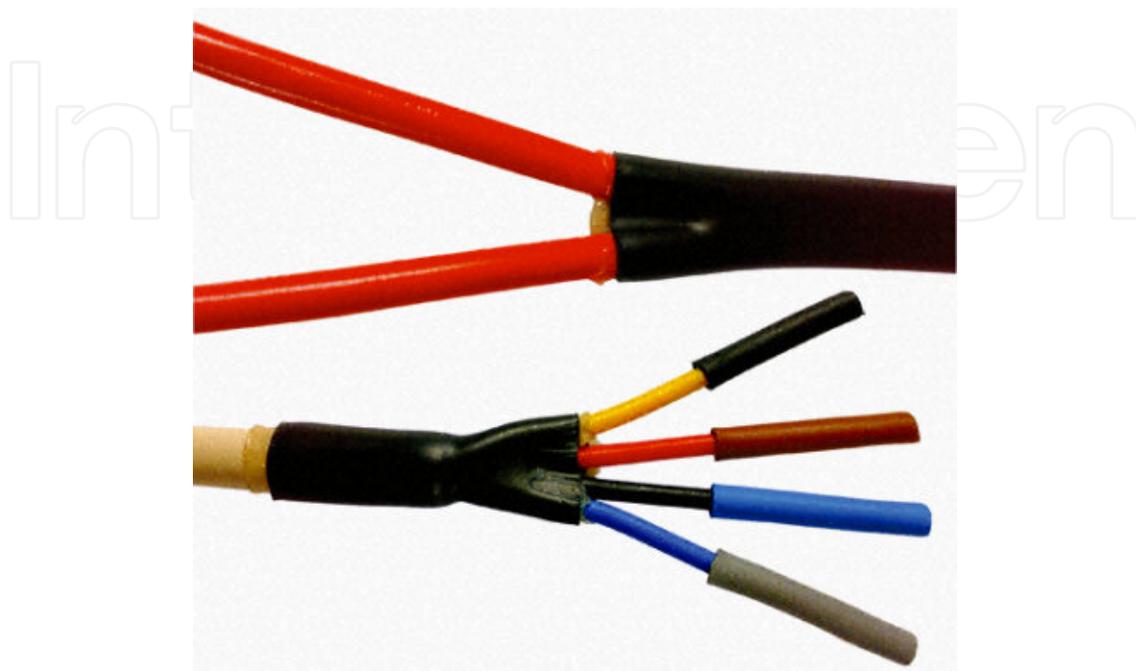
Heat shrink tubing is also available in a wide variety of colors for color-coding of wires and connections. Since long heat shrink tubing has been used for PC to tidy up the interior of computers and provide an appearance considered pleasing. In response to this opening market manufacturers have started producing heat shrink tubing in luminous and UV reactive varieties.

Although heat shrink is usually used for insulation, heat shrink tubing with a conductive lining is available, for use particularly on joints that are not soldered. Heat shrink end caps, closed at one end, are used to insulate the exposed cut ends of insulated wires.



Scheme 5. Heat shrink insulated wires

Cross linked polyolefin heat shrink flame retardant sleeving with an adhesive lining. Designed to provide a permanent encapsulation for protection against moisture in a wide variety of applications once heated. Operating temperature -55°C to $+125^{\circ}\text{C}$. (Source Google)



Scheme 6. Cross linked polyolefin heat shrink flame retardant sleeving

Heat shrinkable Polyolefin tubing with an integrally bonded adhesive inner lining, designed to provide a permanent encapsulation for protection against moisture in a wide variety of applications such as electrical wire splices, cable jackets, wire breakouts, strain reliefs and protection boots for electrical components. (Source Google)

7. Conclusion

Use of TPEs is increasing for wide range of applications. Encapsulation is one of the areas where TPEs are hugely used. About 85% of plastic products in the modern world are made up of TPE materials of which a huge percentage is occupied by TPO's as they provide comparatively high price performance as compared to other natural rubbers. The selection of a TPO material for any particular end application requires a special focus on its physical, chemical, mechanical and electrical properties. Polyolefin elastomers (TPO's) have proven their viability in flexible plastics applications and use in a variety of industries. Further advances in application development, product design, and manufacturing capabilities will provide increasing opportunities for years to come. TPO's has proven to be the best material used for outdoor encapsulation application. One of the major criteria for TPO's suitability in this sector is the heat sensing ability. There is a direct relation between the processing parameters and

the shrinkability of the TPO polymer blends. With increase in crosslinking and the cure time the shrinkability increases. The shrinkability also depends on the curing agent taken into consideration. Addition of flame retardant decreases the stretchability of the material.

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