"COMPARATIVE STUDY OF PS-LDPE BLENDS WITH SBR ADDITION AS COMPATIBLIZER BY TWO STEP CROSSLINKING PROCESS"

By

Muhammad Awais Anwar

NUST201362321MSCME67713F

School of Chemical and Materials Engineering (SCME)

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Muhammad Awais Anwar   NUST201362321MSCME67713F

This thesis is submitted as a partial fulfillment of the requirements for the degree of

(MS Materials and Surface Engineering)

Supervisor:

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National University of Sciences and Technology (NUST),

H-12 Islamabad, Pakistan

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National University of Sciences & Technology (NUST)

Form TH-1

MASTER'S THESIS WORK

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Credit Hours Completed **24** CGPA **3.06**

Course Work Completed

S/No	Code	Title	Core/Elective	CH	Grade
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2	MSE-821	Mechanical Behavior of Materials	Core	3	C+
3	MSE-811	Materials Thermodynamics	Core	3	B+
4	MSE-812	Phase Transformation and Microstructures	Core	3	C+
5	MSE-855	Nano Materials and Nano Processing	Elective	3	B+
6	MSE-862	Electronic and Magnetic Materials	Elective	3	B+
7	MSE-872	Composite Materials	Elective	3	B
8	MSE-880	Corrosion and Protection	Elective	3	B+
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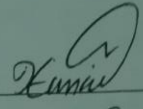
Title: **Comparative Study of PS-LDPE Blends with SBR Addition as Compatiblizer by Two Step Crosslinking Process.**

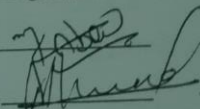Presented on: **30-08-2017**   at: **1500 hrs in SCME Seminar Hall**

Be accepted in partial fulfillment of the requirements for the award of Masters of Science degree in Materials & Surface Engineering.
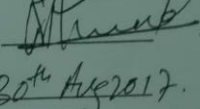
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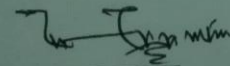Name: **Dr Iftikhar Hussain Gul**   Signature: _____

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Dated: _30th Aug2017_.

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Date 30 . 08. 2017

Dean/Principal
Date 30/8/17

School of Chemical &Materials Engineering (SCME)

V

THESIS ACCEPTANCE CERTIFICATE

Certified that final copy of MS/MPhil thesis written by Mr/Ms Muhammad Awais Anwar (Registration No NUST201362321MSCME67713F), of School of Chemical & Materials Engineering (SCME) has been vetted by undersigned, found complete in all respects as per NUST Statues/Regulations, is free of plagiarism, errors, and mistakes and is accepted as partial fulfillment for award of MS/MPhil degree. It is further certified that necessary amendments as pointed out by GEC members of the scholar have also been incorporated in the said thesis.

Signature: _____

Name of Supervisor: <u>Dr Nasir M. Ahmad</u>

Date: _____

Signature (HOD): _____

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Signature (Dean/Principal): _____

Date:_____

Dedication

I would like to dedicate this work to my Parents and my

Honorable Supervisor

Acknowledgment

ABSTRACT

In this research Polystyrene and Low Density Polyethylene were blended in fixed ratio PS/LDPE (80/20) with the Synthetic styrene butadiene rubber (SBR) in different proportions PS/LDPE/SBR (80/20/2.5), PS/LDPE/SBR (80/20/5), PS/LDPE/SBR (80/20/10), PS/LDPE/SBR (80/20/15). The same is blended with the peroxide by double cross linking method PS/LDPE/SBR/peroxide (80/20/2.5 + 0.05%), PS/LDPE/SBR/ peroxide (80/20/5 + 0.05 %), PS/ LDPE/ SBR/ peroxide (80/20/10+ 0.05 %), PS/LDPE/SBR/peroxide (80/20/15+ 0.05 %).

In this mixing a new method is studied to compatibilize the polymer blends of PS- Polystyrene and LDPE- Low density Polyethylene in the presence of styrene butadiene rubber (SBR). SBR is first crosslinked partially by acute quantity of peroxide in a mixer at 165OC. Then the crosslinked SBR is melted-Blended in the brabender mixer of PS/LDPE having ration 80/20 respectively for another 10 min. this process is called as two step crosslinking process. In the final step of mixing of polymers, the free radicals left in the PE reacts with SBR. The crosslinking that occurs between the polymer blend PS/LDPE and high quantity of SBR has not good effect on the properties of the blends i.e mechanical including other physical/mechanical properties like impact strength, tensile strength, and yield point, elongation at break, hardness and melt flow index. However, the lower amount of SBR enhance all the properties. The scanning electron microscopic results indicate that the adhesion between the inter-facials in decrease event the domain sizes have not changed enough when compared with the non-crosslinking structure. The fracture analysis is done by SEM. This twostep crosslinking process can be used on different blended system with minimum one component and at least one compatiblizer that could be cross linked.

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Aim of Work

Blending of polymers is very useful method for preparing new polymeric materials having not only the main properties of the blended components but also having the modified properties or having the specific properties. The desired properties depends upon the nature of the chosen components, the method of blending and on the conditions of blending. The blending of different polymeric materials is very desired and popular in the commercial groups and in the industry. Mostly, the polymers are blended together to accommodate the commercial interest. In this regard, the two polymers can be blended through chemical means. However, rubbers are usually found in solid state and hence the most favorable method of blending is through mechanical blending and using mixers at specific temperatures.

In the present study, the blend of two polymers PS and LDPE were formed by choosing constant composition of the constituents and blend it with the Synthetic styrene butadiene rubber (SBR), to analyze the effect of SBR on the binary blend. In addition to this work, the same composition of the polymers and rubber is blended with the addition of peroxide to analyze the extent of crosslinking in the blend and the effect on the mechanical properties accordingly.

Synthetic styrene butadiene rubber (SBR), is the amorphous hydrocarbon and general purpose rubbers. It is formed by two monomers and it will not crystallize on stretching as it possess random structure. SBR have extra varying properties depends on the ratio of the two monomers styrene and butadiene.

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CHAPTER-1

1.1 <u>INTRODUCTION</u>

Polymers (poly "many", mer "molecules") are used in the different aspects of life. They have very excellent properties as compared with the conventional materials like wood, cotton and metals etc. they are light weight and could be used easily. They are widely used in the toys and automotive industry and other activities of life. As polymers has wide variety of uses, on the other hand polymers also has disadvantages over these known conventional materials. To overcome these disadvantages, the polymers are used by blending two or more polymers. These blended polymers has new properties and also have the properties of constituents of the blend. The blended technique is widely successfully used in the industry. **(*Gunasekaran et al., 2007*)**

Blending two or more types of polymers is very common method for preparing and developing materials with the enhanced properties which are far superior and useful as compared to the single constituent of the blend. When the rubber is blended in the blend, it has its own advantages and has very unique application due to its chemical composition and its configuration. Thus, it is pretty much cheaper to blend polymers with each other or blend rubber to get the desired properties rather than creating a new elastomer, polymer by using chemical means.

Blending of polymers has very significant in the areas of research due to so many reasons like ease of fabrication, ease of choosing materials, low compound cost,

cheap procedures and having improved results. Polymers have been blended for so long due to these reasons. (*Findik et al., 2004*).

The blended polymers can be prepared by a number of different methods as:

i   Solution Blending
ii Mechanical Blending
iii Latex Blending
iv Copolymerization reaction

The most common and extensively used technique in the industry is Mechanical Blending as it is very easy to operate and have very high capacity of production.(*Pazonyi et al., 1967*).

Polymer blends are of two types on the basis of mixing i.e. homogeneous and heterogeneous.

In the homogenous blends the constituents are totally miscible and compatible with each other and the ingredients are mutually soluble.

However, in the heterogeneous blends the constituents are not miscible and incompatible with each other and the constituents of the polymer blend are not mutually soluble.

In the homogeneous blends, the constituents of the blends is completely transparent and gives a single thermodynamically stable phase in which individual components are completely transparent. On the other hand, heterogeneous blends will be opaque as separate phases. In most cases, compatible blends have better mechanical properties than incompatible blends.

(*Han, 1984*).

The blending of polymers have been used widely appplicalbe in producing new extended polymers by modifying the structure and performance of the polymers and can be used to tailor the bulk properties of the same. A lot of research in this area has been carried out which leads to various applications of commercial and economic importance. **(*George, 2002*).**

Chapter 2:

2.1 <u>Literature Review</u>

The synthesis of polymer blends by two or more than two polymers is very low cost and good method of achieving the required mechanical and other properties like physical etc when it compared with the process of development of new monomers or exploiting alternative polymerization methods and mechanisms. Similar to metallic alloys, polymer blends can produce improver or even synergistic property improvements as compared to their raw components. While most metal alloy components homogeneously mix due to similar atomic sizes and preferred crystal structures, polymeric blends feature components of very large and varying molecule sizes and structural conformations. Fundamental thermodynamic and kinetic factors due to these size and structure variances restrict polymers to more complex blending interactions. Polymer blends are referred to by several alternative classifications,

2.1.1 Types of Polymer Blends

The term polymer blend is generally used for the mixture of two or more polymers to fabricate a new material having different physical or chemical properties. Polymer blends can be classified into five main categories;

1. Thermoplastic–Thermoplastic blends
2. Thermoplastic–Thermosetting blends

The area of polymer blending has gone much attention now days for developing polymer materials having versatile commercial and industrial applications as per customers need. Properties of polymers can be altered by selecting appropriate component polymers. As part of replacement of the traditional polymers, polymer blending involves modern technologies with ultra-high performance machines/equipment like injection molding machines and extruders that can effectively detected or deploy phase-separations and viscosity during the processing stages. Due to this latest and modern blending technology, polymer industry is becoming increasingly sophisticated to generate polymer blends under special conditions (e.g., mechanical, chemical, thermal, electrical) for specific purpose including household products, biomedical devices, automotive interior and exterior components and aerospace applications.

2.1.1.1 <u>Thermoplastic–Thermoplastic blends</u>

Thermoplastic polymer can be defined as a polymer that can soften of melts upon heating and returns to hard solid state when it cools down. Thermoplastic polymer can be recycled and reprocess by applying repeatedly heating and cooling processes. Thermoplastic polymers are used in almost all industrial applications and their roughly consumption is 80% of the total plastic consumption [1]. The most widely used thermoplastic polymers includes polyethylene (PE) and ethylene copolymers, polystyrene (PS), polypropylene (PP), poly(vinyl chloride) (PVC), poly(ethylene terephthalate) (PET), polyamide (PA), poly(butylene terephthalate) (PBT), polycarbonate (PC), and poly(methyl methacrylate) (PMMA). Thermoplastic polymer blends are possibly the most diffused ones and have been widely used in industrial applications. Blends of two or more thermoplastic polymers provide a combination of properties and price which is not found in single polymer, reinforced plastic or copolymer.

2.1.1.2 Thermoplastic–Thermosetting blends

Thermosetting and thermoplastic polymer blends can be prepared by precisely mixing them in the presence of suitable compatiblizers. Both the thermoplastic and thermosetting polymers have different properties e.g thermoplastic materials have good stability under the ultra-violet rays and vacuum but on the other hand they have low thermal stability. Polyurethane (rigid foam), polyester, and polystyrene are the examples of thermoplastic foams. While thermosetting foams are rigid like phenolic, epoxy, and silicone and have excellent thermal stability but they have low stability under the UV-vacuum so they are not suitable for external surfaces of space vehicles. Blend of thermoplastic and thermosetting polymers can have both the properties of individual constituent and UV-vacuum-heat resistant polymer blend can be obtained by eliminating the drawbacks of both the individuals.

Polymer blends can broadly categorize in to three classes:

1. **Miscible polymer blends**

Miscible polymers are homogeneous to polymer segmental level and possess single phase. They are optically transparent and can also undergo phase separation by varying temperature, pressure or composition of the individual constituents in solution. Mechanical properties of miscible blends are proportion to the ratio of their constituents in the blend. The examples of miscible blends are poly(styrene-acrylonitrile) (SAN)–poly (methyl methacrylate) (PMMA) and poly(styrene) (PS)–poly(phenylene oxide) (PPO).
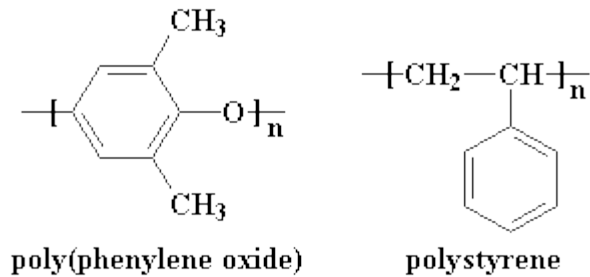
Figure 1Polymer structures of PS and Poly-pheneylene oxide

Both of these polymers have aromatic rings so they can easily stack up and like to associate each other forming a nice blend.

Miscible Polymer blends are related with the negative value of the Gibbs free energy of mixing and have one T_g value.

$$\Delta G_m \approx \Delta H_m \leq 0$$

2. Immiscible polymer blends

Immiscible polymer blends are heterogeneous in nature having free energy of mixing:

$$\Delta G_m \approx \Delta H_m > 0$$

These types of polymer blends have usually two Tg values because of phase separation of individual components. Tg value of blend can help to categorize whether the blend is miscible or immiscible. If only one Tg value is obtained then the blend is miscible but if the two Tg values are observed then the blend is likely to be immiscible in nature.

Examples of immiscible blends are poly(propylene)–poly(ethylene) (PE) and poly(propylene) (PP)– Poly (styrene) (PS).

polyethylene   polypropylene

$$+CH_2-CH_2+_n \quad +CH_2-CH+_n$$
$$CH_3$$

Miscible PB   Immiscible PB
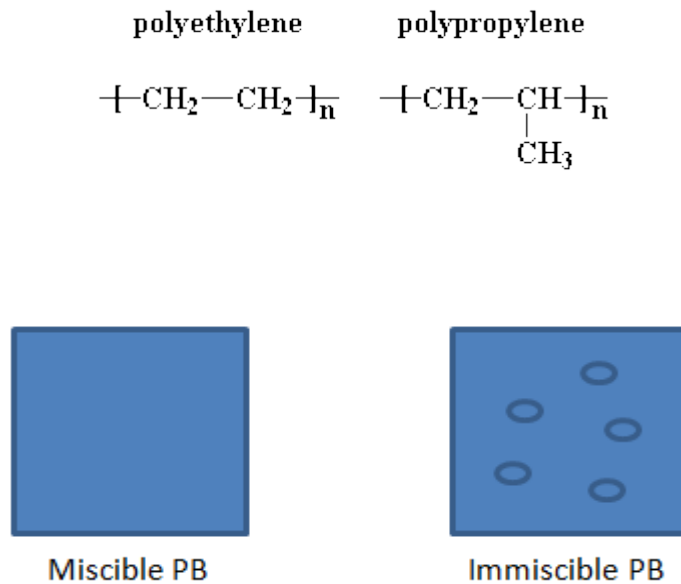
Figure 2 Difference in the miscible and immiscible blends

3. Compatible polymer blends

Compatible polymer blends are basically immiscible polymer blends which exhibits macroscopically constant physical properties. These types of blends are not completely miscible but they have strong interactions between the constituents which leads them to have macroscopically uniform physical properties. Compatible polymer blends have small scale inhomogeneity which is caused by different phases. These types of blends are miscible in certain useful temperature and composition range but immiscible in others. Most of the compatible blends are immiscible in nature and can be made compatible by applying different compatibilization techniques.

2.1.2 Thermodynamics of Polymer Blends

Generally a miscible polymer blend has the properties somewhere between the properties of its constituent individual polymers e.g glass transition temperature.
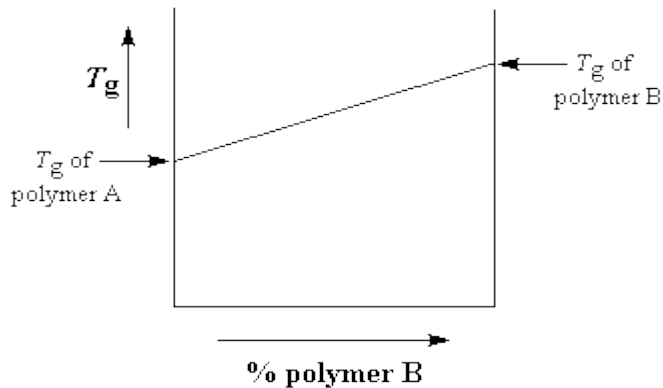
In a blend if one polymer has higher Tg value than other, the Tg value of blend is going to increase with the increased amount of polymer having higher Tg, while the value is going to decrease if the other polymer having low Tg value is in excess.
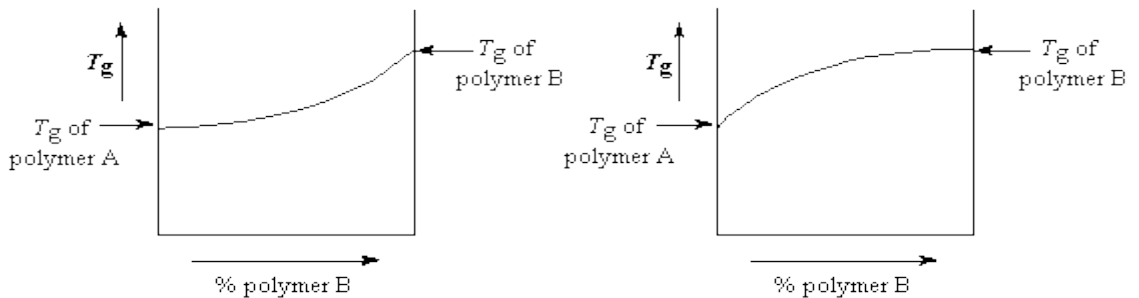
Other properties like mechanical properties, resistance to chemical, heat and radiations also depends upon the relative amount of individual polymers present in polymer blend. By varying the amount of individual constituents in polymer blends, desired properties can be achieved.

Most of the polymer pairs are not miscible with each other. Temperature and composition are the main factors which control to make them mix or not. Amount

of individual polymer is very important as a lot of polymer pairs can only mix when there is large amount of one polymer than the other.
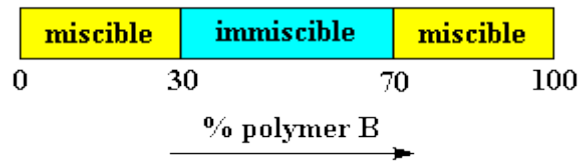
As shown in fig. two polymers were mixed in different compositions. In one phase 30% of polymer B is present while in other contain 70% of polymer B.
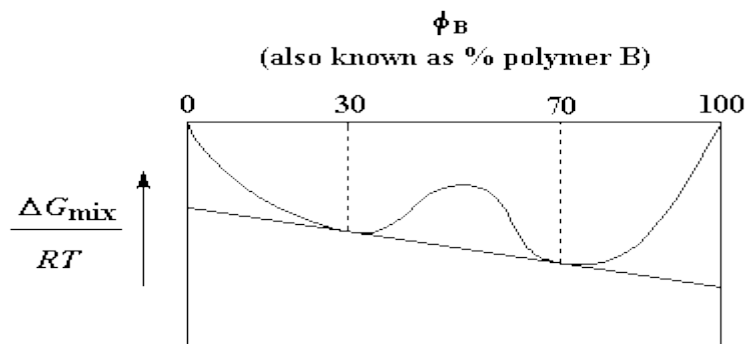
Composition range over which the phase separation of two individual polymer constituents are not constant can be change with temperature. In the case of some polymers this range gets smaller with the increase in temperature. The range of immiscibility becomes smaller when such polymer pairs are heated high enough. This temperature is called the upper critical solution temperature or UCST. On the other hand in some cases the range of immiscibility decreases with decrease in temperature. Upon cooling a temperature range becomes at which immiscibility will disappear. This temperature is called the lower critical solution temperature or LCST.
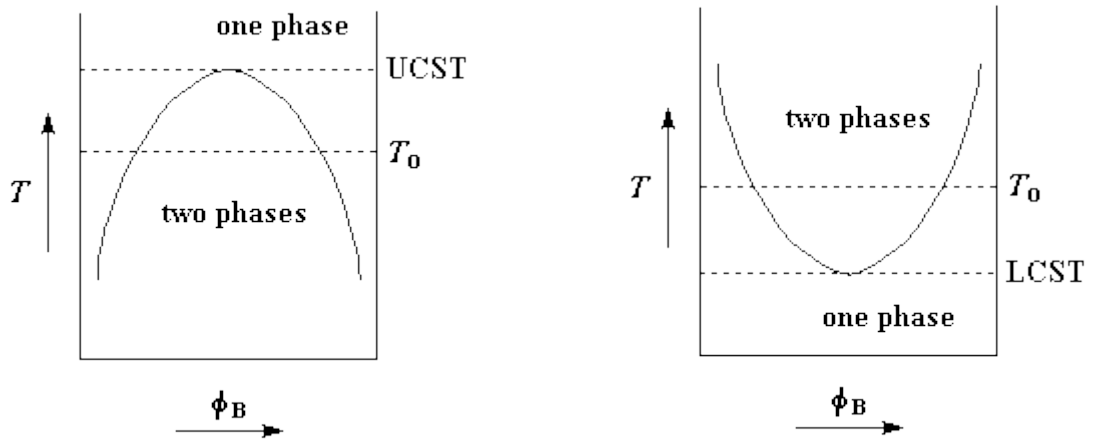
Figure 3 Graphical representation of phases

The compatibility and force of attraction between the individual components of blends play important role in determining the properties of heterogeneous polymer blend. When the interphase tension between polymer phases in a polymer blend approaches zero then the blend become miscible while the large interphase tension causes the blend to become immiscible. Large interphase tension leads to phase separation resulting increase in particle size and decrease in mechanical properties. Interfacial agents called compatiblizers having hydrophobic and hydrophilic regions can increase the interfacial tension by aligning along the interphases causing reduction of interfacial tension and increase in compatibility of the polymer blends. High compatibility between phases leads to decrease in dispersed particle size, increase in mechanical properties and enhance phase stability. Physical properties of polymer blends can be determined through thermogravimetric analysis.

Properties of polymer blends depend upon their final morphology. Generally polymers are miscible, immiscible or partially miscible characterized by their free energy of mixing ΔGm.

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

2.1.3 Types of Blending

Kinetic and thermodynamic studies are important to determine the phase separation of polymers. A general concept was that the polymer pairs are immiscible due to low entropy of mixing which is mostly related to the polymers having long molecular structure. But now the recent studies revealed that the polymer miscibility can be enhanced by using special interactions between the unlike polymers. Other factors like blending also play key role in the miscibility of polymers. There are number of mixing techniques for the preparation of polymer blends including melt-mixing and solution casting etc. in case of two-phase blend with high temperature in melt mixing leads to the formation of miscible polymer blend with a low critical solution temperature (LCST). There are several techniques for the preparation of polymer blends. Some of them are:

1. **Solution-casting**

Films of pure polymers and their blends can be cast from the 4% solution at room temperature in different solvents on a mercury surface to obtain uniform thickness. Solvent should be evaporated slowly in a dust free chamber in the presence of nitrogen. Dry the resulting films under pressure at 100°C until the constant weight has been obtained. At the end pour the blend solutions based on chloroform or THF onto a glass slide preheated to 70°C on a hot plate.

2. **C0-Precipitated blend**

In co-precipitated method pure polymers and their blends can be prepared through precipitation technique from chloroform or the THF using non-solvent methanol. The precipitated powder has been dried on a preheated solid glass on a hot plate.

3. Melt-mixing

Melt-blending has been done by melting the precipitated polymer blend prepared by the coprecipitation method at about 150-170°C for 5 min. In the case of melt-blending, to avoid the thermal degradation octyl tin mercaptide is used as a stabilizer.

4. Copolymers

Immiscible polymers can be blend nicely by using copolymers. For example polystyrene doesn't blend with many polymers but with the use of copolymer it can blend easily.
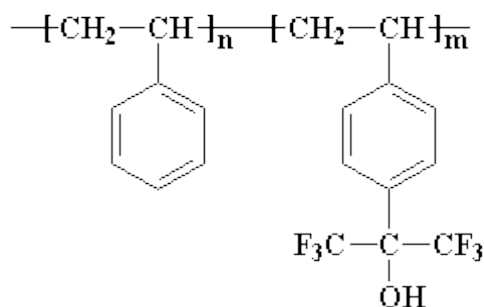
poly[styrene-*co*-(*p*-hexafluoro-2-hydroxyisopropyl)styrene]

Compatibility of polymers in polymer blend may depend on the type and technique of mixing/blending and it varies from polymer to polymer. Compatibility can be increased by using appropriate method of blending, right choice of polymer constituents and use of copolymer.

2.2 <u>**Materials**</u>

2.2.1 ”STYRENE BUTADIENE RUBBER (SBR)”

Styrene-butadiene rubber (SBR), is a most common used synthetic rubber. It is compromises of two copolymers named Styrene and Butadiene. SBR represents one of the synthetic rubbers that are still widely used for manufacturing a wide range of different products such as in the automobile industry, cars and tyres, in production of technical parts, cable insulation material, shoe sole, molded goods etc. generally as an abrasion-resistant instead of natural rubber. SBR is a random copolymer, does not crystallize on stretching due to the fact that it is an amorphous rubber. Therefore, it becomes a requirement of admixing SBR with the filler materials. It is known as a cross-linkable polymer on irradiation. SBR is an amorphous and homogenous polymeric materials and the mechanical properties is depends upon the chemical structure and process conditions. **(Woods et al., 1994)**

Styrene Butadiene generally is the mixture of Butadiene (CH2=CH-CH=CH2) and Styrene (CH2=CHC6H5) in the approximate ration of 75 percent and 25 percent respectively. In most cases, by emulsion process, these two compounds are co-polymerized with each other and linked together to form long multiple unit molecules. In this process, surface like a soap acts as agent, disperses in the solution of water and emulsifies. The other materials which are present in the solution are free-radical initiators which initiate the process of polymerization and act as a stabilizers and also avoid the deterioration of the final product. During the process of Polymerization the repeating units Styrene and Butadiene are arranged in the random positons in the polymer chain. These polymer chains

are crosslinked with each other in the further process called vulcanization process which induces the elastomer properties. Generally in most applications Natural Rubber is used, but on account of performance and economics it can replaces the natural rubber. It includes the excellent abrasion resistance and better aging characteristic. In natural rubber the effect of atmospheric oxygen and ozone weakens the hydrocarbon oils degraded over time but SBR behaves opposite, the main effect of oxidation in increased the crosslinking or interlinking of the polymer chain so it tends to harden the polymer chains instead of softening. The limitation of SBR is that it have very poor mechanical properties without any usage of reinforcement so that it must be used with any filler material. A large amount of SBR is used as latex form as a rubbery adhesive in a number of applications such carpet backing , belting, flooring, wiring and cable insulation.
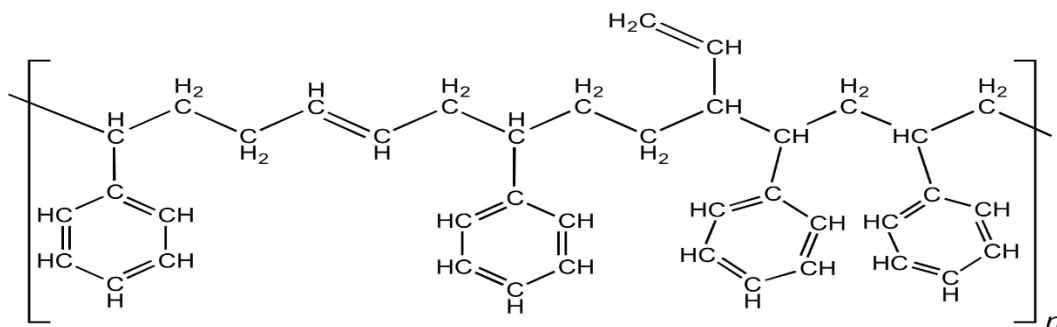
Figure 4: Structure of Styrene Butadiene Rubber
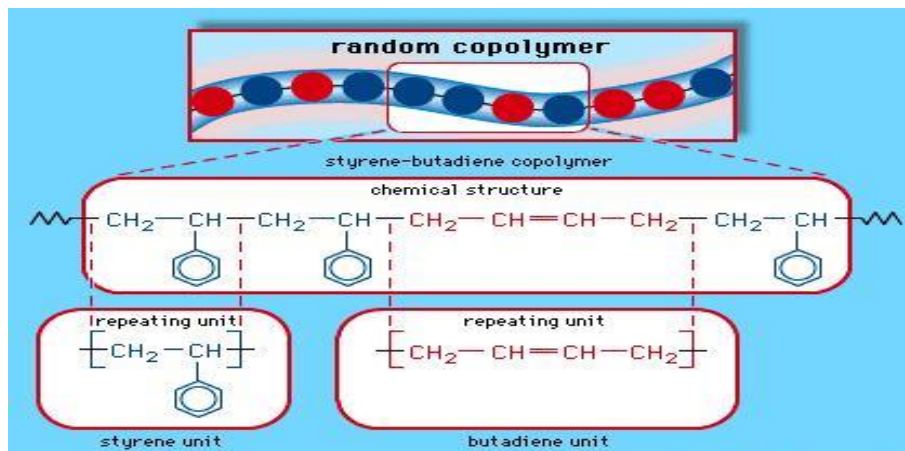
Figure 5: The random copolymer arrangement of styrene-butadiene copolymer.

(Encyclopedia Britannica, Inc.)

2.2.2. <u>Poly Styrene</u>

Polystyrene (PS) is a synthetic aromatic thermoplastic polymer made from a monomer called "styrene". It is hard, clear and brittle materials and very cheap resin. It has very low melting point and one of the most widely used polymer in the world. The scale of production of the PS is exceeding several millions of tons per year. PS naturally a transparent polymer which may be colored by using additives. It is used in the packaging industry, protective packaging, lids, bottles, trays, toys, CDs, CD cases and containers.

Polystyrene is in solid state at the room temperature but it can flows above 100 OC and rigid again upon cooling. The temperature behavior is exploited for extrusion and also used or molding and vacuum forming as it can cast with very fine details.

Structure:

Polystyrene is a flammable polymer. In term of chemical structure it is a long chain hydrocarbon wherein alternating carbon atoms are attached with phenyl group i.e aromatic benzene ring. The chemical formula of the Polystyrene is (C_8H_8). It contains he carbon and Hydrogen atoms

The Polystyrene's properties are induced by the short-range van der Waals forces between the polymers chains. As the thousands of molecules are linked with each other and long hydrocarbon chains are formed, the total attractive force between the molecules is large. On heating, the chains of the polymer are slide past each other and chains are able to take a high level of conformation. The intermolecular weakness and intramolecular strength, it indusced the flexibility and elasticity. The ability of the system to be readily deformed above its glass transition temperature allows polystyrene (and thermoplastic polymers in general) to be readily softened and molded upon heating.
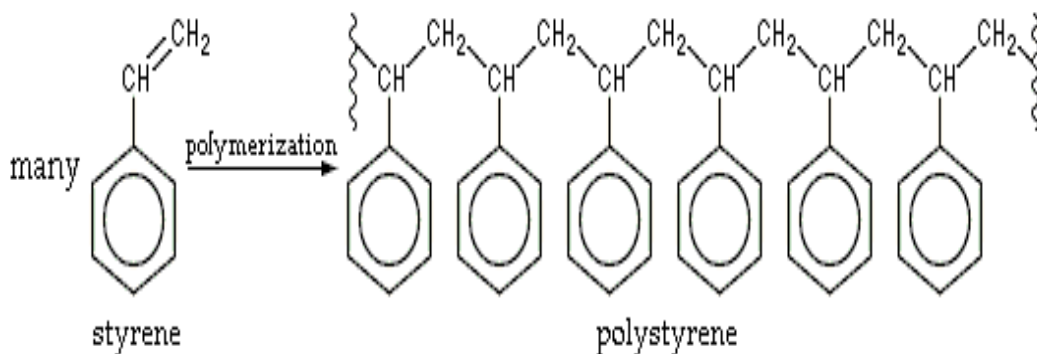
Figure 6: Structure of Poly-Styrene

The extruded polystyrene is very much string as unalloyed aluminum but it is very flexible and in much lighter weight as compared to the metal. (1.05 g/cm3 is for the polymer and in compare 2.70 g/cm3 for aluminum).

As discussed earlier that the main constituent of the polystyrene is the styrene molecule so when the styrene molecules are interconnected with each other, in results Polystyrene is formed, this process is known as polymerization. In polymerization, C-C π bond present in the vinyl group is broken and leads to form a new C-C π (sigma bond) with the other styrene monomer and the resulted sigma bond is stronger than the broken Π bond. Once the polymerization is completed then de-polymerization of the polymer is very difficult. In polymers a few thousand monomers are linked together and giving a molecular weight of 100,000–400,000.

Technical Data Sheet

Supplier: Pak Petrochemical Industries (Pvt.) Ltd

Grade: DIAMOND GP-550 P

Processing:

- Extrusion Grade
- Blue Tined,
- Excellent Clarity
- Good Flow
- Low Volatility

Table 1 Technical data sheet of Polystyrene

TYPICAL PROPERTIES	TEST METHOD	UNIT	VALUES
Mechanical Properties			
Tensile Strength at Yield / at break	ASTM D-638	kgf/cm^2	450
Tensile Elongation	ASTM D-638	%	2
Flexural Strength	ASTM D-790	kgf/cm	900
Izod Impact Strength	ASTM D-256	Kg-cm/cm	1.55
Thermal Properties			
Vicat Softening Temp	ASTM D-1525	ºC	100
Heat Distortion Temp	ASTM D-648	ºC	95
General Properties			
Melt Flow Rate MFR 200/5	ASTM D-1238	gm/10 min	3.0
Processing			
Specific Gravity	ASTM D-792	23/23ºC	1.05
Miscellaneous Properties			
Water Absorption		%	<0.1
Moisture Adsorption (23 C/50% r.h)		%	<0.1

2.2.3 Low Density Polyethylene

Low Density Polyethylene is a thermoplastic polymer which is made from a monomer ethylene. It is polymerized via free radical polymerization. LDPE has density ranging from 0.910–0.940 g/cm3, it is mostly nonreative at room temerature. It is very flexible and tough polymer. The difference between the high density polyethylene and low density polythylene is of brancing approx 2% of the carbon atoms are more branching than HDPE , so the intermoculeur forces i.e dipole dipole attraction are much weaker and In result its mechanical properties like tensile strength is very lower and the resilience in on higher side. It is because of that LDPE's molecule are less tighly packed and also has less crystallineith due to the side branches and its density is also lowers.
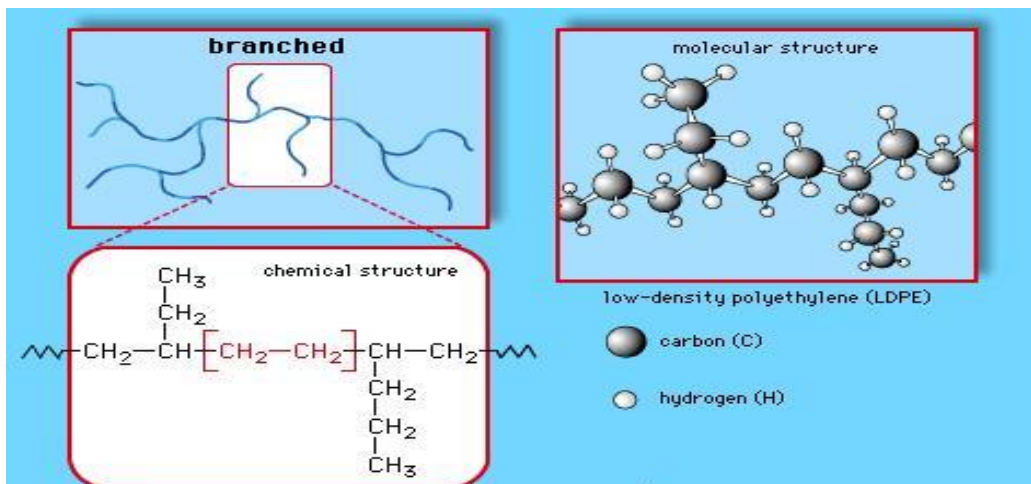
Figure 7: Structure of Low Density Polyethylene

PROPERTIES	VALUE	UNIT	TEST METHOD
Melt Flow Index	70	g/10 min.	ASTM D-1238
Density @ 23 °C	0.918	g/cm3	ASTM D1505
Crystalline Melting Point	102	°C	ASTM E-794
Vicat Softening Point	80	°C	ASTM D-1525
Tensile Strength @ Yield	8	MPa	ASTM D-638
Tensile strength @ Break	7	MPa	ASTM D-638
Elongation @ Break	240	%	ASTM D-638

Table 2: Technical data sheet of LDPE

Chapter 3

3.1 EXPERIMENTAL TECHNIQUES

3.1.1 Materials Used

a. Poly Styrene

Formula: $(C_8H_8)_n$

Density: 1.05 g/cm³

IUPAC ID: poly(1-phenylethene-1,2-diyl)

Supplier: Pak Petrochemical Industries (Pvt.) Ltd

Grade: DIAMOND GP-550 P

Processing:

- Extrusion Grade
- Blue Tined,
- Excellent Clarity
- Good Flow
- Low Volatility

b. Low Density Polyethylene

Melt flow index: 70 g/per min

Density of the polymer: 0.918 g/cm3

Tensile: 8 Mpa

Elongation at Break: 240 %

Supplier: Lotrène® MG70

Grade: MG70 injection molding grade

Properties: High flexibility and glossy surface

c. Peroxide

Peroxide is class of chemical compounds in which oxygen atoms are attached to each other to form a covalent bonds. In this chemical structure minim two atom are linked together to form long structures. Peroxides may be organic and inorganic compounds and these are very useful in different applications such as as a agents, they also play a very important role as a initiator of polymerization reaction, and also used in the synthesis of hydrogen peroxide and oxygen compounds.

d. Styrene Butadiene Rubber (SBR)

Styrene-butadiene rubber (SBR), is a general-purpose synthetic rubber. It is the copolymer of styrene and butadiene. (SBR) represents one of the synthetic rubbers that are still used for production of different products such as in automobile industry , cars and tires ,and in production of other technical parts, cable insulation material, shoe sole, molded goods etc. generally as an abrasion-resistant instead of NR-Natural rubber   .
SBR is a random copolymer, does not crystallize on stretching due to the fact that it is a totally amorphous rubber.

3.1.2 Preparation of Samples:

The compound formation was carried out as follows:

1. All ingredients were actually weighed.
2. Mixing of polymers were carried out on the laboratory scale Bra bender Plastic order internal mixer screw having following parameters.
   - i. Temperature of the side wall 1 : $180^{O}C$
   - ii. Temperature of the side wall 2: $180\,^{O}C$
   - iii. Temperature of the middle part: $160\,^{O}C$
   - iv. No. of Screws: 02 Nos
   - v. Rpm of the screws: 38-40 Cycles /minute
   - vi. Capacity of the chamber: 45 g
   - vii. Time for mixing: 10 minutes

3. The polymers PS and LDPE were taken in separate containers and weighted for 80-20 ratio respectively.
4. The polymers were mixed with the SBR on slow rolls and the temperature at the middle and side walls of the chambers were continuously measured during the mixing.
5. The electrical balance were calibrated before each measurement.

3.1.3 Procedure of Experiments

a. First of all machine / mixer was set at desired temperatures. Shown in (Fig 8)

b. The polymers PS and LDPE were carefully measured to maintain the weight ratio of 80-20

c. The material which used in the process are commercially available and used at it is without any purification process.

d. The blend composition fixed at 80-20 % (PS/PE) and quantity of the SBR varies from 0% to 15 %.

e. Moreover the blends of the same is also synthesize by fixing the ratio of peroxide at 0.05 %

f. The mixer is bra bender internal mixer having maximum capacity of 45g.

g. The mixing of polymer blend was carried out on a mixer. The temperature of the process was 165°C and the screw was operated at 40 rpm.

h. PS/LDPE were injected into the preheated mixer and SBR is added into the system and after 10 min of mixing the compound recovered.

i. SBR and peroxide were introduced into the preheated mixing chamber. After 6 min of mixing, the compound recovered.

j. This resultant initial compound was then blended with PS and LDPE at 165°C and further mix for 10 min.

Figure 8. BRA BENDER INTERNAL MIXER

3.1.4 List of experiments/ Compositions

Following compositions were formed by varying different continents:

1. By varying SBR content

Sr. No	Composition PS/LDPE	PS (Wt %)	LDPE (Wt %)	SBR (Wt %)
1	80-20	80	20	2.5
2	80-20	80	20	5
3	80-20	80	20	10
4	80-20	80	20	15

2. By varying peroxide content

Sr. No	Composition PS/LDPE	PS (Wt %)	LDPE (Wt %)	SBR (Wt %)	Peroxide (Wt %)
5	80-20	80	20	5	0.1
6	80-20	80	20	5	0.15

3. By varying SBR with fixed percentage of peroxide

Sr. No	Composition PS/LDPE	PS (Wt %)	LDPE (Wt %)	SBR (Wt %)	Peroxide (Wt %)
7	80-20	80	20	2.5	0.05
8	80-20	80	20	5	0.05
9	80-20	80	20	10	0.05
10	80-20	80	20	15	0.05

a. Following notes were taken care into consideration during the mixing of experiments:
b. All the polymers were passed through the rollers twice.
c. The chamber temperature was maintained at 165^OC.
d. The time of mixing was controlled and average time was about 10 minutes

e. The weights of blends were checked after mixing to ensure that the loss in weight do not exceed 0.5 %.

f. It is make sure that all the compound was taken and removed from the mixer without any contamination.

3.2. MEASUREMENTS

3.2.1. Mechanical measurement

The specimens for the tensile testing and determination of impact were prepared by a laboratory scale injection molding machine at the processing temperature ranges from 200C to 210C and at pressure at 6 bar. The specimens were prepared as per ASTM standards. The tensile and elongation testing was carried on the Instron Machine at a speed of 2.5mm/min. The tests were performed on the dog bone shaped specimens of 6mm width and total lenigth of 50 mm   with   35mm gauge length. The notched impact strength samples were also prepared on the same injection molding machine in accordance with the ASTM Standard

3.2.1.1 Tensile strength (TS):

The tensile test is known as the Force applied on per unit area of the cross-sectional area. The cross section area is applied and check at the test of performing tests. The unit used in the testing is N/mm2

The tensile strength (TS) of the sample at break point can be calculated as follows:

$$\text{Tensile strength (TS)} = (L/T.W) \text{ N/mm}^2 \text{ Where:}$$

L: Force to cause break

W: width of sample (cm)

T: Thickness (cm)

Figure 9 **Sample Preparation Unit for Tensile and Impact Sample**

3.2.1.2 Elongation at break %

The term of elongation is used to represent the ability of rubber to stretch the polymer without breaking. It is calculated to between the gauge lengths. It is expressed in percentage. Elongation at break is the elongation at the moment of the rupture. In other words, the elongation at break is expressed as the percent elongation of the original bench mark length attained at the moment of rupture. Hence, the elongation at break is given by

$$E_b (\%) = (L-L_0/L_0) \times 100 \text{ Whereas:}$$

L= Length of the sample.

L_0= length between benchmarks

3.2.1.3 Hardness

The hardness test was carried out as per ASTM standards on the flat surfaces of the samples. The unit of hardness is expressed in (Shore D).

Figure 10 **Frank Hardness Tester Shore**

3.2.1.4 Melt flow index:

Melt flow index which is also abbreviated as MFI is a measure of how many grams of polymer flow through the die in 10 minutes. The temperature set at $190^{O}C$ and load at 2160 gram. The force used to push the plastic through the system is supplied by a weight which sits on top of a ram.

Figure 10 Melt Flow Index

3.2.1.5 Impact test:

The impact test is a method for calculation of the toughness and notch sensitivity of the polymers. The units for the impact test are "J/m". it is the capacity that how much material can withstand the sudden load.

Figure 11. Impact Tester

3.2.1.6 Structure morphology by SCANNING ELECTRON MICROSCOPE:

The SEM is used to analyze the structure and morphology of the polymers. In this study, the surface after the tensile strength was examined in detail to analyze the effect of mechanical testing.

Chapter 4

4.1 Results and Discussions

PS/LDPE blends were prepared by same process method while varying the composition of styrene butadiene rubber and peroxide content. The composition for the blend was fixed at PS/LDPE 80/20 and the SBR content varies from 2.5% to 15 % and the same was analyze by the two step cross linking method by the addition of peroxide. In all the samples the ration for PS and LDPE was 1:4 and all the calculations were made on the basis of total weight of PS and LDPE.

4.1.1. Mechanical properties

The above mentioned properties have been studied in this study is the UTS along with elongation % . The hardness and impact tests were also studied in this research. All the testing have been followed as the function of composition variation i.e SBR content.

4.1.1.1 Impact Analysis

Table (3) shows the comparison of the impact values for the different blends and composition. At initial, the impact values of the Polymer blend with no addition of any compatiblizer was studied. The impact values were significally increased by the addition of SBR content but gradually decrease by increasing amount of SBR.

4.1.1.2 Tensile Testing and Elongation percent

Table (4) shows the variation of the Tensile and elongation values for the polymer blends by the varying composition of SBR and peroxide. It is Cleary seen from the table that the values for the tensile tests are gradually decrease with the increase of the SBR content and the effect of the reduced tensile tests continues by the addition of peroxide in the blend.

<u>4.1.1.3 Hardness Testing</u>

The same composition are analyzed for the determination of Hardness of the injected molds. The compound was melted by the injection molding machine and analyzed the surface for the determination of Hardness. As the compound was pass through the injection molding machine the surface of the molds doesn't show any remarkable change. However, the values of the hardness was significantly reduced by the addition of peroxide in the blends. The results for the hardness test shown in Table 3.

Blends PS-LDPE-SBR-Peroxide	Composition	Impact Strength	Hardness
Units	%age	J/m	Shore-D
PS/LDPE	80/20	18.51	65.66
PS/LDPE/SBR	80/20/2.5	23.33	67.33
PS/LDPE/SBR	80/20/5	38.33	65.33
PS/LDPE/SBR	80/20/10	21.43	66
PS/LDPE/SBR	80/20/15	16.08	66
PS/LDPE/SBR/Peroxide	80/20/2.5/0.05	20.18	70.66
PS/LDPE/SBR/Peroxide	80/20/5/0.05	16.20	64.33
PS/LDPE/SBR/Peroxide	80/20/10/0.05	25.78	65
PS/LDPE/SBR/Peroxide	80/20/15/0.05	30.24	65.33
PS/LDPE/SBR/Peroxide	80/20/5/0.05	28.94	64.33
PS/LDPE/SBR/Peroxide	80/20/5/0.05	23.17	63

Table 3: Comparison of the impact and melt flow index values along with hardness

4.1.1.1 _Tensile and Elongation Testing_

Blends PS-LDPE-SBR-Peroxide	Composition (%)	UTS	Elongation
Units	%age	N/mm^2	%
PS/LDPE	80/20	19.36	12.75
PS/LDPE/SBR	80/20/2.5	21.3	17.28
PS/LDPE/SBR	80/20/5	16.21	12.9
PS/LDPE/SBR	80/20/10	17.05	21.26
PS/LDPE/SBR	80/20/15	16.04	15.25
PS/LDPE/SBR/Peroxide	80/20/2.5/0.05	17.83	15.78
PS/LDPE/SBR/Peroxide	80/20/5/0.05	14.94	10.36
PS/LDPE/SBR/Peroxide	80/20/10/0.05	14.08	7.915

Table 4 the effect of SBR content on the Tensile and elongation percentage of the PS/LDPE blends
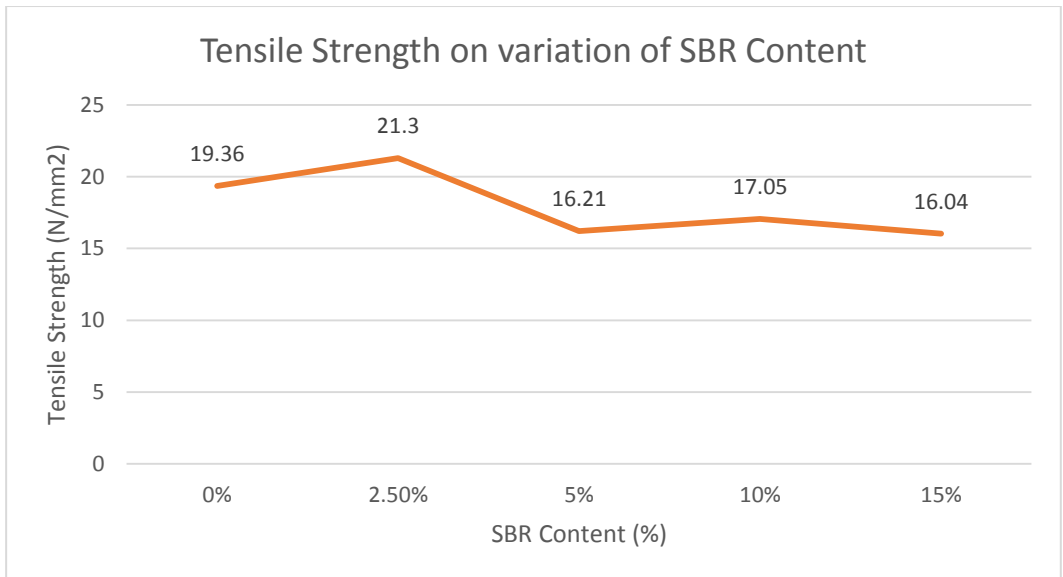
Figure 12 Comparison in the Tensile Strength with the variation of SBR content

In Figure 5, the comparison of the tensile strength of the polymer blends is shown, this comparison is based on the varying content of styrene butadiene content in the polymer blend. The SBR content is the blend is gradually changes from the 0 % to 15 %. In the first experiment there is no addition of any filler or compatiblizers, this is the actual 80/20 blend of the PS/LDPE. The experiment shows that the adhesion between the PS and LDPE blends subsequently reduced with the increase on SBR content. The tensile strength is depends upon the degree of cross linking between the chains of the polymer blend. It is observed the facial adhesion in a multiphase structure doesn't leads to increase in the mechanical properties of the blend. The adhesion between the polymers is weak as the PS and LDPE are not miscible with each other. The tensile strength is decrease with the increase of SBR content. Initially at the lower percentage of the SBR content induced the increase in the tensile properties which is due to the crosslinking between the chains of the constituents. After that the extent of cross linking lowers with the addition of SBR so the optimum value for the SBR addition is this study by two step cross linking method is less than 5 % SBR.
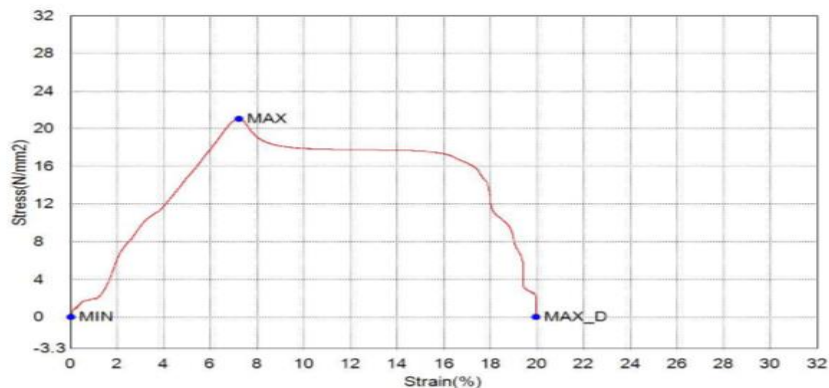

Figure 13 2.5 % SBR content

Similarly, the same composition were again cross linked by the two step cross linking which means that the same composition and SBR gradient was cross linked with the addition of per oxide in the blend. Firstly, the SBR is mixed or cross linked with the peroxide and the chains of the polymer are intend to cross link with each other, as the polymer blend is introduced in the preheated cross linked system , the leftover chains cross linked with the PS/LDPE chains . As shown in Figure (6) the extent of the tensile strength is gradually decrease. In these experiments, the percentage of the peroxide is fixed at 0.05 % and only the SBR content is varies. These series of tests shows that with the addition of peroxide in the SBR, the crosslinking already increased and the leftover chains are cross-linked with the blend. So in result, the values for the tensile strength is gradually decrease due to the poor bond/adhesion between the chains of the polymers on the function of SBR content and peroxide.
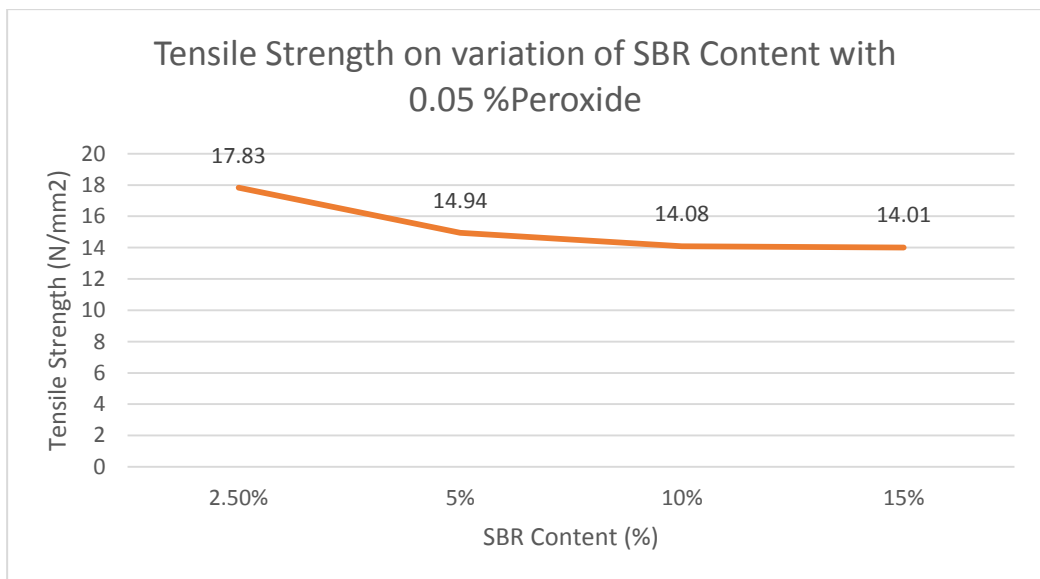
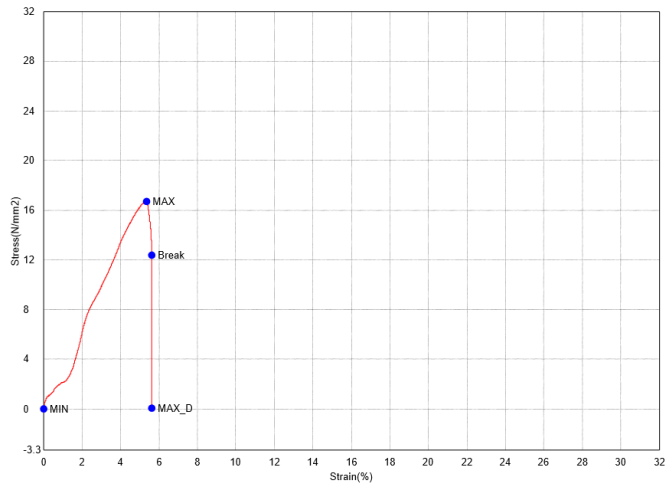Figure 14 Tensile Strength on variation of SBR Content with Peroxide addition

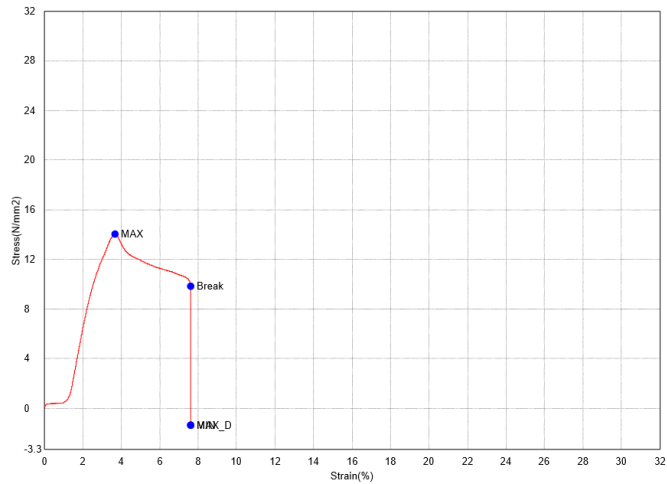**Figure 15 2.5 % SBR with 0.05% peroxide**

Figure 16 2.5 % SBR with 0.05% peroxide

In Figure 7, the values of the impact testing was analyzed and studied. As impact resistance of the polymer blend is significally increased with the addition of SBR into the system due to the extent of crosslinking between the chains. The impact resistance decrease with the increase in the SBR content.

In figure 8, the same experiments were conducted by the addition of peroxide in the system. By adding peroxide, the impact values were increased with the increase of SBR content with the fixed peroxide percentage. The significant increase in the impact strength is endorsed the cross-linking between PE/LDPE Blend and SB-Rubber. It is well recognized that strong interfacial adhesion in a multiphase-structure blend gives rise to an increase of impact strength. The tensile strength of the blends decreases as a function of the SBR composition up to 2.5 wt% of SBR and then decreases in the tensile test on further increase of the SBR content.
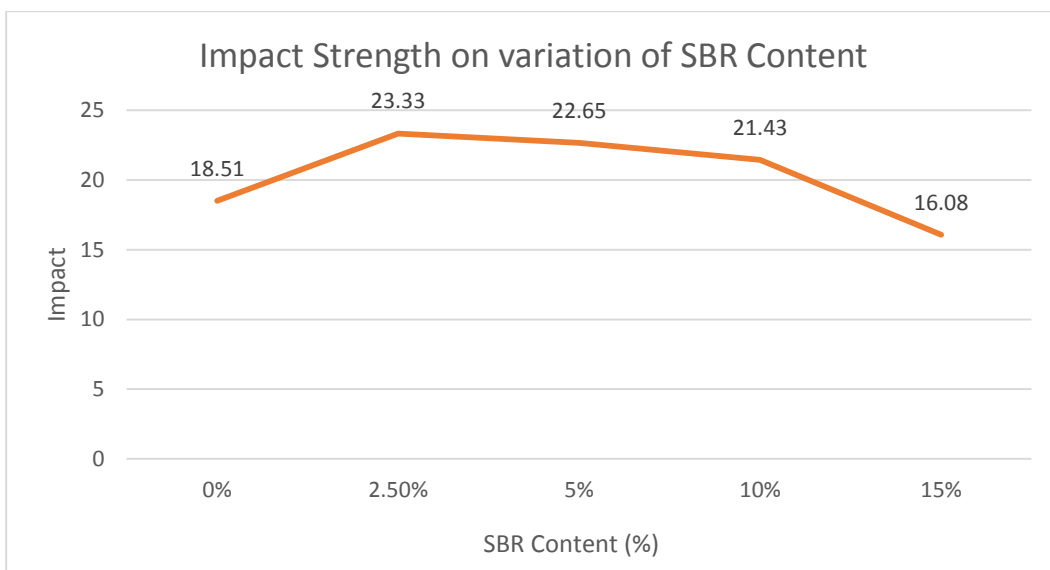
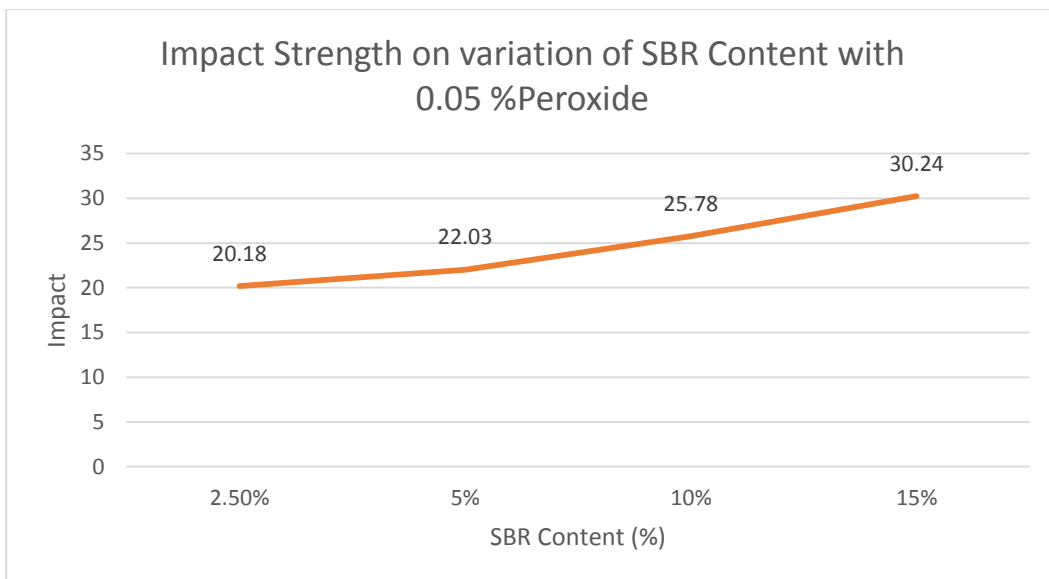*Figure 17 Values for the Impact Strength on variation of SBR Content in the Polymer Blends*

Figure 18 Impact Strength on variation of SBR Content with 0.05 %Peroxide

4.1.2 Physical Testing

4.1.2.1 Melt flow index

The melt flow index of the polymeric blends is studied in this temperature. The parameters for the MFI were 190 ^{O}C and all the tests were carried at load = 2190 g in accordance with the ASTM standard. The results for the MFI is shown in Table 5.

Blends PS-LDPE-SBR-Peroxide	Composition	Melt Flow Index
Units	%age	g/10 min
PS/LDPE	80/20	2.60
PS/LDPE/SBR	80/20/2.5	1.87
PS/LDPE/SBR	80/20/5	1.67
PS/LDPE/SBR	80/20/10	01

PS/LDPE/SBR	80/20/15	2.13
PS/LDPE/SBR/Peroxide	80/20/2.5/0.05	2.13
PS/LDPE/SBR/Peroxide	80/20/5/0.05	2.22
PS/LDPE/SBR/Peroxide	80/20/10/0.05	2.12
PS/LDPE/SBR/Peroxide	80/20/15/0.05	2.00
PS/LDPE/SBR/Peroxide	80/20/5/0.05	1.13
PS/LDPE/SBR/Peroxide	80/20/5/0.05	1.93

Table 5: Melt Flow Index

4.1.4 Characterization

4.1.4.1 Scanning Electron Microscope

All the samples were tested on the SEM to analyze the morphology of the compound. All the specimens were initially tested for the tensile tests and the fracture surface of the tensile specimen were analyzed under the SEM.

In Figure (9-14) the sem images for the 80/20 blends and with SBR addition which varies from 2.5 to 15 % and Figure 14 shows 80/20/2.5 blend with the addition of 0.05% peroxide.
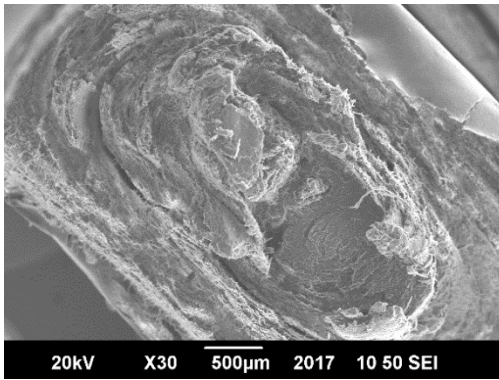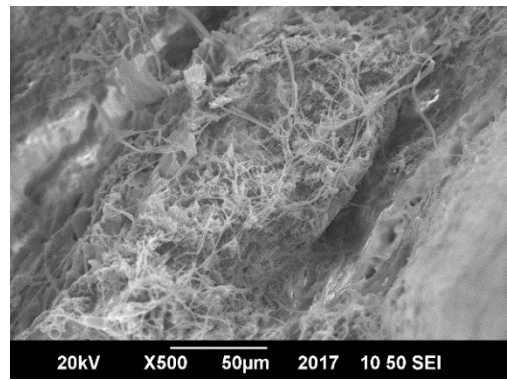

A *B*
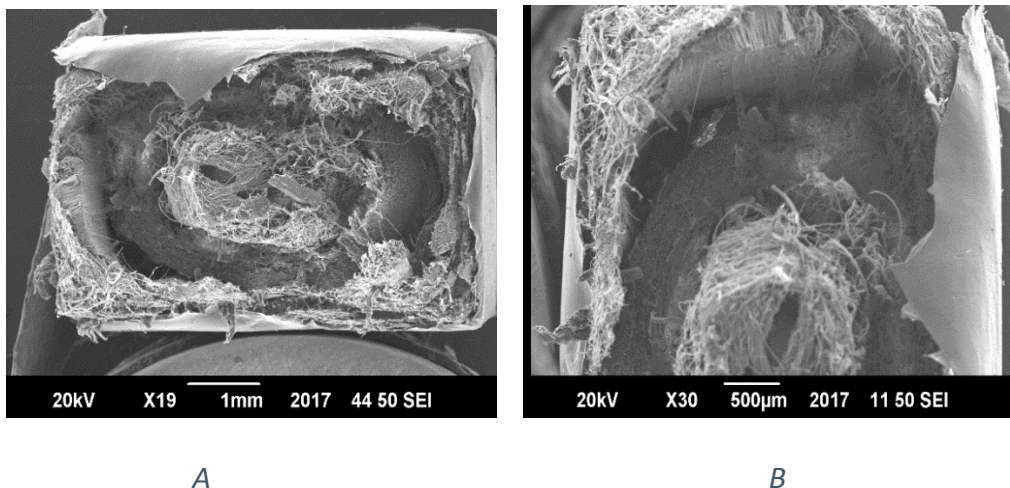
Figure 19 SEM images for PS/LDPE blends of 80/20 with no addition of SBR

A   B

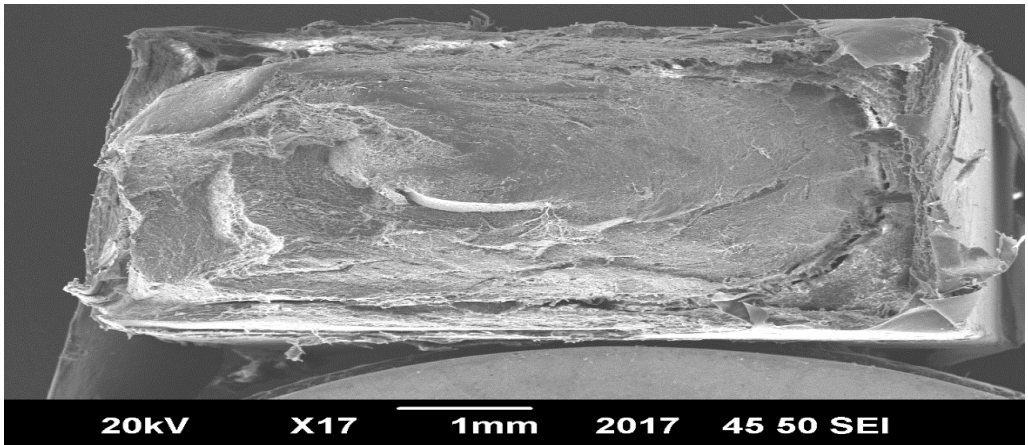*Figure 20 SEM images for PS/LDPE/SBR blends of 2.5 % addition of SBR*

The non-crosslinked polymer blends PS/LDPE and the PS/LDPE/SBR blends is prepared by the two step crosslinking process with the SBR content is varying from the composition ranges 0 to 15 Wight %. For the non-crosslinked PS/LDPE blends, the addition of SB-Rubber shows only a slight improvement in the mechanical properties.
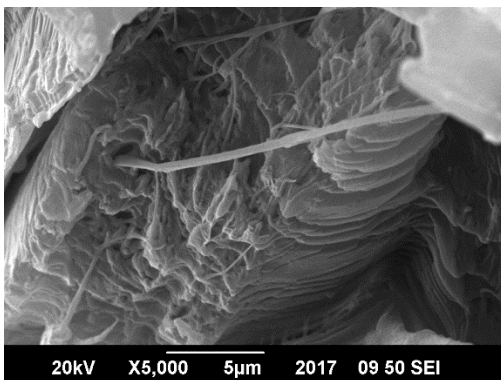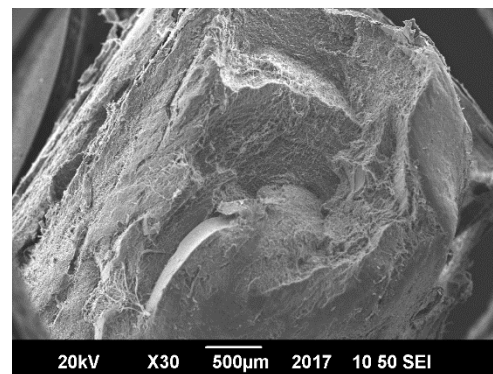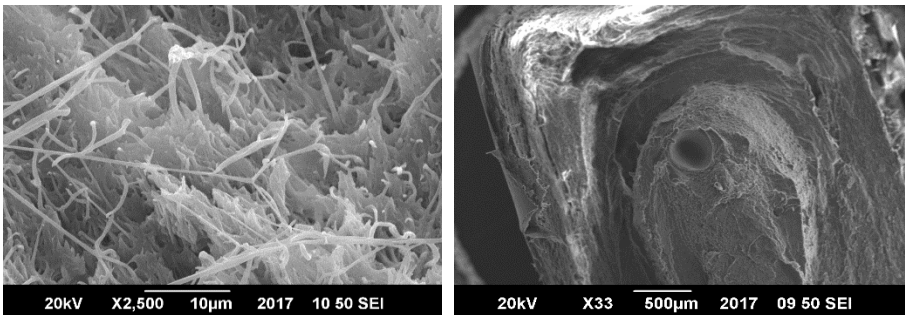

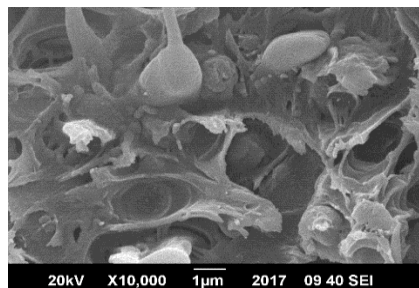A   B

C

Figure 21 SEM images for PS/LDPE/SBR blends of 5 % addition of SBR

In Figure 9 A: the fracture surface of the tensile specimens is observed.

A

B

C

Figure 22 SEM images for PS/LDPE/SBR blends of 10 % addition of SBR

In Figure 12 and Figure 13 the micrographs are PS/LDPE blends with the addition of 10% and 15% of the SBR content respectively. The detachment of the PS phase from LDPE indicates that there is little or zero adhesion in these two phases of polymers. The morphology of the said polymer blend shows that they are incompatible blends as compared to little amount of SBR content. In figure 12, the SBR content is seen in the matrix of the blend.
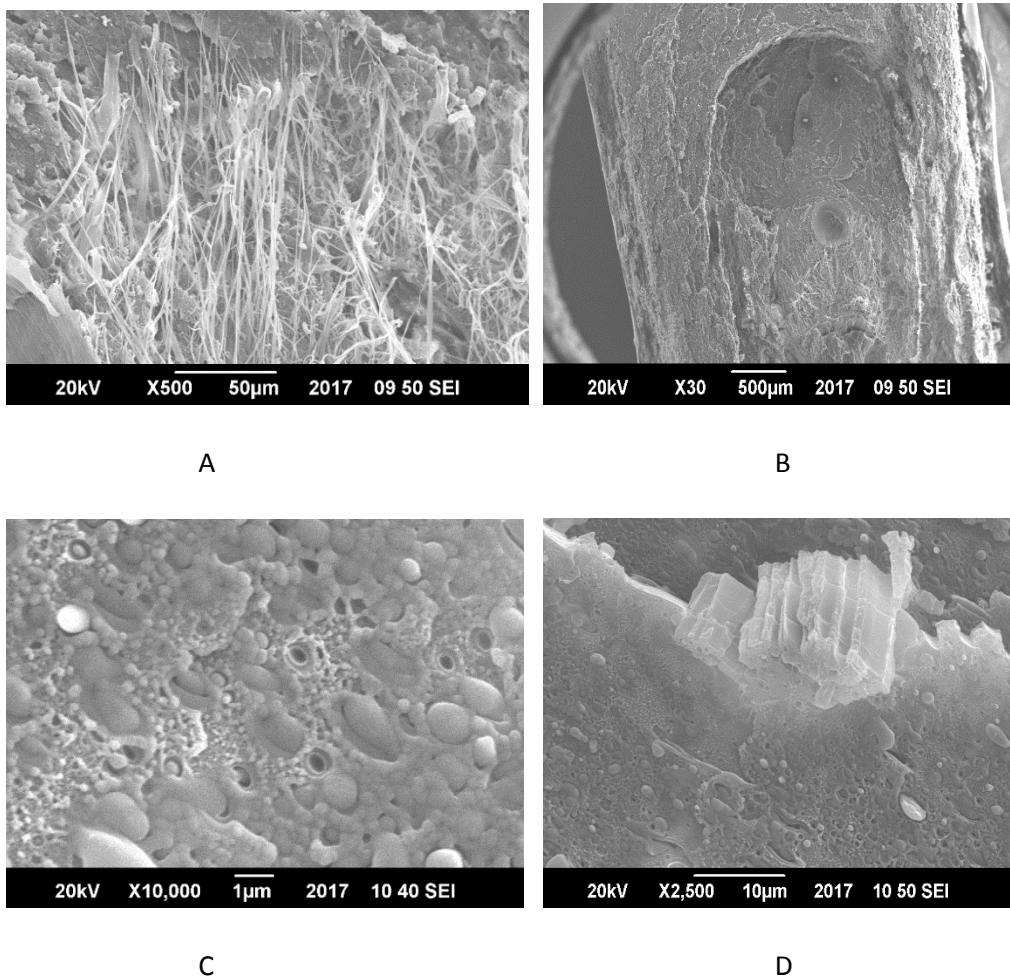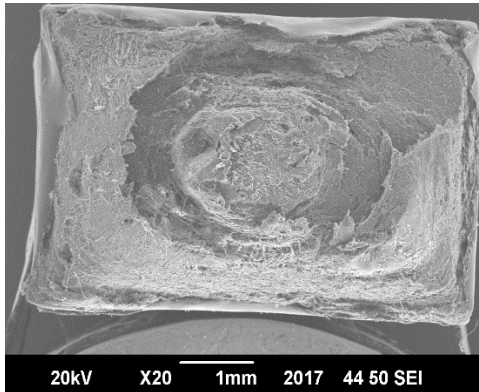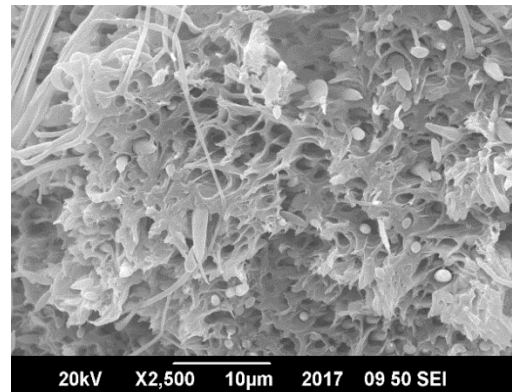

A

B

C

D

Figure 23 SEM images for PS/LDPE/SBR blends of 15 % addition of SBR
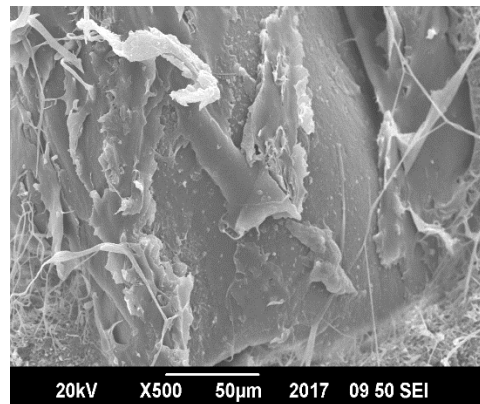
In Figure 13, as the addition of SBR is increased, the SBR particles are seen embedded in the matrix. It is seen that the structure is immiscible and the addition of SBR with higher quantities doesn't took part in the improvement of mechanical properties.

A

B

C

Figure 24 SEM images for PS/LDPE/SBR blends of 2.5 %

Addition of SBR with 0.05 %peroxide

Chapter 5

5.1 Summary & Conclusions

As discussed, the individual polymers have no significant role and various applications. To compete with the metal industry of high durability and performance the blends of polymers are researched and manufactured to achieve the desired properties with much cheaper procedures, low costs and easy to handle . The desired properties can be enhanced by the addition of several compatiblizers in the blend which not only increase the properties as well as the performance of the blend. But in some cases the addition of additives or compatiblizers may cause reduction in several properties as the blends shows zero or no compatibility with each other and the blends are totally immiscible, in order to cater this little amount of additives has been added.

All kinds of polymers have shortcomings in one or more properties. To develop their properties there are two ways, synthesizing a new polymer with new chemical structure or blending different types of polymers having dissimilar properties to obtain polymer blend with required properties. The first process is very difficult and expensive and need a lot of time and the results are not guaranteed. On the other hand the blending of two polymers is very cheap and easy to realize.

 This twostep crosslinking method for the addition of peroxide is not that effective with the increase of SBR content. Similar, the increased amount of SBR content in the blends leads to the immiscibility and have poor effect on the mechanical properties on the blends. The addition of SBR is as the coupling agent between the PS and LDPE chains. The crosslinking enhance the properties of mechanical

but in the small amounts. As soon as the SBR content increased the effect of properties reduced.

In the first experiments the addition of SBR varies from the 0-15 %, the mechanical properties and impact test was analyzed. The small addition of SBR content enhance the mechanical properties but as soon as the SBR content increased the properties gradually reduced and further addition is not favorable due the immiscible behavior of the blend and the addition of SBR doesn't induce any remarkable improvements in the properties.

However, the next experiments are repeated on the principal of two step cross linking in which SBR was crosslinked first with peroxide. Addition of peroxide enhance the crosslinking between the chains and left over chains are crosslinked with polymer blend. This process is also suitable and doesn't influence on the improvement of mechanical properties.

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