THE EFFECT OF RECYCLED THERMOPLASTIC ELASTOMER (TPE) MIXING RATIO ON THE TENSILE STRENGTH OF THERMOPLASTIC ELASTOMER (TPE) POLYMER

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Thesis submitted in partial fulfilment of the requirement for the award of Bachelor of Manufacturing Engineering

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JUNE 2013

ABSTRACT

Recycling polymer has become an important field in a polymer research especially in recent years. This is because, by recycling the polymer, we can prevent pollution from happen. In this research, thermoplastic elastomer (TPE) is used, TPE is a class of copolymers or a physical mix of polymers usually a plastic and a rubber which consist of materials with both thermoplastic and elastomeric properties. The dog-bone shape mould with standard size ASTM D638 designed by using AutoCAD software and fabricated by using electrical discharge machining machine and milling machine to be used as a specimen. The virgin TPE come from raw material of TPE in the resin form where as the recycled TPE come from injection moulded virgin dog-bone shape specimens that have been crushed by using crusher machine. After that, recycled TPE and virgin TPE are then mixed according to the desired mixing ratio and injection moulded by using injection moulding machine. Then, the specimens undergo tensile strength test by using universal testing machine in order to determine which mixing ratio produce highest tensile strength. As a result, the mixing ratio that produce highest tensile strength is 100% virgin TPE and the second highest is 100% recycled TPE. This is due to the ability of material mix together and produces strong bonding within each other.

ABSTRAK

Kitar semula polimer telah menjadi satu bidang penting dalam penyelidikan polimer terutamanya pada tahun-tahun kebelakangan ini. Ini adalah kerana, dengan kitar semula polimer, kita boleh mengelakkan pencemaran daripada berlaku. Dalam kajian ini, "thermoplastic elastomer" (TPE) digunakan, TPE adalah kelas kopolimer atau campuran fizikal polimer biasanya plastik dan getah yang terdiri daripada bahan-bahan dengan kedua-dua termoplastik dan sifat-sifat elastomer. Acuan bentuk "dog-bone" dengan saiz standard ASTM D638 direka dengan menggunakan perisian AutoCAD dan dibuat dengan menggunakan "electrical discharge machining machine" dan "milling machine"untuk digunakan sebagai spesimen. TPE tulen datang dari bahan mentah TPE dalam bentuk resin di mana sebagai TPE yang dikitar semula datang dari suntikan dibentuk spesimen tulen "dog-bone" yang telah dihancurkan dengan menggunakan mesin penghancur. Selepas itu, TPE yang dikitar semula dan TPE tulen dicampur mengikut nisbah yang dikehendaki pergaulan dan suntikan acuan dengan menggunakan mesin pengacuan suntikan. Kemudian, spesimen menjalani ujian kekuatan tegangan dengan menggunakan mesin ujian universal untuk menentukan nisbah pencampuran menghasilkan kekuatan tegangan yang tinggi. Hasilnya, nisbah campuran yang menghasilkan kekuatan tegangan tertinggi adalah 100% dara TPE dan kedua tertinggi adalah 100% dikitar semula TPE. Ini adalah kerana keupayaan campuran bahan bersama-sama dan menghasilkan ikatan yang kuat dalam satu sama lain.

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TPE	Thermoplastic Elastomer
MWD	Molecular Weight Distribution
DP	Degree of Polymerization
Tg	Glass-Transition Temperature
MPR	Melt Processable Rubber
ABS	Acrylonitrile-Butadienne-Styrene
TPV	Thermoplastic Vulcanisates
UTM	Universal Testing Machine
ASTM	American Society for Testing and Materials

CHAPTER 1

INTRODUCTION

1.1 PROJECT BACKGROUND

Currently, a large number of companies consider recycling of materials as an opportunity to maximize profits and to reduce the environmental impact generated by these materials after they are disposed.[1] However, there is a strong constraint on the use of recycled materials mainly due to the lack of technical and scientific information, which would relate their physical properties to their recycling cycle.[1]

Therefore, the recycling cycle of materials is a tool that provides scientific and technical support in the selection of materials.[1] It uses the information related to the mechanical properties of the materials as a parameter for product design.[1]

For this project, the study is about the effect of recycled thermoplastic elastomer (TPE) mixing ratio on the mechanical properties of TPE. The type of TPE used in this study is styrenic block copolymers (TPE-S) or also known as (SBS) which is based on two-phase block copolymers with hard and soft segments.[2] The styrene end blocks provide the thermoplastic properties and the butadiene mid blocks provides the elastomeric properties.[2] SBS is commonly used in footwear, adhesives, bitumen modification and lower specification seals and grips, where resistance to chemicals and aging a lower priority.[2]

The recycled TPE mixed with virgin TPE to know which composition produced the optimum result. The recycled TPE come from the virgin dog-bone shape specimens that have been crushed where as the virgin TPE come from the resin form.

The tensile strength of the specimens test is perform by using Universal Testing Machine (UTM).

1.2 PROBLEM STATEMENT

TPE are durable and degrade very slowly, the chemical bonds that make plastic so durable make it equally resistant to natural processes of degradation.[3] Since 1950s, one billion tons of TPE have been discarded and may persist for hundreds or even thousands of years.[3] This characteristic of TPE make it harmful to the environment and living things.

The industry which is the biggest contributor to this problem must reduce the waste of TPE. They can reduce the waste by recycling it and used it again to produce the new product.

However, not many study done on the mechanical properties of recycled TPE leave a loophole on the performance of recycled TPE product produced.

1.3 OBJECTIVES

The main objectives of this project are:

i. To design and fabricate dog-bone shape mould according to ASTM D638 to be use as a specimens.

ii. To study the effects of mixing percentage of recycled TPE with virgin TPE to the tensile strength by carrying out tensile strength test on the specimens using UTM.

iii. To determine the optimum mixing percentage of recycled TPE with virgin TPE in terms of highest tensile strength.

1.4 PROJECT SCOPE

The main scopes of this project are:

i. Prepare the recycled TPE from the virgin dog-bone shape specimens and virgin TPE from the raw material in the resin form.

ii. Analyze the mechanical properties of recycled TPE and virgin TPE by using UTM.

iii. Performed the project at FKP laboratory.

CHAPTER 2

LITERATURE REVIEW

2.1 POLYMER

A polymer is a chemical compound or mixture of compounds consisting of repeating structural units created through a process of polymerization.[3] The term derives from the ancient Greek word, polus which means many or much and meros which means parts, and refers to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties.[3]

Polymerization is the process of combining many small molecules known as monomers into a covalently bonded chain network.[3] During this process, some chemical groups may be lost from each monomer.[3] There are two important polymerization processes which are condensation polymerization and addition polymerization. In condensation polymerization (Figure 2.1), polymers are produced by the formation of bonds between two types of reacting mers.[4] A characteristic of this reaction is that reaction by-product such as water is condensed out.[4] In addition polymerization (Figure 2.2), bonding takes place without reaction by-product, but an initiator is added to open the double bond between two carbon atoms, which begin the linking process by adding many more monomers to a growing chain.[4]

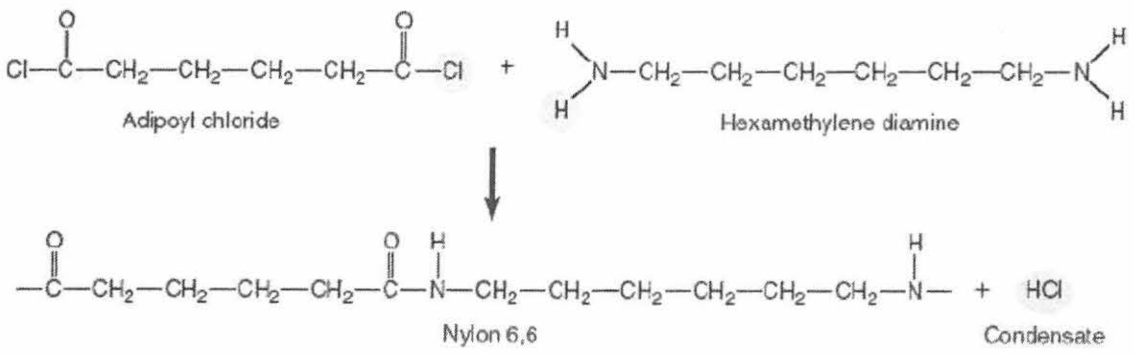


Figure 2.1: Condensation Polymerization

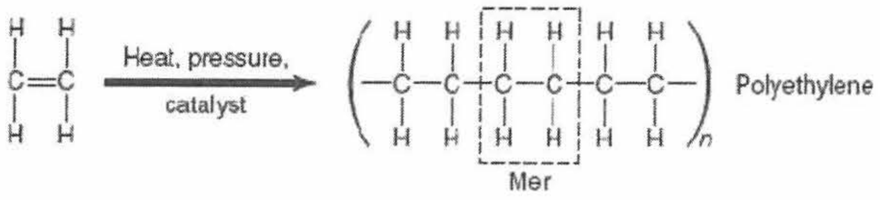


Figure 2.2: Addition Polymerization

The sum of the molecular weights of the mers in a representative chain is known as the molecular weight of the polymer.[4] The higher the molecular weight of a given polymer, the greater the average chain length.[4] Most commercial polymers have a molecular weight between 10,000 and 10,000,000.[4] Because polymerization is a random event, the polymer chains produced are not all equal length, but the chain lengths produced fall into a traditional distribution curve.[4] The average molecular weight of a polymer is determined on a statistical basis by averaging.[4] The spread of the molecular weight in a chain is referred to as the molecular weight distribution (MWD).[4] A polymer's molecular weight and its MWD have strong influence on its properties.[4] For example, the tensile and the impact strength, the resistance to cracking, and the viscosity in molten state of the polymer all increase with increasing molecular weight (Figure 2.3).[4]

Degree of polymerization (DP) is the ratio of the molecular weight of polymer to the molecular weight of the repeating unit.[5] In terms of polymer processing, the higher the DP, the higher is the polymer's viscosity (Figure 2.3).[5] High viscosity adversely affects the ease of shaping and, thus, raises the overall cost of processing.[5]

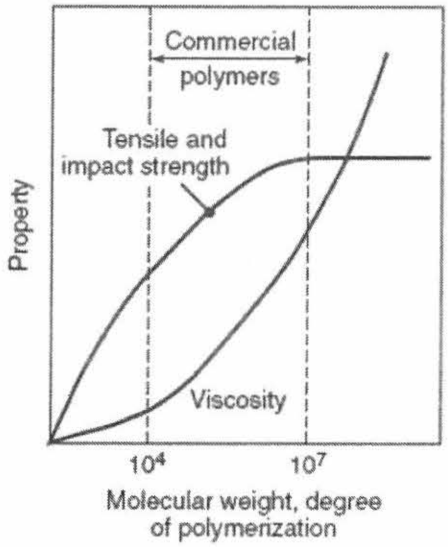


Figure 2.3: Effect of Molecular Weight and Degree of Polymerization on the Strength and Viscosity of Polymers

During polymerization, the monomers are linked together by covalent bonds, forming a polymer chain.[5] Because of their strength, covalent bonds also are called primary bonds.[5] The polymer chains are, in turn, held together by secondary bonds, such as van der Waals bonds, hydrogen bonds, and ionic bonds.[5] Secondary bonds are weaker than primary bonds by one to two orders of magnitude.[5] In a given polymer, the increase in strength and viscosity with molecular weight is due to the fact that the longer the polymer chain, the greater is the energy needed to overcome the combined strength of the secondary bonds.[5]

The chain-like polymers are called linear polymers because of their sequential structure (Figure 2.4).[5] However, a linear molecule is not necessarily straight in shape.[5] Generally, a polymer consists of more than one type of structure, thus, a linear polymer may contain some branched and cross-linked chains.[5] As a result of branching and cross linking, the polymer's properties are changed significantly.[5]

Figure 2.4: Linear Structure of Polymer

The branched polymers (Figure 2.5), side-branch chains are attached to the main chain during the synthesis of the polymer.[6] Branching interferes with the relative movement of the molecular chains.[6] As a result, their resistance to deformation and stress cracking is increased.[6] The density of branched polymers is lower than that of linear-chain polymers, because the branches interfere with the packing efficiency of polymer chains.[6]

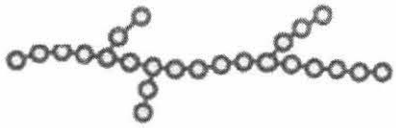


Figure 2.5: Branched Structure of Polymer

The behaviour of branched polymers can be compared to that of linear-chain polymers by making an analogy with a pile of tree branches (branched polymers) and a bundle of straight logs (linear polymers).[6] It is more difficult to move a branch within the pile of branches than to move a log within its bundle.[6] The three dimensional entanglements of branches make movements more difficult, a phenomenon akin to increased strength.[6]

Generally three dimensional in structure, cross linked polymers have adjacent chains linked by covalent bonds (Figure 2.6).[6] Polymers with a cross-linked chain structure are called thermosetting plastic.[6] Cross-linking has a major influence on the properties of polymers, generally imparting hardness, strength, stiffness, brittleness and better dimensional stability as well as vulcanization of rubber.[6]

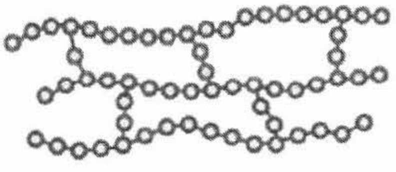


Figure 2.6: Cross-linked Structure of Polymer

Network polymers consist of spatial (three-dimensional) networks of three or more active covalent bonds (Figure 2.7).[6] A highly cross-linked polymer also is considered a network polymer.[6] Thermoplastic polymers that already have been formed or shaped can be cross-linked to obtain higher strength by subjecting them to high-energy radiation, such as ultraviolet light, x-rays, or electron beams.[6] However, excessive radiation can cause degradation of the polymer.[6]

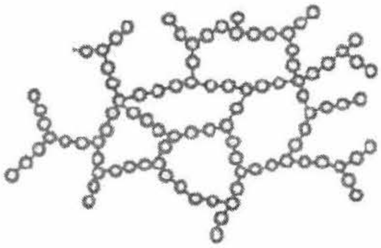


Figure 2.7: Network Structure of Polymer

Homopolymer is the same type of repeating units in a polymer chain.[6] However, as with solid-solution metal alloys, two or three different types of monomers can be combined to develop certain special properties and characteristics, such as improved strength, toughness, and formability of the polymer.[7] Copolymers contain two types of polymers, for example, styrene-butadiene, which is used widely for automobile tires.[7] Terpolymers contain three types, for example, acrylonitrile-butadiene-styrene (ABS), which is used for helmets, telephones, and refrigerator liners.[7]

Polymers such as polymethylmethacrylate, polycarbonate, and polystyrene are generally amorphous, that is, the polymer chains exist without long-range order.[8] The amorphous arrangement of polymer chains often is described as being like a bowl of spaghetti or like worms in a bucket (all interwined with each other).[8] In some polymers, however, it is possible to impart some crystallinity and thereby modify their characteristics.[8] This arrangement may be fostered either during the synthesis of the polymer or by deformation during its subsequent processing.[8]

The crystalline regions in polymers are called crystallites (Figure 2.8).[8] These crystals are formed when the long molecules arrange themselves in orderly manner, similar to the folding of a fire hose in a cabinet or of facial tissues in a box.[8] A partially crystalline polymer can be regarded as a two-phase material, one phase being crystalline and other amorphous.[8]

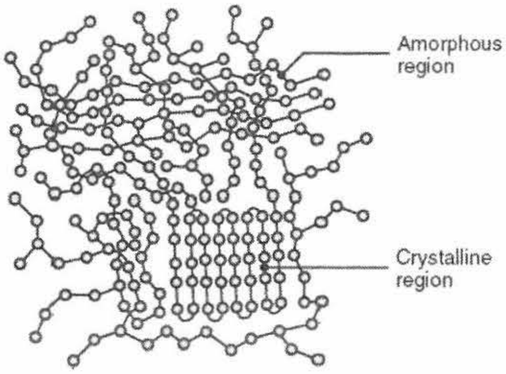


Figure 2.8: Amorphous and Crystalline Region in a Polymer

By controlling the rate of solidification during cooling and the chain structure, it is possible to impart different degrees of crystallinity to polymers, although never 100%.[8] Crystallinity ranges from an almost complete crystal (up to about 95% by volume in the case of polyethylene) to slightly crystallized (mostly amorphous) polymers.[8] The degree of crystallinity also is affected by branching.[8] A linear polymer can become highly crystalline, but a highly branched polymer cannot, although it may develop some low level of crstallinity.[8] It will never achieve high crystallite content because the branches interfere with the alignment of the chains into a regular crystal array.[8]

The mechanical and physical properties of polymers are greatly influenced by the degree of crystallinity, as crystallinity increases, polymers become stiffer, harder, less ductile, less dense, less rubbery, and more resistant to solvent and heat.[9] The increase in density with increasing crystallinity is called crystallization shrinkage and is caused by a more efficient packing of the molecules in the crystal lattice.[9]

Optical properties of polymers also are affected by the degree of crystallinity.[9] The reflection of light from the boundaries between the crystalline and the amorphous regions in the polymer causes opaqueness.[9] Furthermore, because of the index of refraction is proportional to density, the greater the density difference between the amorphous and crystalline phases, the greater is the opaqueness of the polymer.[9] Polymers that are completely amorphous can be transparent, such as polycarbonate and acrylics.[9]

Although amorphous polymers do not have a specific melting point, they undergo a distinct change in their mechanical behaviour across a narrow range of temperature.[9] At low temperatures, they are hard, rigid, brittle, and glassy, where as at high temperatures, they are rubbery or leathery.[9] The temperature at which a transition occurs is called the glass-transition temperature (Tg), also called the glass point or glass temperature.[9] The term glass is used in this description because glasses, which are amorphous solids, behave in the same manner.[9] Although most amorphous polymers exhibit this behaviour, an exception is polycarbonate, which is neither rigid nor brittle below its Tg.[9] Polycarbonate is tough at ambient temperatures and is used for safety helmets and shields.[9]

To determine Tg, the specific volume of the polymer is determined and plotted against temperature, and marked by a sharp change in the slope of the curve (Figure 7.9).[9] In the case of highly cross-linked polymers, the slope of the curve changes gradually near Tg, and hence, it can be difficult to determine Tg for these polymers.[9] The glass-transition temperature varies with different polymers (Table 2.1).[10] For example, room temperature is above Tg for some polymers and below it for the others.[10] Unlike amorphous polymers, partly crystalline polymers have distinct melting point, (Tm), (Figure 2.9, Table 2.1).[10] Because of the structural changes (first order changes) occurring, the specific volume of the polymer drops suddenly as its temperature is reduced.[10]

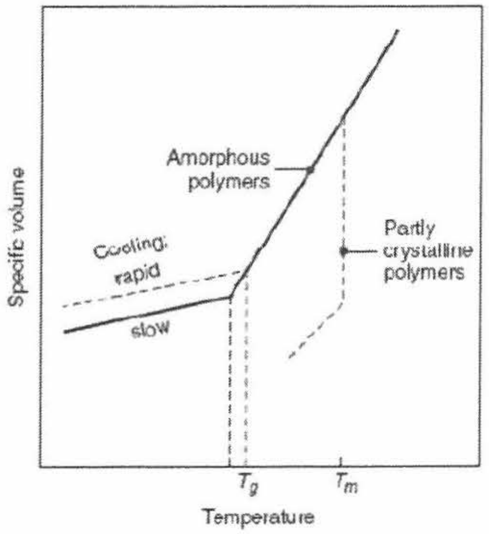
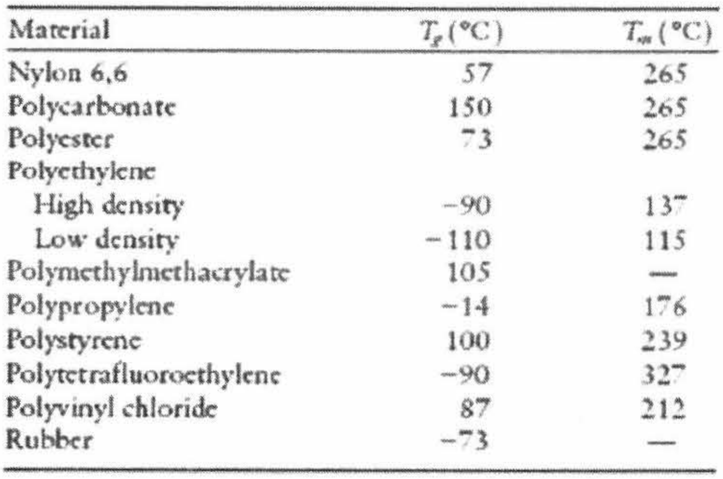


Figure 2.9: Specific Volume of Polymers as a Function of Temperature

Table 2.1: Glass Transition and Melting Temperatures of Some Polymers



Material	T_g (°C)	T_m (°C)
Nylon 6,6	57	265
Polycarbonate	150	265
Polyester	73	265
Polyethylene		
High density	−90	137
Low density	−110	115
Polymethylmethacrylate	105	—
Polypropylene	−14	176
Polystyrene	100	239
Polytetrafluoroethylene	−90	327
Polyvinyl chloride	87	212
Rubber	−73	—

2.1.1 Thermoplastic

Thermoplastic is a polymer that becomes pliable or mouldable above a specific temperature, and returns to a solid state upon cooling.[11] This is happen because of the increased temperature weakens the secondary bonds and adjacent chains.[12]

When the temperature of a thermoplastic is raised above its Tg, it first becomes leathery and then, with increasing temperature, rubbery.[12] Finally, at higher temperatures, it becomes a viscous fluid, its viscosity decreases with increasing temperature.[12] At still higher temperatures, the response of a thermoplastic can be linked to ice cream, it can be softened, moulded into shapes, refrozen, resoftened, and remoulded a number of times.[13] In practice, however, repeated heating and cooling cause degradation, or thermal aging, of thermoplastic.[13]

The typical effect of the temperature on the strength and elastic modulus of thermoplastics is similar to that of metals, with increasing temperature, the strength and the modulus of elasticity decrease and the toughness increases (Figure 2.10).[13]

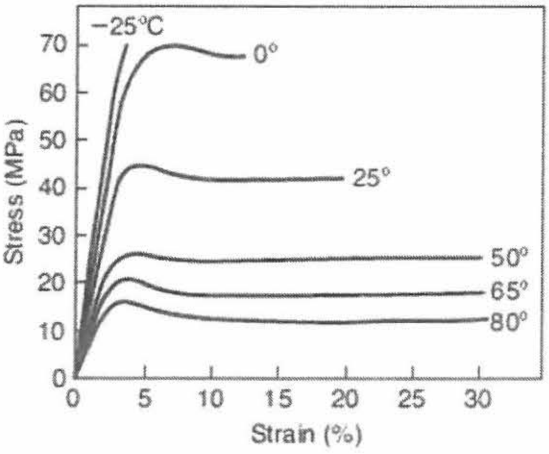


Figure 2.10: Effect of Temperature on the Stress-Strain Curve for Cellulose (Thermoplastic)

The behaviour of thermoplastics is similar to the strain-rate sensitivity of metals, indicated by the strain-rate sensitivity exponent m equation $\sigma = C\varepsilon^{m}$.[14] In general, thermoplastics have high m values, indicating that they can undergo large uniform deformation in tension before fracture (Figure 2.11).[14] Note how the necked region elongates considerably.[14] This phenomenon easily can be demonstrated by stretching a piece of the plastic holder for a 6-pack of beverages cans.[14] This characteristic enables the thermoforming of thermoplastics into such complex shapes as meat trays, lighted signs, and bottles for soft drinks.[14]

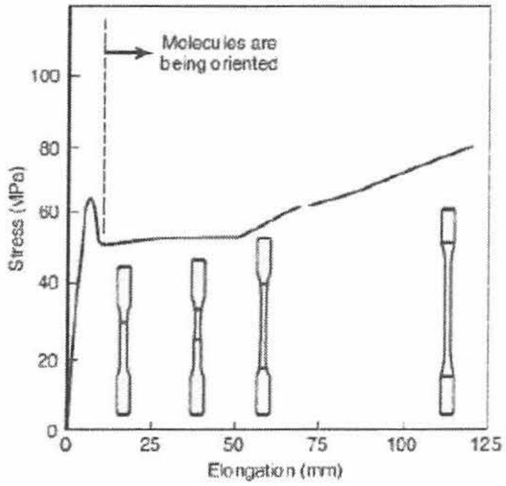


Figure 2.11: Load-Elongation Curve for Polycarbonate (Thermoplastic)

Orientation is the process when the long chain molecules tend to align in the general direction of the elongation when the thermoplastics are deformed (stretching).[14] As in metals, the polymer becomes anisotropic, so the specimen becomes stronger and stiffer in the elongated (stretched) direction than in its transverse direction.[14] Stretching is an important technique for enhancing the strength and toughness of polymers.[14]

Because of their viscoelastic behaviour, thermoplastics are particularly susceptible to creep and stress relaxation and to a larger extent than metals.[14] The extent of these phenomena depends on the polymer, stress level, temperature, and time.[14] Thermoplastic exhibit creep and stress relaxation at room temperature, most metals do so only at elevated temperatures.[14]

Some thermoplastic, such as polystyrene and polymethylmethacrylate, when subjected to tensile stresses or to bending, develop localized, wedge-shaped, narrow regions of highly deformed material, called crazing.[14] Although they may appear to be like cracks, crazes are spongy material, typically containing about 50% voids.[14] With increasing tensile load on the specimen, these voids coalesce to form a crack, which eventually can lead to a fracture of the polymer.[14] Crazing has been observed both in transparent, glassy polymers and in other types.[15] The environment, particularly the presence of solvents, lubricants, or water vapour can enhance the formation of crazes, environmental-stress cracking and solvent crazing.[15] Residual stresses in the material also contribute to crazing and cracking of the polymer, radiation especially ultraviolet radiation can increase the crazing behaviour in certain polymers.[15]

A phenomenon related to crazing is stress whitening.[15] When subjected to tensile stresses, such as those caused by folding or bending, the plastic becomes lighter in colour, a phenomenon usually attributed to the formation of microvoids in the material.[15] As a result, the material becomes less translucent (transmits less light) or more opaque.[15] This behaviour easily can be demonstrated by bending plastic components commonly found in coloured binder strips for report covers, household products, and toys.[15]

An important characteristic of some polymers, such as nylons, is their ability to absorb water.[15] Water acts as a plasticizing agents, it makes the polymer more plastic.[15] In a sense, it lubricates the chains in the amorphous region.[15] With increasing moisture absorption, the glass-transition temperature, the yield stress, and the elastic modulus of the polymer typically are lowered severely.[15] Dimensional changes also occur, especially in a humid environment.[15]

Compared to metals, plastics generally are characterized by low thermal and electrical conductivity, low specific gravity (ranging from 0.90 to 2.2), and a high coefficient of thermal expansion.[15] Because most polymers have low electrical conductivity, they can be used for insulators and as packaging material for electrical components.[15]

The electrical conductivity of some polymers can be increased by doping, introducing impurities, such as metal powders, salts, and iodides, into the polymer.[16] Discovered in the late 1970s, electrically conducting polymers include polyethylene oxide, polyacetylene, polyaniline, polypyrrole, and polythiophene.[16] The electrical conductivity of polymers increases with moisture absorption, their electronic properties also can be changed by irradiation.[16] Applications for conducting polymers include adhesives, microelectronic devices, rechargeable batteries, capacitors, catalysts, fuel cell, fuel-level sensors, deicer panels, radar dishes, antistatic coatings, and thermoactuating motors.[16]

Thermally conducting polymers also are being developed for applications requiring dimensional stability and heat transfer as well as for reducing cycle times in moulding and processing of thermoplastics.[16] These polymers are typically thermoplastics, such as polypropylene, polycarbonate and nylon, and are embedded with non-metallic thermally conducting particles which their conductivity can be as much as 100 times that of conventionally.[16]

2.2 THERMOPLASTIC ELASTOMER

TPE, sometimes referred to as thermoplastic rubber, are a class of copolymers or a physical mix of polymers, usually a plastic and a rubber which consist of materials with both thermoplastic and elastomeric properties.[17]

Besides TPE, there is another type of elastomer called thermosetting elastomer. The principal difference between TPE and thermosetting elastomer is the type of crosslinking bond in their structures.[17] Crosslinking is a critical structural factor which contributes to impart high elastic modulus.[17] The crosslink in TPE is a weaker dipole or hydrogen bond or takes place in one of the phases of the material, where as the crosslink in thermosetting elastomer is a covalent bond created during the vulcanization process.[17]

In order to qualify as TPE, a material must have these three characteristics.[17] The characteristics are processable as a melt at elevated temperature, absence of significant creep and the ability to be stretched to moderate elongations and upon the removal of stress, return to something close to its original shape.[17]

TPE can be divided into two main types which are block copolymer TPE (Figure 2.12) and blended TPE (Figure 2.13).[18]

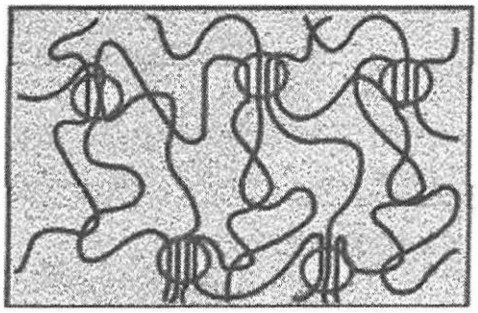


Figure 2.12: Molecular Structure of TPE Block Copolymer