

## CHAPTER II

### THEORY AND LITERATURE SURVEY

#### 2.1 Production of High Impact Polystyrene (HIPS)

Rubber is incorporated with polystyrene in commercial high impact polystyrene (HIPS). In order to provide a rubber with better compatibility with the continuous polystyrene phase, it is advantageous to graft the rubber with polystyrene. The most common commercial rubbers are pure polybutadiene or copolymers with styrene; cis-polybutadiene is particularly popular.

In mass-produced rubber modified polystyrene, the rubber is dissolved in the styrene. As the polymerization of the styrene proceeds, two phases are formed: a rubber-rich phase and a polystyrene-rich phase. Grafting occurs during the polymerization of styrene when some of the free radicals react with the rubber as shown in Figure 2.1. Grafting is important because the graft copolymer concentrates at the interface and strongly affects particle size, morphology and toughness. Some radical transfer reaction probably involves the allylic hydrogen of the diene.

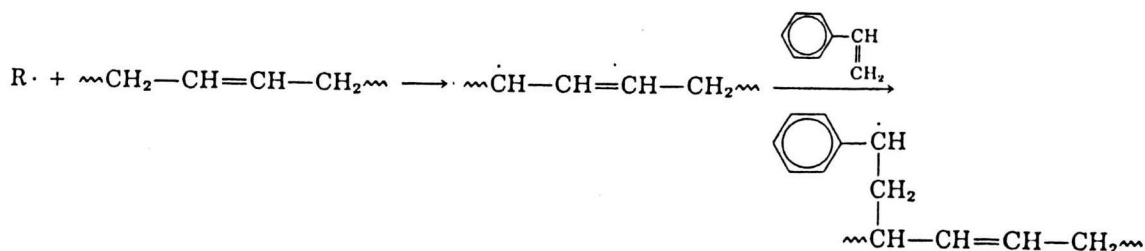


Figure 2.1 : Grafting of polystyrene chain on rubber.

When the polymerization proceeds, with proper agitation, phase inversion begins to occur: the polystyrene becomes continuous and contains small domains of rubber solution. Because the equilibrium of styrene between the two phases tends to favor a higher concentration of styrene in the rubber phase, the phase inversion generally occurs when the amount of polystyrene is two to three times the initial amount of rubber.

Shortly after phase inversion, particle boundaries become fixed and polymerization continues both inside the rubber particle and in the continuous phase. As conversion approaches completion, the temperature tends to increase. As a result, cross-linking of the rubber phase takes place, yielding a final rubber particle that remains stable during subsequent forming operations. The phase inversion sequence for a polybutadiene-styrene system is shown by phase-contrast photomicrographs, as shown in Figure 2.2 [3]. The photomicrographs show the dark phase as the polystyrene and the light phase as the polybutadiene. Without agitation, phase inversion does not occur and the rubber phase remains continuous.

Particle size, particle size distribution, and particle morphology are all important in determining the balance of properties of a rubber-modified polystyrene.

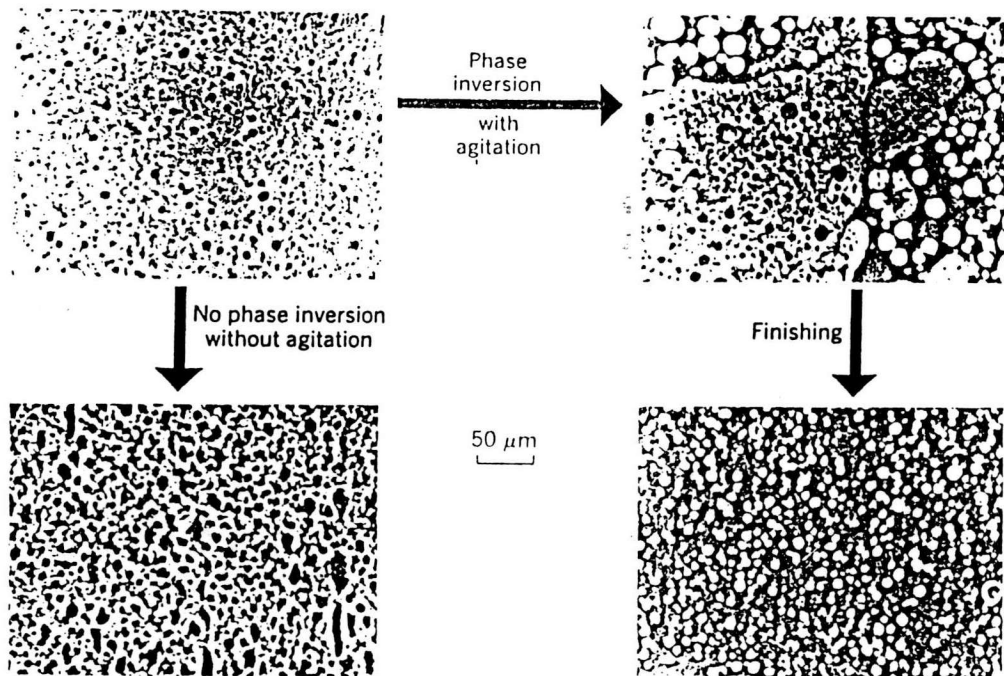


Figure 2.2 : Phase-contrast photomicrographs showing particle formation via phase inversion with agitation.

## 2.2 Degradation of High Impact Polystyrene

The growth of polymer recycling has led to considerable efforts in studying the changes in the properties of processed polymers. High impact polystyrene (HIPS) represents a common polymer with a relatively high proportion of waste in the local processing industry in Thailand.

Scraps can be classified into two types : post fabricating scraps and post consumer scraps. After polystyrene has passed the processing or the fabricating steps, usually degradation can happen and it tends to limit the possibilities for plastic waste recycling. Post industrial scraps are more easily reused than post consumer

scraps because of their high quality. Post consumer scarp is often contaminated with foreign matters which are usually difficult and costly to separate. Sometimes, the post consumer scraps may have aged to an uncontrolled extent and are structurally damaged.

Several papers have been published on the subject of degradation. La Mantia et al. [4] studied the effect of flow on the degradation of polystyrene using capillaries of different length. They also discussed the possible breakage of C-C links under elongational flow. Murthy and Raghavendra [5] concluded that increased degradation of polystyrenes is caused by higher shearing in extrusion and pelletization processes, Inaba and Inoue [6] investigated the changes of molecular weight of polystyrene degraded at 340-380 °C. F. A. Jamil and S. D. A. Shubber [7] also studied the changes in the rheological and the mechanical properties of recycled HIPS. Their results showed that the recycling of HIPS caused a decrease in the shear stresses and consequently in the viscosity at constant shear rate. The higher pressure capillary rheometer gave a greater decrease in the shear stress than with the Brabender plasticorder. Tensile stress values were progressively decreased with the laboratory extruder but increased in the case of Brabender mixers.

The most important factors affecting degradation of polymers are thermal treatment, the amount of shear stress acting on the polymer and the residence time, i.e. the time for which the polymer melt is subjected to certain thermal and shear effects.

## 2.3 Impact Modifier for HIPS

### 2.3.1 Impact Modifier

Earlier papers had studied and provided guidelines for improving the properties of recycled plastics. S. Fellahi, S. Boukobbal and M. M' Hala [8] studied the improvement of flows and the mechanical properties of recycled mixed plastics by adding titanates coupling agents, CPE, Peroxide and Novolak. D. J. Seitz [9] studied the modification of impact properties of an old, abandon liner of refrigerators made of HIPS.

Appropriate impact modifier is believed to enable polymers to withstand greater high-speed stress before failing catastrophically. Generally, low-speed stress is resisted by the matrix polymer. Most impact modifiers function by introducing discontinuous domains of low-modulus polymers such as elastomers into the resin system. The discontinuous nature of the domains minimizes the negative effects on the tensile strength, modulus, and heat-deflection temperature. The additives are therefore said to improve a system's property balance.

SBS block copolymer are used to improve the performance of polyolefins, styrenics and engineering thermoplastics. By the use of polymer blends, physical properties can be altered to produce useful materials with a wide range of applications. Desirable properties can be achieved more easily in many instances by proper blend selection than by polymerization of a new polymer. This being the case, a major thrust of the technology on rubber thermoplastic blends is to provide materials to meet specific applications as efficiently as possible. Moreover, certain rubbery

thermoplastic blends possess a combination of physical and rheological properties that are unavailable in a single polymer. This happens when one modifies styrene-butadiene-styrene block copolymers by addition of butadiene or styrene homopolymers. The butadiene homopolymer resides in the polybutadiene phase of the block copolymer and the modulus is reduced. Styrene homopolymer is incorporated in the polystyrene phase and the modulus is increased.

### 2.3.2 SBS Block Copolymer

#### 2.3.2.1 Structure of SBS Block Copolymer

Most of the polystyrene/polydiene block copolymers that are thermoplastic elastomers have the basic structure of poly(styrene-b-butadiene-b-styrene) or poly(styrene-b-isoprene-b-styrene). For convenience, they will be referred to here as S-B-S and S-I-S respectively. The most important result of this structure is that they are phase separated systems, quite unlike the corresponding random copolymers. The two phases, polystyrene and polydiene, retain many of the properties of the respective homopolymers. For example, such block copolymer have two glass transition temperatures ( $T_g$ ) reflecting the characteristics of the respective homopolymers whereas the equivalent random copolymers have a single intermediate  $T_g$  as shown in Figure 2.3 [10]. This means that in S-B-S and S-I-S block copolymers, at room temperature the polystyrene phase is strong and rigid while the polydiene phase is soft and elastomeric.

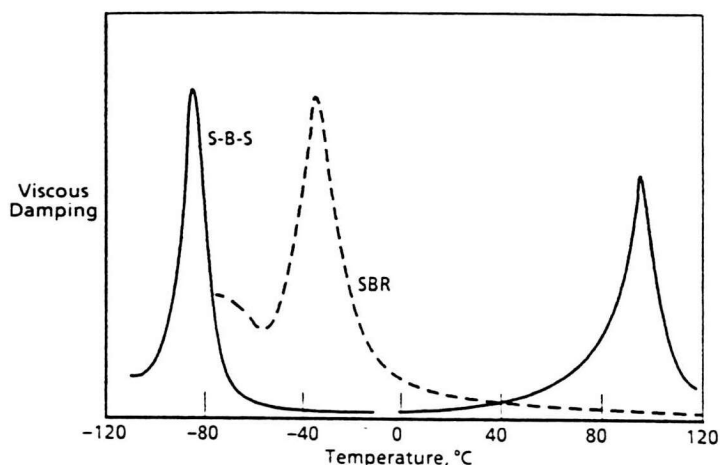


Figure 2.3 : The glass transition temperatures of S-B-S and SBR copolymers.

If the polystyrene phase is only a minor part of the total volume, it is reasonable to postulate a phase structure as shown, in idealized form, in Figure 2.4 [10]. In this structure, the polystyrene phase consists of separate spherical regions or domains. Since both ends of each polydiene chain are terminated by polystyrene segments, these rigid polystyrene domains act as multifunctional junction points to give a crosslinked elastomer network similar to that of a conventional vulcanized rubber. However, in this case the crosslinks are formed by a physical rather than a chemical process and so are labile. At room temperature, a block copolymer of this type has many of the properties of a vulcanized rubber. However, when it is heated, the domains soften, the network loses its strength and eventually the block copolymer can flow. When the heated block copolymer is cooled down, the domains become hard again and the original properties are regained.

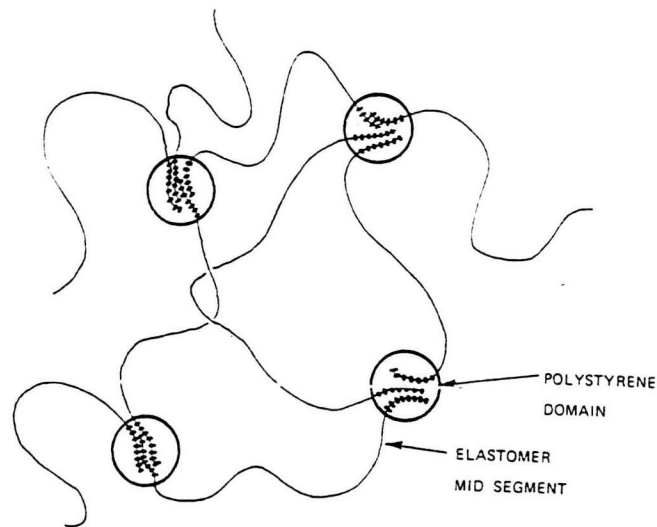


Figure 2.4 : Phase structure of S-B-S block copolymer.

This explanation has been given in terms of S-I-S and S-B-S block copolymers but it should apply, with similar restrictions on relative phase volumes, to other block copolymers such as S-I-S-I-S-I... and  $(S-B)_n$  (where x represents a multifunctional junction point), since these should be able to form continuous network structures similar to that shown in Figure 2.4. On the other hand, block copolymers such as S-I and B-S-B cannot form these structures, since only one end of each polydiene chain is terminated by a polystyrene segment. Because of this, these block copolymers are weak materials with no resemblance to conventional vulcanized rubbers.

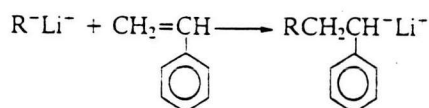
When this explanation was first postulated, it was generalized to include all block copolymers with alternating hard and soft segments. Specifically it was applied to polycarbonate/polyether and poly(dimethyl siloxane)/poly(silphenylene siloxane) block copolymers. A similar explanation was applied by analogy to segmented polyurethanes and it is now accepted as the underlying mechanism which gives most thermoplastic elastomers their valuable properties.



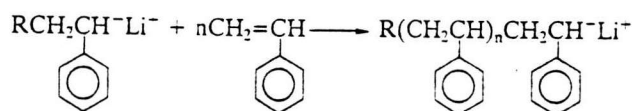
### 2.3.2.2 Synthesis of SBS Block Copolymer

S-B-S, S-I-S and similar block copolymers are made by anionic polymerization. This reaction is limited to only three common monomers - styrene (including substituted styrenes), butadiene and isoprene. It is usually carried out in an inert hydrocarbon solvent such as cyclohexane or toluene and it is necessary to rigorously exclude oxygen, water or any impurity that can react with the highly reactive propagating species. Under these conditions the polymeric molecular weights can be precisely controlled. This is in contrast to other block and graft copolymers which generally contain a broad distribution both of the segment molecular weights and also of their arrangements in the polymer molecule. The preferred initiators are organolithiums, although others can be used.

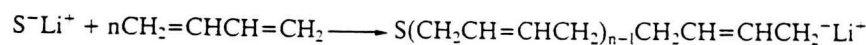
Sec-butyl lithium is the preferred initiator because it initiates the polymerization very readily. That is to say, the rate of the initiation reaction is high compared to that of the subsequent polymerization. This initiator first reacts with one molecule of styrene monomer. This is known as the initiation reaction.



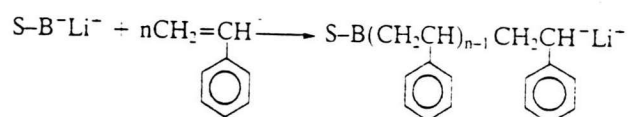
The product can then continue polymerization of the styrene and this is known as the propagation reaction.



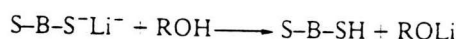
The new end product is termed polystyrol lithium (the effects of the terminal sec-butyl radical are ignored) and we will denote it as  $S^-Li^+$ . If a butadiene is added, the  $S^-Li^+$  can initiate further polymerization:



For the above reaction, we will denote the product  $S-B^-Li^+$ . It also is an initiator, so that if more styrene monomer is now added, it will polymerize onto the “living” end of the polymer chain:



When this last reaction is complete, the product  $(S-B-S^-Li^+)$  can be inactivated by the addition of a protonating species such as an alcohol. This terminates the reaction:



### 2.3.2.3 SBS Block Copolymer Used in This Study

SBS block copolymer used in this study is styrenic block copolymers produced by anionic polymerization from styrene and butadiene. They are extremely versatile base polymers which may be compounded with many different materials, such as other polymers oils and fillers to produce elastomeric compounds.

In the plastics and elastomers industries, new products are often treated by mixing different ingredients: this is known as compounding. The objective of this

mixing process is to produce a compound which combines the positive properties of each element of the mixture and has good homogeneity and stability.

The fundamental advantage of compounding is that it enables the compounder to tailor make a compound to satisfy the requirements of the end-user. The principal compounding ingredients are other plastics (frequently polystyrene), oil, fillers, and stabilizers.

SBS thermoplastic elastomers are styrenic block copolymers. Three feedstocks are needed to produce styrenic block copolymer (SBCs), namely styrene and butadiene. The styrene is polymerized in sophisticated sequential reaction with butadiene. Styrene-butadiene-styrene (SBS), for example, is the material suitable for footwear and the modification of bitumen.

SBS block copolymer are produced by anionic polymerization. The reaction is, started by an alkyl lithium initiator. Lithium alkyls ionize, initiation of the reaction takes place and continues in a propagation process whereby monomers are joined together in chains to form polymers. One characteristic of the anionic polymerization is to produce a "living entity". The subsequent addition into the reactor of another monomer results in the production of a block copolymer.

The reaction of styrene monomer with alkyl lithium followed by a butadiene results in polystyrene-polybutadiene-polystyrene block copolymer as shown in Figure 2.5.

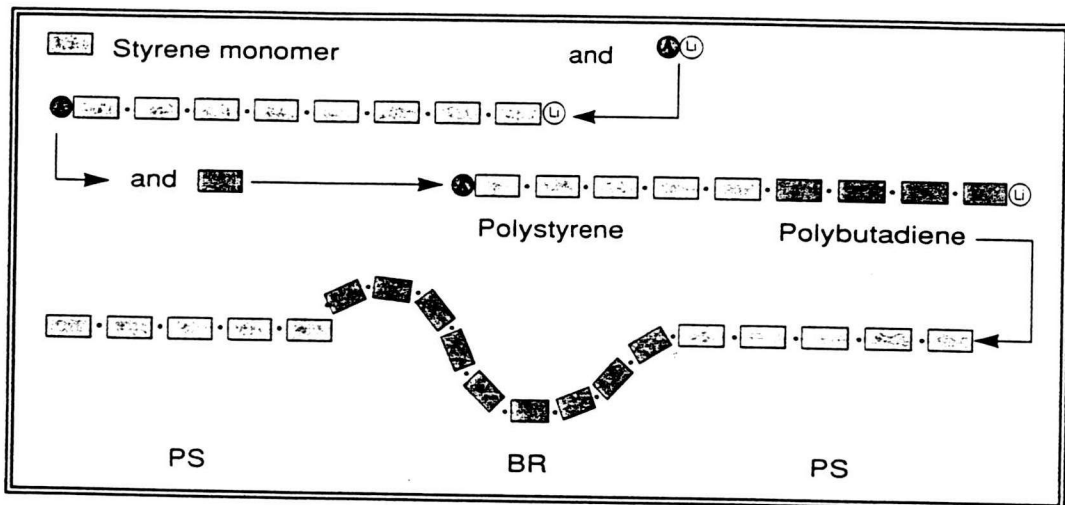


Figure 2.5 : Polymerization of thermoplastic elastomers.

SBS block copolymer typically contain a larger volume of elastomer phase than of polystyrene phase. On a microscopic scale, the hard polystyrene domains are embedded in the continuous elastomeric matrix and act as physical crosslinks. During processing in the presence of heat and shear forces or solvent, the polystyrene domains soften and permit flow. After cooling or solvent evaporation, the polystyrene domains re-form and harden, locking the elastomeric network in place again.

As an additive, it can improve the impact toughness of plastics, the high and low temperature viscosities of motor oils or the shrink characteristics of polyester thermosets. At high enough concentrations, it can improve the flexibility, softness, elasticity and feel of certain plastics.

SBS block copolymer are extremely versatile base polymers which can be compounded with a wide variety of other polymers, oil and fillers to produce compounds which find outlets in the areas of footwear, medical, automotive and

moulded and extruded technical goods. It toughens and improves the impact properties of these plastics in room and low temperature conditions. SBS block copolymer are used as additives to improve impact resistance and hot strength, which helps avoid damage in demoulding operations.