CHAPTER 1 : INTRODUCTION

1.1 Plastics

1.1.1 General Concept Of Plastics

According to the ASTM D883, a plastic is a material that contains as an essential ingredient one or more organic polymeric substances of high molecular weight. It is solid in its finished state and, at some stage in its manufacture or processing into finished articles, can be shaped by flow.[1] The shaping by "flow" usually involve heat as well as pressure.[1,2]

1.1.2 Plastic Materials

Plastics contain not only polymers but also additives intended to enhance the processing or the physicochemical or mechanical properties.[1]

The polymer is usually over 95% of the formulation.[3] Examples of polymers are acrylonitrile butadiene styrene, acetals, acrylics, cellulosics, fluorocarbons, polyphenylene oxides, polyallomers, polyamides, polyaryl ether, polyaryl sulfone, polycarbonates, polyester, polyethylenes, polyimides, polyphenylene sulfide, polystyrenes, polysulfone, vinyls, alkyds, allyls, melamines, phenolics, polyesters, silicones, ureas, epoxies.[4]

The typical additives for plastics are

- *Fillers* [4] - Cheap, inner substance added to a plastic to make it less costly, increase bulkiness as well as improve mechanical, physical and electrical properties such as strength characteristics, hardness, density and dielectric strength. They can be inorganic, organic, mineral, natural and synthetic. Table 1 shows the details of fillers. A filler is usually added to between 10 and 50% of the weight of the mix.

Purpose	Filler
Bulk	Wood flour Sawdust Wood pulp Sisal-jute Purified cellulose Mica-rock
Reinforcement	Glass fibers and spheres Asbestos fibers Cellulosic fibers Cotton fabric Paper Synthetic fibers
Hardness	Inorganic pigments Mineral powders Metallic oxides Powdered metals Graphite Silica
Thermal insulation	Asbestos Diatomaceous earths Ceramic oxides Silica
Chemical resistance	Glass fibers and fabrics Synthetic fibers and fabrics Graphite Metallic oxides
Appearance	Colour pigments Dyestuffs Carbon blacks Powdered metals Phosphorescent minerals Woven fabrics

Table 1 : Fillers for plastics[4]

- *Plasticizers* [4] - A material incorporated in a plastic to increase its workability and its flexibility or distensibility. The most popular general purpose plasticizers are the phthalates. Epoxies, phosphates, adipate diesters, sebacates, polyesters are other examples of plasticizers.

- *Colourant* [4] - A material added to the plastics in measured quantity in order to produce a precise, predetermined colour of the finished articles to be molded. Broadly speaking, there are two types of colourants used in plastics, namely, dyes and pigments. Dyes are organic chemicals that are soluble in plastics while the pigments are inorganic chemical being insoluble, are dispersed throughout the mass.
- *Heat stabilizers* [4] - a material uses to prevent the degradation of resins during processing, when melts are subjected to high temperatures, or used to extend the life of end products of which they become a part.
- *Antioxidants* [4] - a chemical substance used to protect materials from deterioration through oxidation brought on by heat, light, or chemically induced mechanisms. Such chemical attack by oxygen may render a plastic brittle or cause melt flow instability, loss of tensile properties, and discolouration. The three main preventive mechanisms to control deterioration of plastics operate by absorbing or screening ultraviolet light, deactivating metal ions and decomposing hydro peroxides to non radical products.
- *Ultraviolet Light Absorbers* [4] - The function of ultraviolet light absorbers is to stabilize colour and to lengthening the life of a product under sunlight. Benzophenones and benzotriazoles are examples of ultraviolet light absorbers. The concentration of ultraviolet light absorber in any formulation run in the order of 0.25-1% .
- *Antistatic agent* [4] - A chemical substance that can be applied to the surface of a plastic article, or incorporated in the plastic from which the article is to be made. Its function is to render the surface of the plastic article less susceptible to accumulation of electrostatic charges which attract and hold fine dirt or dust on the surface of the plastic article. The most common antistatic agents for plastics are amines, quaternary ammonium compounds, phosphate esters, and polyethylene glycol esters.

- *Flame retardants* [4] - a resin which is compounded with certain chemicals to change its burning characteristics. The most common flame retardants are antimony, boron, halogens, nitrogen and phosphorus. Flame retardants work on four basics principles : either they insulate, create an endothermic cooling reaction, coat the product by excluding oxygen, or actually influence combustion through a reaction with materials that have different physicals.
- *Blowing agents* [4] - A blowing or foaming agent is used alone or in combination with other substance to produce a cellular structure in a plastic mass. Chemical blowing agents range from simple salts such as ammonium or sodium bicarbonate to complex nitrogen releasing agents.
- *Lubricants* [4] - Lubricants are used to enhance resin processibility and the appearance of end products. Lubricants fall into five categories : metallic stearates, fatty acid amides and esters, fatty acids, and hydrocarbon waxes, and low molecular weight polyethylenes. Underlubrication will cause degradation and frequently higher melt viscosities, but overlubrication can cause too much slippage and lower outputs. An imbalance of lubricant and stabilizer can cause plateout or the migration of pigment from a melt system.

1.1.3 Types Of Plastics

Based on ASTM D 883, plastics are divided into the following main groups :-

(A) With regard to their chemical and technological behavior.

- *Thermoplastics* : " A plastic that can be repeatedly softened by heating and hardened by cooling through a temperature range which is characteristic of the plastic and that in the softened state can be shaped by flow into article by molding or extrusion".[1]

- *Thermosets* : " A plastic that, after having been cured by heat or by other means, is substantially infusible and insoluble".[1]

(B) With regard to their mechanical behavior as tested by specific ASTM methods at room temperature.

- *Rigid plastics* : plastics that have an elastic modulus greater than 700 MPa (100,000 psi)[1]
- *Semirigid plastics* : plastics that have an elastic modulus between 70 to 700 MPa (10,000 - 100,000 psi)[1]
- *Nonrigid plastics* : plastics that have an elastic modulus of not more than 70 MPa (10,000 psi) [1]

1.2 Tyre

1.2.1 General Introduction

A pneumatic tyre is a composite structure of compounded rubber, fabric and steel.[5] It is fitted to a rim and wheel to support a vehicle and its load on a cushion of compressed air which is contained within the tyre. The principle of a pneumatic tyre is to confine compressed air to form a cushion between the vehicle and road.[5]

The pneumatic tyre performs a variety of functions that are essential to the effective operation of most modes of transportation which includes the following : [6]

i. Supporting the vehicle load.

ii. Transmitting driving and braking forces to the road surface.

iii. Producing lateral forces for cornering and vehicle handling control to help guide the direction of travel.

iv. Providing safety through maneuverability, durability, wet and dry traction, snow traction and high speed performance.

v. Maintaining dimensional stability by undergoing only inappreciable change of size or shape upon inflation

vi. Providing economy through long tread life (wear resistance) and low rolling resistance (energy consumption).

To perform these functions, the tyre must have enough rigidity to develop substantial forces in all directions, enough flexibility to be able to envelope obstacles without sustaining damage and a long fatigue life in flexing from a doubly curved shell to a flat surface and back. [6]

1.2.2 Application of Tyres

Tyres can be classified by the type of vehicle on which they are applied.[6] Major classifications include automobile, truck, off-road, farm, aircraft and race tyres. Other classifications include bicycle, motorcycle and industrial tyres.

1.2.3 Tyre Components

The major components of a typical pneumatic tyre are carcass, beads, tread, belts, chafers, inner tube, inner liner, sidewall, shoulder and crown which perform distinctly different functions in service.[6] These components are as shown in Figure 1.

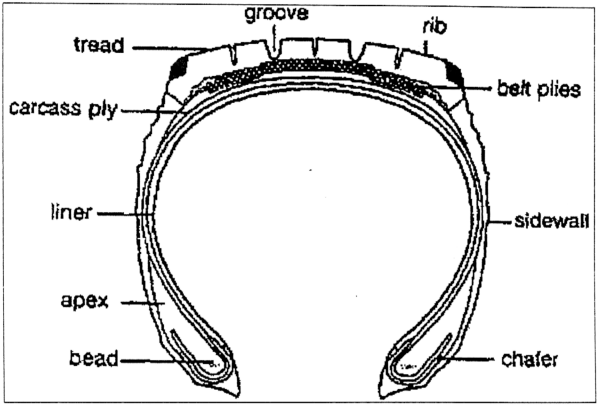

Figure 1 : Major components of a typical pneumatic tyre[6]

Each component of a tyre is required to provide some performance attributes for customer satisfaction and / or for fabrication in a specific manufacturing process. Table 2 shows the different properties required for different components in a tyre.[7]

Tyre Component	Compound Requirements
Tread	1. Resistance to abrasion 2. Good wet and dry traction 3. Resistance to chunking, tearing and groove cracking 4. Low heat build up 5. Low rolling resistance 6. Good extrusion characteristics
Sidewall	1. Excellent flex fatigue resistance 2. Resistance to kerb cutting 3. Good weathering performance 4. Good extrusion characteristics
Belt	1. Good adhesion to steel or fabric 2. Good retention of adhesion upon ageing 3. Good tear strength 4. Moderate to high modulus 5. Good flex resistance 6. High green strength and tack
Carcass/Ply	1. Good adhesion to carcass cords 2. Good tear strength 3. Good flex resistance 4. Excellent ageing performance 5. Good green strength and good tack 6. Excellent calendering behaviour
Apex	1. Very high hardness 2. High modulus 3. Low compression set
Inner Liner	1. Excellent ageing performance 2. Good flex resistance 3. Good tear strength 4. Excellent permeability resistance 5. Good tack and green strength

Table 2 : Compound requirements for different components in a tyre [7]

1.2.4 Tyre Compounding

Compounds are mixtures of materials such as elastomers, carbon black and / or silica and a cure system. [6] Other ingredients are added to aid process, to develop specific properties or to provide compound stability.

The objectives of compounding are : [8]

i. to facilitate processing and fabrication;

ii. to ensure quality with minimal reject rate;

iii. to achieve the required properties in the vulcanizate, and

iv. to provide durability at competitive cost

Compounding ingredients can be classified into nine major categories, which are defined as follows :

- *Elastomers* [9, 10] : The basic component of all rubber compounds, it may be in the form of rubber alone, or " masterbatches" of rubber-oil, rubber-carbon black, or rubber-oil-carbon black, reclaimed rubber, or thermoplastic elastomers. Today there are more than twenty different elastomers commercially available. Their properties differ widely, so do their prices. Examples of elastomers are natural rubber(NR), styrene butadiene rubber(SBR), butyl (IIR), butadiene rubber (BR).
- *Processing Aids* [9, 10] : Materials used to modify rubber during the mixing or processing steps, or to aid in a specific manner during extrusion, calendering, or molding operations. Table 3 is a list of typical processing aids and their function.

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Composition	Example (tradenames)	Function
Activated Dithi-bisbenzanilide	Pepton 44	Peptizer for NR
Poly-paradinitrosobenzene	Polyac	Chemical conditioner for IIR
Xylyl mercaptans	RPA 3	Peptizer for NR, IR, SBR and NBR. Stabilizer for cement viscosity
Low molecular weight polyethylene	A-C Polyethylene 617A	Release agent, lubricant
Calcium oxide	DesiCal P	Desiccant
Aliphatic-napthenic-aromatic resins	Strucktol 60NS	Homogenizing agent for all elastomers
Paraffin wax	Numerous	Release agent, lubricant
Polyethylene glycol	Carbowax PEG3350	Activator for silica lubricant
Petroleum hydrocarbon	Petrolatum	Release agent, lubricant

Table 3 : Processing aids of rubber compound [10]

Vulcanization Agents [9,10] : With the exception of thermoplastic elastomers, these materials are necessary for vulcanization, since without the chemical crosslinking reactions involving these agents, no improvement in the physical properties of the rubber mixes can occur. Through chemical crosslinking, an elastomeric compound is converted from a soft, tacky thermoplastic to a strong temperature stable thermoset. Sulfur is by far the most widely used vulcanizing agent. Sulfur bearing materials such as thiuram disulfides (TMTD) and dithiodimorpholine (DTDM) are sometimes used as complete or partial replacements of elemental sulfur in a low sulfur or sulfur less cure system to improve heat resistance of a compound. Table 4 shows each popular type of vulcanizing agent and its use.

Type	Common Use
Sulfur or sulfur bearing materials	Natural rubber, Isoprene, SBR, Butyl, Butadiene, EPDM, Nitrile, Norsorex
Organic Peroxides	Urethane, Silicone, Chlorinated Polyethylene, Crosslinked Polyethylene, Vamac, Vynathene, PVC/Nitrile
Metallic Oxides	Neoprene, Hypalon, Thiokol
Organic Amines	Acrylic, Fluorocarbon, Epichlorohydrin, Vamac
Phenolic Resins	Butyl

Table 4 : Vulcanizing Agents of rubber compound [10]

Accelerator [9, 10] : In combination with vulcanizing agents, these materials reduce the vulcanization time (cure time) by increasing the rate of vulcanization. In most cases, the physical properties of the products are also improved. Most accelerators being used today are organic substance containing both nitrogen and sulfur. Table 5 shows each major category of organic accelerators, examples of them and their typical use.

Activators [9, 10] : These ingredients form chemical complexes with accelerators, and thus aid in obtaining the maximum benefits from an acceleration system by increasing vulcanization rates and improving the final product's properties. The most widely used activators are zinc oxide, stearic acid, litharge, magnesia, and amines

Type	Example	Typical Use
Aldehyde amine	Reaction product of butyraldehyde and aniline	Fast curing accelerator for reclaim, hard rubber and self curing cements
Amines	Hexamethylene tetramine	Delayed action slow accelerator for natural rubber
Guanidines	Diphenyl guanidine (DPG)	Secondary accelerator to activate thiazole type accelerator
Thioureas	Ethylene thiourea (ETU)	Fast curing accelerator for Neoprene, Hypalon and Epichlorohydrin
Thiazoles	Benzothiazyldisulfide (MBTS)	Safe processing moderately fast curing accelerator for natural rubber, isoprene, SBR, nitrile and EPDM
Thiurams	Tetramethylthiuram disulfide (TMTD)	Fast curing sulfur bearing accelerator for SBR, Nitrile, Butyl and EPDM
Sulfenamides	N-cyclohexyl-2-benzothiazy lsulfenamide (CBTS)	Safe processing, delayed action accelerator for natural rubber, SBR and Nitrile
Dithiocarbamates	Zinc dimethyldithiocarbamate (ZDMC)	Fast curing accelerator for SBR and Butyl
Xanthates	Dibutylxanthogen disulfide	Fast curing, low temperature accelerator for natural rubber and SBR

Table5 : Organic accelerators of rubber compound[10]

Age-Resistors (Antidegradants) [9, 10] : Antioxidants, antiozonants, and other materials used to reduce aging processes in vulcanizates. They function by slowing down the deterioration of rubber products. Deterioration occurs through reactions with materials that catalyze rubber failure, i.e., oxygen, ozone, light, heat, radiation, and so forth. Table 6 shows each widely used type of antidegradant, an example of it, and its relative effectiveness in various areas of protection.

Type	Example	Resistance to Staining	Resistance to Oxygen	Resistance to Heat	Resistance to Flexing	Resistance to Metal Catalysis	Resistance to Ozone
Hindered Phenols	2,6-Di-t-butyl-p-cresol	None to slight	F	F	F-P	P	P
Hindered Bisphenol	2,2'-Methylene-bis-(4-methyl-6-t-butylphenol)	None to slight	G-F	G-F	F-P	G	P
Hindered Thobisphenols	4,4'-thiobis(6-tert-butyl-m-cresol)	Slight	G-F	G-F	F-P	F	P
Hydroquinones	2,5-di(tert-amyl) hydroquinone	None to slight	G-F	F	F-P	P	P
Phosphites	Tri(mixed mono and dinonyl-phenyl) phosphite	None to Slight	G-F	F	F-P	P	P
Diphenylamines	Octylated diphenylamine	Slight to moderate	G-F	G-F	F	P	P
Naphthylamines	Phenyl-alpha-naphthylamine	Moderate	G	G	G-F	F	P
Quinolines	2,2,4-trimethyl-1, 2-dihydroquinoline	Slight to moderate	G	E	F	P	F-P
Carbonyl amines condensation product	Reaction product of diphenylamine & acetone	Considerable	G	E	E-G	P	F-P
Paraphenylenediamines	Mixed Diaryl-p-phenylenediamines	Considerable to severe	E-G	E-G	E-G	E	E-G

E=Excellent; G=Good; F=Fair; P=Poor

Table 6 : Antidegradant of rubber compound [10]

Fillers [9, 10] : These materials are used to reinforce or modify physical properties, impart certain processing properties, or reduce cost. Table 7 is a list of widely used fillers.

	Fillers
Reinforcing type	Carbon black, silica, zinc oxide, magnesium carbonate, aluminum silicate, sodium Aluminosilicate, magnesium silicate
Extending type	Calcium carbonate, Barium sulfate, Aluminum Trihydrate, Talc and Soapstone

Table 7: Fillers of rubber compound [10]

Softeners [9] : Any material that can be added to rubber to aid in mixing, promote greater elasticity, tack, or to extend (or replace) a portion of the rubber hydrocarbon (without a loss in physical properties) can be classified as a softener.

Miscellaneous Ingredients [9] : Materials that can be used for specific purposes but are not normally required in the majority of rubber compounds can be included in this group. It includes retarders, colours, blowing aids, abrasives, dusting agents, odourants, homogenizing agents, and so forth.

1.2.5 Tyre Industry in Malaysia

There are four major tyre factories in Malaysia. They are

- Silverstone in Taiping (Perak),
- Sime Tyre in Alor Setar(Kedah),
- *DMIB in Petaling Jaya (Selangor) and*
- Good Year in Shah Alam (Selangor)

1.3 Plastics In The Tyre Industry

Basically, plastics can be available in tyre factories in various forms. The solid and bale form of elastomers are packed with plastic wrappers. Plastic bags are used to fill rubber ingredients such as antidegradant, vulcanizing agent, activators prior to tyre compounding. Raw tyres before moulding are covered with a plastic sheet to prevent dust collecting. Plastic tapes are used to wrap finished tyres. Plastic bags are also used in laboratory to keep remnant test samples.

1.4 Effect Of Plastics On Tyres

Studies have shown that tyres are sensitive to plastics contamination.[11] Unmelted plastics in tyres lead to poor bonding of tyre compounds during tyre curing. Plastics present in tyres due to an improper mixing temperature during the compounding process can result in the presence of unmelted plastic wrappers of elastomers and from plastic bags of rubber ingredients or due to tyre operators, who accidentally or intentionally contaminate the tyres with plastics. The presence of unmelted plastics on an adhesion-failure tyre can be identified by using the Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX) and Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR).

Appendix I shows a study on adhesion-failure tyre. The presence of unmelted plastics were detected by analysing the good areas as well as the bad areas by using the SEM, the EDX and the FTIR-ATR. The conclusion was made based on the following observations :-

- SEM detected sheet form contaminants on the defect area.
- EDX detected C element on the contaminant on the defect area.
- The defect area has a peak at 1462.29 cm^{-1} and a doublet at about 720 cm^{-1}.

1.5 Objective Of Project

This project aims to investigate the elastomers in plastic wrappers and in plastic bags used in tyres. The instruments used in the investigation are :-

- Fourier Transform Infrared - Transmission
- Fourier Transform Infrared - Attenuated Total Reflectance
- Differential Scanning Colorimeter
- Softening point apparatus

The composition of plastics can be detected by Fourier Transform Infrared - Transmission and Fourier Transform Infrared - Attenuated Total Reflectance. Differential Scanning Colorimeter is used to identify the melting point of plastics. The softening point apparatus as implied by its name is used to determine the softening point.

All the information collected are intended to contribute towards troubleshooting in the tyre industry.