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# Mémoire

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## Master

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***Effects of Interfacial Interaction on the Rheological, Mechanical, Dynamic Mechanical, Thermal, and Morphological Development in a Blending Process of the Compatibilized PVC/SBR Blends***

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*Dedication*

# *Dedications*

*We would like to dedicate our Master-thesis:*

- To our family especially our parents whose unbelievable endurance, unconditional love, and untouchable devotion have been monumental;*
- To all our brothers and sisters;*
- To those who will be happy with this new goal in our study career;*
- To all our best friends;*
- To anyone who has ever taught us anything.*

*There are many friends and other family members who need to be listed for their part in this Master-thesis.*

*Finally, this Master-thesis is dedicated to all those who believe in the richness of learning, and, we would like also to dedicate this modest review to all those who have devoted their lives to bringing the faded light of ambiguity to the complete shininess of clarity.*

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*In the name of Allah, The Most Beneficent and the Most Merciful.*

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To this end, we fully take all responsibility for any mistakes that may have occurred in this work.

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**List  
Of  
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Abbreviations**

# List of Notations and Abbreviations

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<b>Abbreviations</b>	<b>Description</b>
<b>BR</b>	Butadiene Rubber
<b>DMA</b>	Dynamic mechanical analysis
<b>DSC</b>	Differential scanning calorimeter
<b>ENR</b>	Epoxidized Natural Rubber
<b>EPDM</b>	Ethylene propylene diene rubber
<b>EPR</b>	Ethylene propylene rubber
<b>HDPE</b>	High density polyethylene
<b>LLDPE</b>	Linear Low Density Polyethylene
<b>NBR</b>	Acrylonitrile butadiene rubber
<b>NMR</b>	Nuclear magnetic resonance
<b>NR</b>	Natural rubber
<b>PE</b>	Polyethylene
<b>PLA</b>	Poly lactide
<b>PMMA</b>	Poly(methyl methacrylate)
<b>PP</b>	Polypropylene
<b>PVC</b>	Polyvinyl Chloride
<b>PS</b>	Polystyrene
<b>SBR</b>	Styrene Butadiene Rubber
<b>SAN</b>	Styrene-acrylonitrile
<b>TGA</b>	Thermogravimetric Analysis
<b>TPEs</b>	Thermoplastic Elastomers
<b>T<sub>g</sub></b>	Glass transition temperature
<b>VCM</b>	Vinyl chloride monomer

<b>Symbols</b>	<b>Description</b>
<b><math>\Delta G_m</math></b>	Free energy of mixing
<b><math>\Delta H_m</math></b>	Melting enthalpy of sample
<b><math>\Delta S_m</math></b>	Entropy of mixing
<b>T<sub>c</sub></b>	Crystallization temperature
<b>T<sub>g</sub></b>	Glass transition temperature
<b>T</b>	Temperature
<b>MPa</b>	Megapascal
<b>P</b>	Pressure
<b>R</b>	universal gas constant
<b>°C</b>	Degree Celsius
<b>wt%</b>	Percent by weight
<b>X</b>	Flory-Huggins interaction parameter
<b><math>\varnothing</math></b>	Volume fraction of the component
<b><math>\phi_i</math></b>	Volume fraction of component

# **General Introduction**

# General Introduction

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## I. General Introduction

A polymer blend is a mixture of two or more polymers that have been blended together to create a new material with different physical properties. Generally, there are five main types of polymer blend: thermoplastic–thermoplastic blends; thermoplastic–rubber blends; thermoplastic–thermosetting blends; rubber–thermosetting blends; and polymer–filler blends, all of which have been extensively studied. Polymer blending has attracted much attention as an easy and cost-effective method of developing polymeric materials that have versatility for commercial applications. In other words, the properties of the blends can be manipulated according to their end use by correct selection of the component polymers. Today, the market pressure is so high that producers of plastics need to provide better and more economic materials with superior combinations of properties as a replacement for the traditional metals and polymers. Although, plastic raw materials are more costly than metals in terms of weight, they are more economical in terms of the product cost. Moreover, polymers are corrosion-resistant, possess a light weight with good toughness (which is important for good fuel economy in automobiles and aerospace applications), and are used for creating a wide range of goods that include household plastic products, automotive interior and exterior components, biomedical devices, and aerospace applications.

The development and commercialization of new polymer usually requires many years and is also extremely costly. However, by employing a polymer blending process—which is also very cheap to operate – it is often possible to reduce the time to commercialization to perhaps two to three years. As part of the replacement of traditional polymers, the production of polymer blends represents half of all plastics produced in 2010. Today, the polymer industry is becoming increasingly sophisticated, with ultra-high-performance injection molding machines and extruders available that allow phase-separations and viscosity changes to be effectively detected or manipulated during the processing stages. Whilst this modern blending technology can also greatly extend the performance capabilities of polymer blends, increasing market pressure now determines that, for specific applications, polymer blends must perform under some specific conditions (e.g., mechanical, chemical, thermal, electrical). This presents a major challenge as the materials must often function at the limit of the properties that can be achieved; consequently, in-depth studies of the properties and performance of polymer blends are essential.

Interest in the development of polymer blends stems from the economic and environmental advantages in producing improved polymeric materials through the blending of existing

## General Introduction

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polymers, rather than through development of new synthetic polymers. Blending may be used to combine the attractive properties of two polymers and/or to improve the deficient properties of a given polymer. Imparting solvent resistance to an amorphous material through addition of a crystalline phase and improving the impact resistance of brittle materials through incorporation of a dispersion of rubber particles are examples of improvements which may be made through blending of polymers.

While some pairs of polymers exhibit complete miscibility over all ranges of temperature and blend composition, the majority of polymer pairs do not. Most polymer pairs are thermodynamically incompatible due to the small mixing entropy in mixtures of long chain molecules. Typical useful blends are usually mixtures of two (or more) immiscible or partially miscible polymers, and exhibit a microscopically inhomogeneous structure. The properties of immiscible blends are strongly dependent on the size and distribution of phases and the strength of the interphase interface(s). The development of many useful blends depends on the control of two important aspects of their structure. First, a stable dispersion of one polymer in the other must be realized, and second, the interface between the two polymeric components of the blend must be strong enough to support load transfer. The typical approach to managing this problem is to add block copolymer 'compatibilizers' to the mixture. This technique involves adding a block copolymer of the type A-B to a mixture of polymers A and B. The copolymers segregate to the A/B interfaces and act as an emulsifier thereby lowering the A/B interfacial tension, improving the resistance to particle coalescence, and stabilizing the dispersion. If the blocks of the A-B copolymers are sufficiently long then they can extend into the homopolymer phases and entangle causing mechanical linking which leads to a strong A/B interface. The drawbacks to traditional compatibilization are: 1) separate fabrication of A-B copolymers is required, which is prohibitively expensive in most cases, 2) it is difficult to properly disperse the block copolymers during processing so that they are positioned at the interfaces, and 3) the amount of compatibilizer which may be added is limited to low concentrations by the formation of copolymer micelles.

A novel approach to the modification of interfaces in incompatible blends which has been recently receiving much attention is reactive compatibilization, in which compatibilizers are formed in-situ at the interfaces. Homopolymer blend components which have reactive groups incorporated along the chains are utilized. Functional pendant or end groups are inherent to many types of polymers and may be added to others through relatively cost efficient processes such as small-molecule grafting, conversion of existing moieties or copolymerization. The

## General Introduction

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functional groups come in contact during mixing of the two polymers and react, forming bonds between the homopolymers at the interfaces. Recent studies have concentrated on the control of blend morphology which may be achieved through this type of reactive compatibilization scheme. It has been demonstrated that the dispersion of the minor polymer blend component decreases in average size with increasing concentration of functional groups, and that a homogeneous material may be achieved at sufficiently high functional group concentrations.

Polyvinylchloride (PVC) is one of the three most important polymers currently used worldwide. This is because PVC is one of the cheapest polymers to make and has a large range of properties. It plays an important role in every field such as agriculture, electrical, irrigation, house roofs, shoe soles and many other fields. It is having limited thermal stability.

Styrene butadiene rubber (SBR) is a synthetic rubber made from the polymerization of styrene and butadiene. It is a thermoplastic elastomer, meaning it can be melted and molded, then will return to its original shape. It is resistant to abrasion, oil, and heat, and has good tensile strength. It is used in products such as tires, hoses, belts, and gaskets.

As we know, these two polymers are thermodynamically incompatible; this incompatibility can be improved by means of different strategies of compatibilization such as: Physical, Chemical, and Technological compatibilization.

This master thesis is composed of four chapters. The first chapter presents a theoretical background on Poly (vinyl chloride); Styrene Butadiene Rubber; as well as thermoplastic elastomeric blends, the second chapter presents the thermodynamics principles of polymer blends, and the third chapter presents the strategies for compatibilization of polymer blends. The fourth chapter presents a brief presentation of **few** of the works that have been published and which covered different aspects of the subject.

The overall conclusion of this bibliographic research is discussed in the last part.

**CHAPTER I**  
**Theoretical**  
**Background**  
**(An Overview of**  
**PVC; SBR; and**  
**TPEs Blends)**

## **Chapter I : Theoretical Background**

### **An Overview of PVC; SBR; and TPEs Blend**

#### **I. General Introduction**

PVC is a thermoplastic, meaning that it has the property of softening or fusing when heated and hardening when cooled. Thermoplastic materials, correctly formulated, can undergo this process many times without undergoing any appreciable chemical change. PVC has primarily an amorphous structure, i.e., lacking positional order on the molecular scale, and shows typical characteristics of dimensional stability up to the glass transition temperature ( $T_g$ ): creep resistance, low shrinkage, impact resistance but notch sensitive and good transparency.

Styrene Butadiene Rubber (SBR) is a synthetic elastomer that belongs to the family of synthetic rubbers. It is commonly used in a wide range of applications due to its excellent combination of properties, including durability, flexibility, and resistance to abrasion and heat. SBR is produced by the copolymerization of styrene and butadiene monomers. Styrene provides rigidity and hardness to the rubber, while butadiene imparts elasticity and resilience. The ratio of these monomers can be adjusted to achieve different grades of SBR with varying properties. One of the primary uses of SBR is in the manufacturing of tires.

In this chapter we present an overview of the polymers involved in this study. Emphasis is made on thermoplastic elastomers (TPEs) and those based on PVC; SBR and the different strategies used for compatibilization.

#### **I.1.Poly (vinyl chloride)**

PVC is a synthetic thermoplastic polymer derived from the monomer vinyl chloride. Because of its versatility, durability, and low cost, it is one of the most frequently used polymers on the planet.

PVC was discovered in the late nineteenth century, but industrial manufacture of PVC did not begin until the 1920s. PVC is now employed in a wide variety of products, ranging from building materials to medical gadgets to clothes and upholstery. One of the most important characteristics of PVC is its capacity to be modified with additives to improve attributes such as flexibility, color, and resistance to heat, chemicals, and UV radiation. These additions include plasticizers, stabilizers, and colors.

However, PVC has been a source of contention due to environmental concerns, notably over its disposal and the potential release of dangerous chemicals.

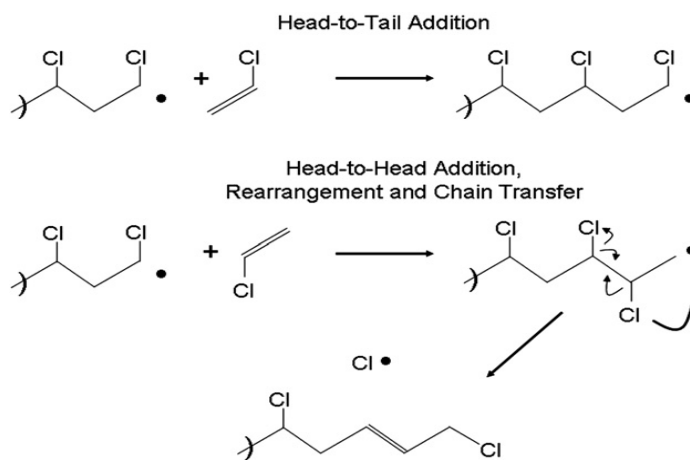
Because to the existence of additives and contaminants, recycling PVC can be difficult, and cremation might produce harmful gases.

Despite these obstacles, PVC remains an important material in many industries due to its versatility, durability, and low cost.[1]

### I.1.1 Synthesis Methods of Poly (vinyl chloride)

VCM is polymerized by free radicals to create PVC. A PVC chain generally has 1000 monomer units. Normally, monomer units are added head-to-tail; however, when head-to-head addition takes place, the expanding chain's unstable end rearranges to produce a terminal double bond and a chlorine atom. As a free radical, the chlorine atom initiates the polymerization of another chain (**Figure I.1**)

Chain transfer and molecular weight regulation are mediated by head-to-head addition activation energy, and hence by polymerization temperature alone. The only significant commercial polymer in which molecular weight and molecule weight distribution are controlled by polymerization temperature is PVC.



**Figure I.1:** Addition of VCM to growing PVC chain.

#### I.1.1.1 Emulsion/Microsuspension Polymerization

True emulsion or microsuspension polymerization can both be used to create small-particle PVC (less than 1 micron in diameter). Water is added to a reactor together with VCM, a surfactant (often a detergent like sodium lauryl sulfate), and a peroxide or azo initiator. Latex produced by polymerization has 40% or less particles and is steam stripped before being spray-dried.

Small-particle PVC is a powder with particles that are between 0.1 and 10 microns in size and agglomerates that are between 50 and 60 microns in size. The fundamental particles typically have a diameter of 1 micron. Although it is usual practice to pulverize dried material, not all agglomerates are eliminated during the post-processing. Surfactant or other surface residues are present on every particle as a byproduct of the production process.

Most often, a paste is created using different small-particle PVC materials.

### **I.1.1.2 Suspension Polymerization**

Suspension polymerization is the primary method of PVC production. The shearing action of an agitator produces VCM droplets in water that are roughly 50–100 microns in size.

These puddles Temperatures between 40 and 70 C are commonly required for polymerization. All PVC polymerization occurs at high pressure, but only to a level of around 100 psig as VCM boils at 13 C.

In theory, vinyl chloride, like polypropylene for instance, might exhibit tacticity because it is a monosubstituted ethylene and not a symmetric molecule. In reality, however, a protective colloid, typically a functionalized cellulose or partially hydrolyzed poly (vinyl acetate), stabilizes vinyl chloride polymerized.

Free-radical initiation in suspension polymerization often results from the breakdown of an azo or peroxide initiator.

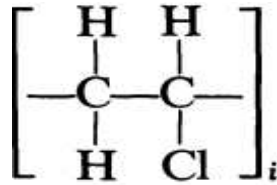
### **I.1.1.3 Mass Polymerization**

Without the use of water or any other dispersion, VCM can be polymerized. The majority of the time, mass or bulk polymerization is accomplished in two steps. To make PVC seed particles as a suspension in VCM, a low-solid prepolymerization is first performed. This prepolymer is put to a bigger postpolymerization reactor together with extra monomer, where it initiates and stirs the polymerization process to produce PVC powder.

Despite its seeming simplicity, mass polymerization has some special problems, including reactor fouling, heat transfer, VCM removal, and particle porosity. Most of those problems have been solved through the development of methods, although mass polymerization only accounts for a tiny portion of the world's PVC production.[2-4]

### I.1.2 Chemical Structure of Poly (vinyl chloride)

PVC polymer chain's fundamental repetition unit is



Where  $i$  represents the degree of polymerization—or, more specifically, the number of repeat units—in the molecular chain. Virtually all of the links between the units are "head-to-tail," or  $-\text{CH}_2-\text{CHCl}-\text{CH}_2-\text{CHCl}-$ . [5]

### I.1.3 Properties of Poly (vinyl chloride)

- **Physical properties**

PVC (polyvinyl chloride) is a synthetic polymer with a variety of physical properties, including:

1. PVC has a density of 1.3-1.45 g/cm<sup>3</sup>, making it one of the heavier polymers.
2. Hardness: PVC is a relatively hard plastic, with a Shore A hardness of 70-95.
3. Tensile strength: PVC has a comparatively high tensile strength of 50-80 MPa.
4. Flexibility: PVC is also malleable and can be formed into a wide range of shapes and forms.
5. Chemical resistance: PVC is resistant to a wide range of chemicals, including acids, bases, and salts.
6. Electrical characteristics: PVC is a great insulator with outstanding electrical qualities.
7. Flame resistance: PVC is naturally flame-resistant and can be manufactured to fulfill a variety of fire requirements.
8. Weather resistance: PVC is resistant to sunshine, ozone, and other environmental factors.
9. Thermal properties: Depending on the grade of PVC, PVC has a comparatively low melting point of 100-260 °C.

Overall, PVC is a flexible plastic with a wide range of physical qualities that make it useful for a wide range of applications, including building, packaging, and medical equipment.

- **Chemical properties**

Polyvinyl chloride (PVC) is a thermoplastic polymer that is widely used in building, packaging, electronics, and the automotive industries. Its key chemical features include:

1. **Chemical resistance:** PVC is chemically resistant to a wide range of substances, including acids, alkalis, and solvents. This feature makes it beneficial in applications where chemical exposure is likely.
2. **Flammability:** PVC is a highly flammable polymer that, when burned, emits harmful fumes. To solve this issue, flame retardants and other additives are frequently added to PVC compositions.
3. **Thermal stability:** PVC has a low melting point of around 212°C (414°F). It can, however, sustain high temperatures without degrading, making it useful for applications requiring heat resistance.
4. **Electrical insulation:** Because PVC is a good electrical insulator; it can be used in electrical and electronic applications.
5. **Weatherability:** PVC is resistant to weathering, including sun, rain, and high temperatures. This quality makes it suited for outdoor use.

In general, the chemical qualities of PVC make it a versatile material that is widely employed in a variety of sectors. However, its flammability and potential environmental effect are issues that must be handled through careful handling, disposal, and recycling.

- **Mechanical properties**

PVC is a synthetic polymer with good mechanical properties, which include:

1. **Tensile strength:** PVC has a high tensile strength, making it excellent for applications involving tension, such as the building of fences or tents.
2. **Flexural strength:** PVC has a high flexural strength, which means it can bend without breaking. Because of this, PVC is a common material for applications such as plumbing and window frames.

3. Impact resistance: PVC has great impact resistance, making it suited for use in applications involving sudden impacts, such as the manufacture of safety helmets or protective gear.

4. Compression strength: PVC has strong compression strength, which means it can endure compressive forces without deforming. Because of this feature, PVC is a popular material for use in construction materials such as roofing membranes and flooring.

5. Hardness: PVC is a hard material that is resistant to abrasion and wear. This feature makes PVC acceptable for use in applications where it will be subjected to wear, such as the fabrication of conveyor belts or gaskets.

In all, PVC is a versatile material with a wide range of mechanical qualities that allow it to be used in a wide range of applications. However, the mechanical characteristics of PVC might vary depending on the formulation and manufacturing conditions.

- **Thermal properties**

Due to its diverse physical and chemical properties, polyvinyl chloride (PVC) is a synthetic polymer with a wide range of industrial applications. PVC is well-known for its heat stability, making it an excellent material for high-temperature applications. PVC has the following thermal properties:

1. Melting point: Because PVC has a low melting point of 212-220°C (414-428°F), it is easy to process by melting and molding.

2. Glass transition temperature (T<sub>g</sub>): PVC has a T<sub>g</sub> of about 82°C (180°F), which is low when compared to other thermoplastics. This means that PVC softens and rubberizes at temperatures above its T<sub>g</sub> and stiffens and brittles at temperatures below it.

3. Thermal conductivity: PVC has a low thermal conductivity, which means it is a strong heat insulator. At normal temperature, PVC has a thermal conductivity of 0.14 to 0.16 W/mK.

4. Thermal expansion: PVC has a thermal expansion coefficient of  $7.5 \times 10^{-5}$  /K, which means it expands and contracts with temperature changes. When designing PVC materials for high-temperature applications, this feature should be considered.

5. Flammability: Although PVC is a generally fire-resistant material, it can nonetheless catch fire under certain settings. PVC has a heat of combustion of roughly 15,000 kJ/kg.

To summarize, PVC is a thermally stable material that can endure high temperatures and is an excellent heat insulator. It is easy to produce due to its low melting point and glass transition temperature, but its coefficient of thermal expansion must be considered when designing for high-temperature applications.

- **Electrical properties**

Polyvinyl chloride (PVC) is a thermoplastic polymer having a wide range of electrical characteristics. Here are a few of PVC's main electrical properties:

1. Dielectric constant: Depending on the frequency of the applied electric field, the dielectric constant of PVC ranges from 3.1 to 3.6. This characteristic makes PVC an excellent insulator in electrical applications.
2. Dielectric strength: Because PVC has a strong dielectric strength, it can sustain high voltage without deterioration. PVC is suited for high voltage electrical applications because of its characteristic.
3. Volume resistivity: Depending on the temperature and humidity, the volume resistivity of PVC ranges from  $10^{13}$  to  $10^{15}$  ohm-cm. PVC is a good insulator against electrical current because of this characteristic.
4. Surface resistance: Depending on the surface treatment and environmental circumstances, PVC has a surface resistivity ranging from  $10^{11}$  to  $10^{13}$  ohms/square. Because of this feature, PVC is an excellent material for electrostatic discharge (ESD) protection.
5. Electrical conductivity: Because PVC has a poor electrical conductivity, it is an excellent insulator against electrical current. PVC, on the other hand, can be made conductive by adding conductive fillers like carbon black or metal particles.

Overall, PVC is a flexible material with a wide range of electrical qualities that allow it to be used for a variety of electrical applications such as insulation, wiring, and electrostatic discharge protection.[6]

### **I.1.4 Major Advantages of Poly (vinyl chloride)**

PVC offers a number of key advantages to sectors, cementing its position as one of the most popular and commonly utilized plastics on the market.

These benefits include:

1. Polyvinyl Chloride is easily accessible and reasonably priced.
2. Compared to other plastics, polyvinyl chloride is exceptionally thick and consequently quite durable, and it resists impact deformation very well.
3. Polyvinyl Chloride has an exceptionally high tensile strength.
4. Polyvinyl chloride is chemical and alkali resistant.

PVC's advantages contributed to its status as one of the most widely used plastics in the world. However, even though it is widely effective and popular, some factors must be considered when using the material.[7]

#### **1.1.5 Drawbacks of Poly (vinyl chloride)**

PVC, or poly (vinyl chloride), is a synthetic thermoplastic polymer that is widely utilized in a range of applications, including building, packaging, electronics, and automobiles. However, PVC has various downsides, including:

1. Environmental impact: PVC is derived from petroleum, a nonrenewable resource that requires a large amount of energy to manufacture. Furthermore, the manufacturing process can emit dangerous chemicals into the environment, such as dioxins and phthalates, which have been associated to cancer and other health issues.
2. Toxicity: PVC has the potential to emit toxic compounds such as vinyl chloride and phthalates, both of which are known to be hazardous to human health. These substances can cause respiratory issues, liver and kidney damage, and cancer.
3. Durability: While PVC is a long-lasting substance, it is not as robust as other polymers like polyethylene or polypropylene, and it can grow brittle with time. This might result in cracks and breaks that are difficult to fix.
4. Recycling: PVC is difficult to recycle due to the presence of additives such as plasticizers, stabilizers, and pigments that might interfere with the recycling process. This can lead to PVC items winding up in landfills, where they can take hundreds of years to degrade.

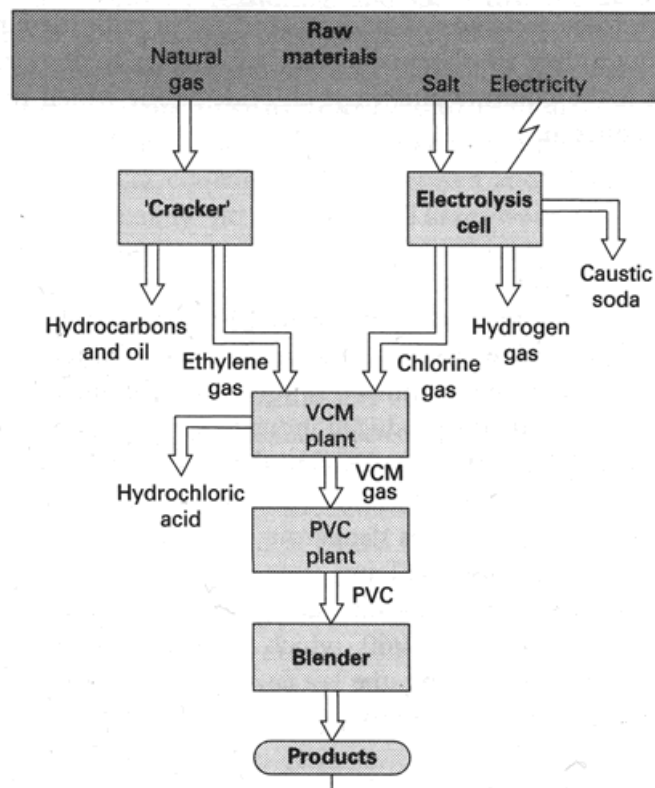
5. Fire hazard: PVC is a highly flammable polymer that emits hazardous fumes when burned, giving it a fire hazard. This is especially problematic in applications like building construction, where fires can spread quickly and cause severe damage

Overall, while PVC has many helpful features and is widely used in industry, it also has substantial negatives in terms of environmental effect, health hazards, and recycling difficulties.[8]

### I.1.6 Manufacturing of Poly (vinyl chloride)

PVC is the second most important commodity plastic after polyethylene, with global output currently exceeding 18 million tonnes per year.

The chemical method for producing PVC consists of three steps: first, the manufacturing of the monomer, vinyl chloride; second, the joining of these monomer units in a polymerisation process; and finally, the polymer blending with additives. (**Figure I.2**)



**Figure I.2:** The production process of PVC

### ✓ Producing Chlorine

Brine is formed when salt (sodium chloride) from dried-up prehistoric oceans is dissolved in water. This solution is placed in a cell and an electric current is sent through it. In one part of the cell, chlorine gas bursts out, while sodium metal is formed in the other. Caustic soda (sodium hydroxide) and hydrogen gas are formed when sodium combines with water. Both have substantial commercial applications.

The production of chlorine gas requires the liquid metal mercury (compounds of which are poisonous) and can have devastating environmental consequences. One such occurrence occurred in the 1950s in Japan at Minamata Bay, when mercury leaked and tainted fish, eventually entering the food chain and killing many locals. Industrial factories take great care to prevent mercury from escaping, but some mercury is inevitably lost, which is why a new method of producing chlorine is currently utilized. This innovative approach uses an asbestos diaphragm in a porous cell that allows an electric current to flow while also preventing corrosion from chlorine and caustic soda. This procedure is safer because no asbestos is lost and the diaphragm can be disposed of safely and efficiently. However, one disadvantage of this method is that it produces a more dilute solution of caustic soda, which necessitates steam heating to remove excess water and make it more concentrated before it can be sold for commercial use.

PVC production accounts for 30% of industrial chlorine production. Because of the presence of chlorine, PVC is compatible with a wide range of different materials, making it exceedingly versatile. Furthermore, chlorine makes PVC flame retardant and distinguishable when sorting plastics for recycling. However, chlorine is a highly corrosive and lethal gas. It is hazardous to handle, and people have perished in industrial accidents using chlorine. Chlorine is thus subjected to stringent safety precautions, even during shipment.

### ✓ Ethylene Gas Producing

Ethylene is derived from oil or natural gas after it has been processed and 'cracked' by heating ethane, propane, butane, or naphtha from oil. For example, the methane cracking process can be described as follows:



Propylene is recovered as it is valuable from the by-products of these operations, which also include hydrogen that can be burned to provide electricity locally. Although these byproducts are flammable, they do not cause cancer or are toxic.

### ✓ Producing PVC

Vinyl chloride, which is disseminated in water as a suspension or an emulsion, is subjected to pressure in high pressure chambers at temperatures between 50 and 70 °C. Water's function in the polymerization process is to reduce and regulate the heat that is produced. PVC is created by small particles growing to the proper size, at which point the reaction is terminated and any remaining vinyl chloride is distilled off and reused. A white powder is created once the PVC is separated out and dried.

### ✓ Producing Vinyl Chloride

Chlorine and ethylene are mixed to create ethylene dichloride, which is heated to produce vinyl chloride, which is then separated from the vinyl chloride to produce hydrogen chloride gas;



Side reactions occur, resulting in the formation of organochlorine chemicals, some of which are collected for commercial purposes. The leftover by-products are burned in order to recover hydrogen chloride, which can then be recycled and reacted with additional ethylene to generate new ethylene dichloride. Although vinyl chloride gas is less toxic than chlorine, it has been linked to angiosarcoma, a type of liver cancer, in people who have worked with it. Workers who are exposed to it are now protected, and leaks and losses of vinyl chloride gas in plants are kept to a bare minimum, with residual traces in the product PVC eradicated to the greatest extent possible. These enhancements ensure that the general population is not at any risk from this chemical. [9-11]

## I.1.6 Applications of Poly (vinyl chloride) in Industrial Fields

Over half of all processed PVC is now used in construction, in products such as pipes, wiring, siding, flooring, and wallpaper. When compared to more traditional building materials (e.g., wood, concrete, and even clay), PVC offers cost savings and ease of installation and replacement (Thornton, 2002).

➤ **PVC pipes**

PVC is utilized to produce raincoats, shower curtains, and, of course, water pipes due to its natural water resistance. PVC is widely used for municipal water supply/sewage pipes, spouts, and other applications because its mechanical qualities, such as tensile strength and tensile modulus, are superior to those of other general-purpose olefin polymers, and it is resilient and durable. Home plumbing systems use various piping materials for various purposes, such as home water supply, waste drainage, appliances, irrigation, and so on. PVC is a stiff plastic that is commonly used in sanitary waste lines, vent pipes, and drain traps for both residential and commercial purposes. PVC rigid pipe is easily cut (with a hacksaw or tube cutter) and fitted, and it is frequently used to repair sections of broken old cast iron waste pipes. Its pieces can be linked mechanically (using plastic pressure fittings for later removal) or permanently (using a specific chemical solvent) (**Figure I.3**).

Under typical settings, PVC pipes are expected to survive substantially longer (up to or exceeding 100 years), lowering both maintenance costs and environmental effect (Makino, 1998). Global annual demand for plastic pipe, the majority of which is made of PVC, is expected to reach 20.3 Mt (million tons) by 2015, with an annual increase of about 7% and continued strong prospects in developing countries, particularly China, which accounted for 30% of overall profits for plastic pipe between 2007 and 2012 (Anon., 2011c). In fact, rising demand for PVC piping in China is being driven primarily by increases in construction spending as well as advances in consumer spending; and it is worth noting that China surpassed the United States to become the world's largest consumer of PVC in 2005 (Anon., 2007a).



**Figure I.3:** PVC pipe and fittings

➤ **PVC profiles**

Due to the high level of product performance required, window and door profiles are two additional demanding applications for rigid PVC (uPVC). Window frames, doors, conservatories, fascias, skirting boards, architraves, soffits, guttering, rainwater systems, fences, and decking are all made of uPVC profiles. PVC, which has a variety of colors and an attractive wood-grain finish, as well as effective heat and sound insulation qualities, provides for all such applications a lightweight, inexpensive, and maintenance-free alternative. As a result, it has already replaced long-used conventional materials like wood, steel, and aluminum. PVC window profiles are anticipated to survive for more than 40 years under typical circumstances, significantly lowering maintenance costs and environmental effect. uPVC is a far more effective thermal insulator than aluminum, steel, and wood, which also shows that it has the lowest values of  $k$  and, consequently, the highest values of  $R$ .

➤ **PVC flooring and tiles**

PVC flooring (also known as PVC floor coverings, vinyl-polyvinyl floors and tiles), which may be used practically everywhere that requires a durable floor, is quite popular for residential applications. The traditional linoleum (or lino) floor coverings, which were constructed of renewable elements including linseed oil, pine rosin, cork dust, wood flour, and mineral fillers, have been replaced by PVC as a preferred flooring material in North America for more than 40 years. PVC tiles and floors can survive even the worst climatic conditions and large loads, and their commercial and industrial grades are available for usage in locations like offices and other high traffic areas (for both pedestrians and automobiles), sports areas, hospitals, etc. PVC floors offer alternatives for soundproofing and waterproofing. In large-floored structures like schools, offices, and public buildings, where durability and cheap maintenance are essential, they are nearly an obvious choice. There are PVC anti-slip mats available. With its additional 'antistatic' grades, vinyl flooring also provides an economical and effective option for situations where sensitive electrical and computer equipment is located and static charges are a major issue.

PVC siding

PVC (or vinyl or uPVC weatherboard) siding is a type of plastic cladding that is used on the outside of a house for weatherproofing, insulation, and decoration. Since the late 1950s, PVC siding has been the most often installed external cladding for residential construction in the

United States and Canada. It is a designed product with a variety of color and finish options that is utilized as an alternative to traditional siding materials such as wood, aluminum, and fiber cement. Approximately 80% of the weight of PVC siding is PVC resin, with the remainder made up of additives required for system properties such as color, opacity, gloss, impact resistance, flexibility, and durability. Small amounts of various plasticizers, as well as stabilizers such as lead compounds, may be used in these additives to make the system more flexible. Furthermore, when vinyl sidings burn (for example, in a fire), they can emit toxic fumes, particularly dioxins.

### **Other PVC applications in construction**

#### **➤ *PVC liners***

PVC have the advantage of combining high chemical resistance and physical qualities, as well as the ease of heat or radiofrequency (RF) weldability. PVC liners are used in a variety of applications, notably as geomembranes, such as landfill liners, secondary waste containment liners, pond liners (for both hazardous and non-hazardous substances), and liners for artificial lagoons. In addition to a variety of other practical and vital applications, flexible PVC liner systems used to insulate city potable water tanks have been demonstrated to significantly extend the life of these tanks (Anon., 2008). Geo-fabrics or geotextiles are systems connected with permeable fabrics that, when utilized in the soil, have the potential to separate, filter, reinforce, protect, or drain. [12]

## **I.2 Styrene Butadiene Rubber**

Styrene-butadiene rubber (SBR) is the most commonly used synthetic rubber and may be manufactured by copolymerizing butadiene (75%) and styrene (25%) with free radical initiators. A random copolymer is formed. The polymer has a microstructure that is 60%e68% trans, 14%e19% cis, and 17%e21% 1,2-. Wet techniques are typically employed to characterize polybutadiene polymers and copolymers. Solid-state NMR is a more convenient method of determining polymer microstructure. More SBR is currently created by copolymerizing the two monomers with anionic or coordination catalysts. The formed copolymer has improved mechanical properties and a narrower molecular weight distribution. Butyl-lithium can also be used to make a random copolymer with an ordered sequence in solution, as long as the two monomers are charged slowly. Block copolymers of butadiene and styrene may be synthesized in solution using coordination or anionic catalysts.

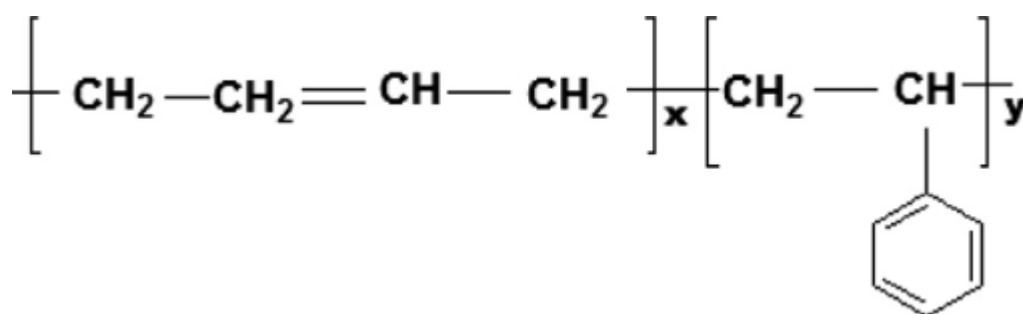
Butadiene polymerizes initially until it is depleted, at which point styrene begins to polymerize. The tensile strength of SBR produced by coordination catalysts is higher than that of SBR produced by free radical initiators.

SBR is mostly used in tire manufacturing. Footwear, coatings, carpet backing, and adhesives are some of the other applications.

### I .2.1 Synthesis Methods of Styrene Butadiene Rubber

Styrene-butadiene rubber (SBR) is a general-purpose synthetic rubber made from a styrene-butadiene copolymer. SBR, which outnumbers all other synthetic rubbers in terms of consumption, is widely used in vehicle and truck tires, primarily as an abrasion-resistant alternative for natural rubber (made from polyisoprene).

SBR is composed of roughly 75% butadiene ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ ) and 25% styrene ( $\text{CH}_2=\text{CHC}_6\text{H}_5$ ). Through the majority of cases, these two compounds are copolymerized (their single-unit molecules are joined to form long, multiple-unit molecules) through an emulsion process, in which the materials are dispersed, or emulsified, in a water solution using a surface-acting agent that resembles soap. Free-radical initiators, which start the polymerization process, and stabilizers, which stop the end product from degrading, are additional components in the solution. Styrene and butadiene repeating units are randomly placed along the polymer chain after polymerization. The vulcanization process cross-links the polymer chains. **(Figure I.4) [14]**

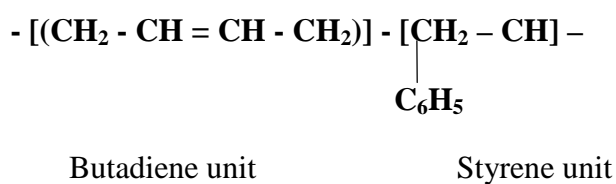


**Figure I.4:** Repeating unit of SBR

### I .2.2 Chemical Structure of Styrene Butadiene Rubber

SBR is produced using three processes: polymerization, monomer recovery, and finishing. The basic properties of SBR are determined by the polymerization process, whereas the product form (latex or dry rubber, oil extended or not) is determined by the finishing process.

SBR is created by adding butadiene and styrene monomers together during an emulsion or solution process. The copolymer's glass transition temperature (T<sub>g</sub>) and consequent stiffness are governed by the styrene/butadiene ratio. **(Figure I.5)**



**Figure I.5:** Chemical structure of styrene-butadiene rubber.

Styrene's T<sub>g</sub> ranges from -80°C (butadiene) to 100°C (styrene), hence the stiffer the copolymer, the higher its styrene content. SBR's chemical structure is depicted in Fig. 5. Because butadiene has two carbon-carbon double bonds, 1,2, and 1,4 addition reactions can occur. The 1,2 addition forms a pendant vinyl group on the copolymer chain, increasing T<sub>g</sub>. The 1,4 addition can occur either in cis or trans. The cis to Trans ratio in free radical emulsion polymerization can be changed by adjusting the temperature (at low temperatures, the trans form is preferred), and roughly 20% of the vinyl pendant group persists in both isomers.

The pendant vinyl group in solution polymerization can be changed from 10% to 90% by selecting the appropriate solvent and catalyst system. Gel formation should be avoided in general. Crosslinking of polymer chains during the growth step of emulsion polymerization causes gel formation. Changing the temperature, modifying the monomer to polymer conversion, and adding chain transfer agents can all be used to control the gel content. However, the gel portion of SBR polymers is frequently sufficient to provide good strength and creep resistance without curing. [15]

### I .2.3 Properties of Styrene Butadiene Rubber

#### ❖ Physical properties

Styrene-butadiene rubber (SBR) has the following physical properties:

1. Density: SBR has a density that ranges between 0.93 and 0.96 g/cm<sup>3</sup>, depending on the formulation and processing method utilized.
2. Melting point: Because SBR is a thermosetting polymer, it does not have a defined melting temperature. When heated, it instead undergoes a slow change from a solid to a viscous condition.
3. Glass transition temperature: The glass transition temperature (T<sub>g</sub>) of SBR ranges from -55°C to -45°C, depending on the formulation.
4. Solubility: SBR is insoluble in water and most organic solvents. However, it can be dissolved in polar solvents such as dimethylformamide and tetrahydrofuran.
5. Electrical conductivity: SBR is an insulator with limited electrical conductivity.
6. Optical properties: SBR is a clear or translucent material that can be tinted with pigments or dyes.
7. Water absorption: SBR has low water absorption, which means it does not readily absorb water even when soaked in water for extended periods of time.
8. Weather resistance: SBR has good weather resistance and can endure exposure to sunshine, ozone, and other environmental variables without degrading or losing its physical qualities.

Some of these physical qualities, such as density and solubility, may change depending on the grade and formulation of SBR utilized.

#### ❖ **Chemical properties**

SBR is a synthetic elastomer that is widely employed in a variety of industrial applications. Some of its chemical features are as follows:

1. Polymerization: Styrene and butadiene monomers are copolymerized to form SBR. Polymerization can be accomplished using a variety of processes, including emulsion, solution, and bulk polymerization.
2. Chemical structure: SBR is a thermoplastic polymer composed of varying quantities of styrene and butadiene units. Styrene concentration can range from 10% to 50%, with butadiene accounting for the remainder.

3. Chemical resistance: SBR has strong acid, base, and alcohol resistance. It is not, however, approved for use with oils, solvents, or aromatic hydrocarbons.

SBR has moderate thermal stability and can sustain temperatures of up to 100°C without substantial deterioration. It is not, however, appropriate for high-temperature applications.

4. Weathering resistance: SBR is resistant to weathering and can endure exposure to sunshine and ozone. However, continuous exposure to UV light is not advised.

5. Electrical properties: SBR offers good electrical insulation and can be used in electrical applications.

6. Adhesion characteristics: SBR has excellent adhesion properties and may form strong bonds with metals and polymers.

7. Water resistance: SBR is not water resistant and can absorb water, affecting its mechanical qualities.

Overall, SBR is a flexible synthetic elastomer with a wide range of chemical properties that allow it to be used in a variety of industrial and consumer applications, including as automobile parts, footwear, and sealing goods.

#### ❖ **Mechanical properties**

Styrene butadiene rubber (SBR) is a synthetic elastomer with varying mechanical properties based on formulation and processing. SBR's common mechanical features include:

1. Tensile strength: SBR has a high tensile strength, which means it can sustain stretching and pulling forces without breaking or deforming. SBR has tensile strengths ranging from 10 to 25 MPa.

2. Elongation at break: SBR has a high elongation at break, which means it can stretch greatly before breaking. SBR elongation at break can range from 300% to 800%.

3. Hardness: SBR has a range of hardness levels depending on the formulation and processing. The Shore A scale is commonly used to quantify hardness, and SBR can range from 30 to 90 Shore A.

4. Tear strength: SBR has a high tear strength, meaning it can withstand tearing forces. SBR's tear strength can range from 25 N/mm to 60 N/mm.

5. Compression set: SBR has a tendency to compress after being subjected to compression forces, which means it might become irreversibly distorted. SBR compression sets range from 20% to 50%.

6. Abrasion resistance: Because SBR is abrasion resistant, it can sustain frictional forces without quickly wearing out. SBR has an abrasion resistance range of 100 mm<sup>3</sup> to 300 mm<sup>3</sup>.

It is important to note that the mechanical properties of SBR can be adjusted to meet specific application needs by altering its formulation and processing conditions.

#### ❖ Thermal properties

Styrene-butadiene rubber (SBR) is a synthetic elastomer that is widely utilized in the production of tires, footwear, and a wide range of other items. It has a number of thermal properties as a polymer that are relevant for its use and processing. SBR's primary thermal features include:

1. Melting Point: Because SBR is an amorphous polymer, it does not have a sharp melting point. As it is heated, it softens and becomes more fluid. The melting temperature of SBR can vary depending on the formulation and manufacturing circumstances, although it normally ranges between 75 and 110 °C.

2. Glass Transition Temperature: The glass transition temperature (T<sub>g</sub>) is the temperature at which an amorphous polymer transforms from a hard, glassy state to a soft, rubbery state. T<sub>g</sub> for SBR is normally in the -55 to -45 °C range, depending on the formulation.

3. Thermal Conductivity: Because SBR has a low thermal conductivity, it is a good insulator. This feature is important in applications requiring thermal insulation, such as building construction or the manufacture of refrigeration equipment.

4. Thermal Stability: SBR is normally stable at temperatures between 100 and 120 °C, although it can degrade and lose mechanical qualities at higher temperatures. The exact thermal stability of SBR is determined by the formulation and processing conditions.

5. Heat Capacity: SBR has a relatively low heat capacity when compared to metals and other materials, which means it may heat up and cool down quickly. This feature is important in applications requiring quick temperature fluctuations, such as the production of rubber products.

SBR's thermal qualities make it a versatile and valuable material for a variety of applications. Its low thermal conductivity and high thermal insulation qualities make it particularly suitable in temperature-controlled applications.

#### ❖ **Electrical properties**

The electrical characteristics of styrene-butadiene rubber (SBR) vary based on its composition, production circumstances, and other factors. SBR's primary electrical features include the following:

1. **Electrical conductivity:** SBR is a low-conductivity insulating material. It can, however, be made conductive by adding conductive fillers like carbon black or metal particles.
2. **Dielectric constant:** Because SBR has a low dielectric constant, it does not store a large amount of electrical charge when an electric field is applied. Because of this feature, SBR is helpful as an insulator in electrical applications.
3. **Dielectric strength:** Because SBR has a high dielectric strength, it can endure high electric fields without breaking down. In high voltage applications, this feature is critical.
4. **Surface resistance:** SBR has a high surface resistivity, which means that electric current cannot flow across its surface. Because of this feature, SBR is helpful as an insulator in electrical applications.

**Volume resistivity:** SBR has a rather high volume resistivity, which implies it does not allow electric current to flow through its bulk. This characteristic makes SBR useful as an insulator in electrical applications.

Overall, SBR is a versatile material with a variety of electrical qualities that make it helpful in a variety of electrical applications such as insulation, gaskets, seals, and wiring.[16]

#### **I .2.4 Major Advantages of Styrene Butadiene Rubber**

Styrene-butadiene rubber (SBR) has various advantages over other forms of rubber, including:

1. **Low cost:** SBR is less expensive than many other synthetic rubbers, making it a popular choice for a wide range of applications.

2. Good abrasion resistance: SBR offers good abrasion resistance, making it appropriate for use in tires and other high-wear applications.
3. Good resilience: SBR has good resilience and can restore its shape after being stretched, making it appropriate for usage in a variety of applications, including shoe soles.
4. Water resistance: SBR has strong water resistance, making it useful for applications that need exposure to water or other liquids.
5. Simple to process: SBR is simple to process and can be easily blended with other materials, making it appropriate for use in a wide range of applications.
6. Good electrical insulation: SBR has good electrical insulation qualities, which makes it suitable in electrical applications.
7. Adhesive: SBR has strong adhesive qualities, making it ideal for adhering to other materials. [17]

### **I .2.5 Drawbacks of Styrene Butadiene Rubber**

Due to its superior mechanical and chemical characteristics, styrene-butadiene rubber (SBR) is a synthetic elastomer that finds extensive use in numerous industrial applications. However, SBR has several disadvantages as well, some of which are as follows:

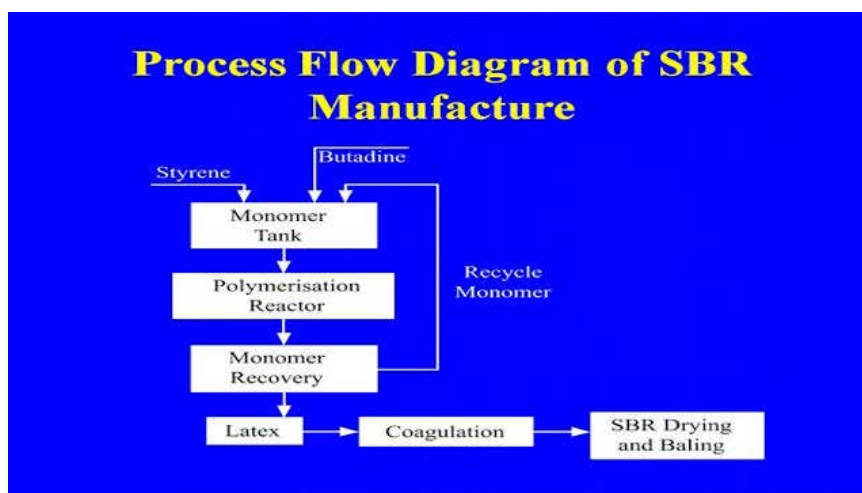
1. Poor weathering resistance: SBR is susceptible to UV light, ozone, and weathering, which can cause it to degrade and lose mechanical qualities over time.

SBR has weak resistance to oil and other hydrocarbon-based fluids, which can cause it to bloat and lose its elasticity.

2. High glass transition temperature: Because SBR has a relatively high glass transition temperature ( $T_g$ ), its low-temperature performance is limited.
3. Poor tear and abrasion resistance: When compared to other elastomers, SBR has comparatively poor tear and abrasion resistance.
4. Limited chemical compatibility: Due of its weak chemical resistance, SBR is not advised for use with certain chemicals, such as strong acids and organic solvents.[18]

### I .2.6 Manufacturing of Styrene Butadiene Rubber

The production of styrene-butadiene rubber involves three distinct steps: polymerization, monomer recovery, and finishing. The polymerization step determines the basic properties of the polymer, which are detailed below, and the product form, whether latex or dry rubber, oil extended or not, is a result of the finishing process.(**Figure I.6**) [19]



**Figure I.6:** Process flow daigram of SBR manufacture.

### I .2.7 Applications of Styrene Butadiene Rubber in Industrial Fields

Conveyor belts, molded shoe soles, microcellular shoe soles, water proof materials, adhesive, molded and extruded items, passenger car tire treads, motorcycle and scooter tire treads, tire bead compound, light truck tire treads.

**Table I.1:** Some SBR types and their application areas [20].

Type	Application Area
SBR 1500	Tread rubber, technical rubbery materials
SBR 1502	Tehcnical material which has lighter colour
SBR 1507	Materials which are used in extrusion or calender
SBR 1509	Cable and electricalgoods
SBR 1516	Extruded materials with shining surfaces (Higher styrene content
SBR 1573	Clutch/Brakelinings, adhesives
SBR 1707	Hoses, profiles, shoes, flooring

SBR 1712	Treadrubber, conveyorbelts
SBR 1778	Lighter colour or transparent technical rubbery materials, flooring
SBR 1618	Technical rubbery materials, extruded materials
SBR 1803	Treadrubber, electricalmaterials
SBR 1843	V-belts

### I.3 Thermoplastic Elastomer from Rubber, Plastics Blends

#### I .3.1 Definition of Thermoplastic Elastomer

TPE, or thermoplastic elastomer, is a rubber-like substance that processes like plastic. TPEs are real thermoplastics that do not need vulcanization or curing. Plastic production equipment such as injection molding, extrusion, and blow molding are used to process thermoplastic elastomers. A TPE can be applied to more complex processing methods like overmolding and two-shot molding, as well as to auxiliary procedures like welding and gluing to diverse materials. The flexibility of part design and ease of adhering to different thermoplastic substrates are two benefits of thermoplastic elastomers.[21]

#### I.3.2 Properties of Thermoplastic Elastomer

Thermoplastic elastomers (TPEs) are a class of materials that have both thermoplastic and elastomeric qualities. They can be molded and shaped in the same way that typical thermoplastics can, but they also have elastic qualities akin to rubber. TPEs have the following properties:

1. Flexibility: TPEs are extremely flexible and may be stretched and bent without cracking or breaking. They can also be compressed and returned to their original shape.
2. Resilience: TPEs have high resilience, which means they can restore their original shape after being deformed.
3. Chemical resistance: TPEs are resistant to a wide range of chemicals, including oils, greases, and solvents.

4. Weather resistance: TPEs are also resistant to weathering and UV radiation, making them perfect for outdoor applications.

5. Low temperature resistance: TPEs retain their flexibility and elastic properties at low temperatures, making them appropriate for use in cold situations.

TPEs are easily processed utilizing injection molding, extrusion, and other standard thermoplastic processing processes.

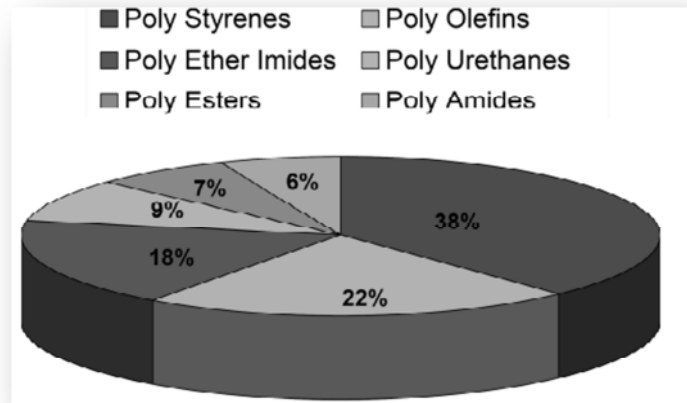
6. Recyclability: TPEs are recyclable and can be reused in different applications, decreasing waste and impact on the environment.

TPEs include styrenic block copolymers (SBCs), thermoplastic polyolefins (TPOs), and thermoplastic polyurethanes (TPUs). TPEs are employed in a variety of industries, including automotive, medical, consumer goods, and construction. [22]

### **I.3.3 Advantages of Thermoplastic Elastomer**

TPE materials offer a wide range of design alternatives and improved cost-saving prospects since they have performance characteristics similar to thermoset rubbers but with the process and design flexibility of plastics.

They can be handled quickly, effectively, and affordably. Thermoplastics and can be insert molded without the need of adhesives with other olefin-based polymers, such polypropylene. Other benefits include being lightweight, having elastic recovery properties within a specific temperature range, replacing metal, reducing noise through self-lubrication, having very good electrical insulation properties, having heat resistance within a specific temperature range, having oil resistance, having improved adhesion, having a tear-resistant surface, having low permeability, being colorable, and being made in a range of hardness grades. For the year 2009, it was estimated that 3.2 million metric tons of TPE rubbers of all types were consumed worldwide. In **Figure I.7**, a pie chart depicting the percentage share of each type is displayed.[23]



**Figure I.7** Percentage share of different TPE materials in global consumer market.

- TPE scrap can be reused with negligible loss of properties. However thermoset rubberscrap cannot be reprocessed.
- TPEs are flexible and break at large elongation.
- TPEs have good compression set and superior vibration damping characteristics.
- TPEs can be reinforced with fillers such as carbon black and silica.
- TPEs have good resistance to impact, compressive and flexural loads.
- TPEs have high fatigue to failure resistance [24]

### I.3.4 Drawbacks of Thermoplastic Elastomer

Countering these advantages of TPEs are certain disadvantages which must be considered:

1. Thermoplastic processing methods and equipment, foreign to the rubber industry, are required for their fabrication. TPE fabrication by a thermoset rubber processor thus requires a capital investment in thermoplastics equipment, and operators must learn how to use this equipment.
2. The good processing economics of TPEs generally need a relatively high production volume to justify the costs of molds, extrusion dies, and development effort.
3. Drying is usually required before TPE processing. This step, familiar to thermoplastics processors, is unknown in conventional rubber processing [25]

### I.3.5 Preparation Methods of Thermoplastic Elastomer

Thermoplastic elastomers are particularly appealing technologically because they can be processed as thermoplastics; this is their fundamental advantage over cross-linkable

elastomers. They can be remelted or devitrified, then reshaped. As a result, they are typically treated using extrusion and injection moulding, which are the most prevalent thermoplastic processing processes. TPE has a disadvantage in that its working temperature is lower than that at which the hard phase becomes dimensionally unstable.

Several factors must be considered when processing TPEs, such as the viscosity or rheology of the two-phase polymer, the temperature at which the hard phase can be processed, thermal stability because the complex structures may have several weak chemical links, thermal conductivity because the hard phase is surrounded by soft phase, crystallinity in the hard phase that must be melted with excess enthalpy, and moisture, which may cause hydrolysis at protons.

### **I.3.5.1 Extrusion**

Extrusion is a high-volume manufacturing process used to make items out of thermoplastic elastomers. This processing technology is critical in the melting of raw materials and shaping them into various continuous profiles. The most popular extrusion processes include film and sheet extrusion, blow film extrusion, cast film extrusion, coextrusion, tubing extrusion, and extrusion coating. Extrusion produces pipe/tubing, wire insulation, film, sheets, adhesive tapes, and window frames as end products. Extrusion is essentially the process of heating a thermoplastic over its melting temperature and forcing it through a die. The extruder is a heating and pressurizing device that consists of one or more screws that operate within a heated barrel. The screw is the most important predictor of extruder performance. It has three basic functions: feeding and conveying the raw material feed, melting, compressing, and homogenizing the material, and metering and pushing it at a steady pace through the extrusion die. Raw thermoplastic elastomer material is put into the extruder barrel and makes contact with the screw. As a melt delivery mechanism, the rotating screw forces the polymer forward into a barrel that is heated to the correct temperature. After exiting the screw, the molten metal passes through a screen pack/plate breaker, where impurities in the melt are removed. The breaker plate also generates back pressure in the barrel, which is required for uniform melting and optimal polymer mixing. The molten metal then enters the die, where the cross section of the extruded product is determined.

### **I.3.5.2 Injection molding**

Due to its great productivity, injection molding is by far the processing method most frequently utilized to produce parts from thermoplastic elastomers. Because of the high pressures needed and the intricate process control, injection molding machines and molds are exceedingly expensive. However, this method's ability to quickly and efficiently produce a complex finished part offsets its drawback.

Injection molding works on a pretty straightforward principle. The plastic substance is gravity-fed through a hopper into the injection barrel. The polymer is heated to melting point as soon as it enters the barrel. It is subsequently pressed into a closed mold that created the shape of the finished product. Continuous cooling is applied to the mold to maintain a temperature that permits the molten material to solidify. After cooling, the mold is opened, the final item is expelled, and the process is then repeated.

The injection molding technique can produce a wide range of parts, from the smallest pieces to whole automobile body panels in a single molding step. Threads, springs, storage bins, mechanical components, and automobile dashboards are a few additional part designs produced via injection molding.

### **I.3.5.3 Compression molding**

One of the earliest techniques for molding plastic objects was compression molding. However, compared to injection molding, it is much less popular. This process typically consists of four steps. First, a heated, open mold cavity is filled with the raw polymer materials in pellet or powder form. Pressure is employed to drive the materials into contact with all mold surfaces while the mold is closed with the opposite half of the mold. High pressure and temperature cause the materials to soften and flow into the mold. Before removal, the part is cooled in the mold to solidify it under pressure so that it keeps its shape.

There are six crucial factors to keep in mind: the right amount of material, the least amount of energy needed to heat the material, the shortest amount of time needed to heat the material, the right heating method, the force required to ensure that the shots take on the right shape, and the design of the mold for quick cooling. TPEs have high melting points, hence compression molding typically necessitates more heating and cooling time. To address this issue, separate platens could be utilized; one for a hot press that is heated electrically and another for a cold press that is cooled by water. The component is pressure-heated in the hot

press before being instantly moved to the cold press to cool it. To speed up the entire cycle, the hot press is typically warmed.

#### **I.3.5.4 Transfer molding**

In the process of transfer molding, the polymer is melted in a separate room called a pot before being pushed into a heated mold through a sprue and taking the shape of the mold cavity. It is chilled before opening the mold. Due to their typical high viscosity, thermoplastic elastomers require longer transfer times. To prevent premature cooling or freezing before the transfer is finished, the temperature of the mold should be kept above the polymer's melting point. The type of polymer, melting point of the polymer, pot hold time, transfer pressure, transfer rate, and mold cooling time are crucial factors throughout the transfer molding process.

#### **I.3.5.5 Blow molding**

Plastic pieces with hollow interiors can be produced using the manufacturing method known as blow molding. High density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), poly (vinyl chloride) (PVC), and poly (ethylene terephthalate) (PET) are just a few of the materials that can be employed in this process. The fundamental procedure starts with melting thermoplastic and extruding it through a die head to create a parison, which is a hollow tube. After being closed around by two mold halves, the parison is then clamped between them. Pressurized air is then used to inflate the parison until it takes on the internal shape of the mold cavity. Finally, the molds open, releasing the finished component. The parison is essentially formed using three different types of blow molding. Extrusion blow molding uses a rotating screw to force molten plastic through a die head that creates the parison. Plastic is melted and extruded this way. Injection blow molding, the molten plastic is first injection molded around the core pin and then moved to a blow molding station where the pin is inflated. There are two distinct stretch molding methods. The perform is injected into the blow mold, transferred there, and then blown and removed from the machine in a one-stage operation. In the two-stage procedure, the perform is injection molded, quickly stored, and then blown into the container using a reheat blow machine.

#### **I.3. 5.6 Thermoforming**

Thermoforming is a technique that turns a thermoplastic flat sheet into the necessary three-dimensional pieces by applying heat, pressure, or vacuum. The sheet is taken out of big rollers or an extruder, transported, and heated to the temperature at which it will soften. The heated sheet is then moved to a temperature-controlled, previously heated mold. The sheet is deformed into the mold chamber using vacuum to release the trapped air, and then it is cooled

to keep the produced shape. After then, a burst of reverse air pressure is applied to break the vacuum and help the formed item out of the mold. The primary parameters in this process are the forming force, mold type, sheet prestretching, material input form, and process phase condition. These elements have a significant impact on the final product's quality and attributes.

### **I .3.5.7 Calendaring**

Calendaring is the process of forming huge amounts of molten plastic into sheets by moving the polymer between a set of rollers. The rollers are heated and maintain the polymer semi-molten. This permits the molten metal to be rolled multiple times until the desired thickness is achieved. The sheet is then passed over cold rollers to harden it before being wrapped up into rolls. Thermoplastic calendars are often built in four-roll units with three banks, each one broader than the one before it. Calendar has a higher output than extruder and can make embossed films, sheets, and laminates. Cling film, shrink film, clear, translucent firm sheets for blister packaging, and opaque flexible film are some of the end products.[26]

### **I.3.6 Classifications of Thermoplastic Elastomer**

Thermoplastic elastomers are divided into six types based on their chemistry.

1. Polystyrene polymers
2. Polyolefins are a kind of polyolefin.
3. Imides of Poly Ether
4. Polyurethanes are a type of polyurethane.
5. Poly Esters
6. Poly Amides

Each category has a tiny chemical difference and hence offers varied properties. Chemical cross linking is achieved in thermoset rubbers through the vulcanization process. Vulcanization is an irreversible and gradual process that occurs during heating. The thermoplastic elastomers are generated by the physical mixing and/or cross linking of two components, which is a reversible process that occurs after the reactants are cooled. TPE materials can be polar (copolyesters, copolyamides, polyurethanes) or non-polar (PP, PE EPM, EPDM, NR, BD). [27-30]

### I.3.7 Factors off acting The Properties of Thermoplastic Elastomer

- ❖ **Composition:** The composition of thermoplastic elastomers (TPEs) can greatly affect their properties .The ratio of the hard and soft segments in the polymer chain can determine the overall flexibility, strength, and durability of TPE.
- ❖ **Molecular weight:** The molecular weight of the TPE can also impact its properties . Higher molecular weight TPEs tend to have better mechanical properties , such as higher tensile strength and elongation at break.
- ❖ **Processing conditions** : The processing conditions used during the production of TPEs can affect their properties .Factors such as temperature, pressure, and cooling rate can influence the final properties of the material.
- ❖ **Additives:** The addition of additives such as fillers, plasticizers, and stabilizers can alter the properties of TPEs .For example, adding fillers can improve stiffness and strength, while plasticizers can increase flexibility andsoftness.
- ❖ **Environmental conditions:** The environmental conditions that the TPE will be exposed to can also affect its properties. Factors such as temperature, humidity, and exposure to chemicals can impact the material’s performance over time.
- ❖ **Crosslinking:** Crosslinking is a process that can be used to improve the mechanical properties of TPEs .By introducing chemical bonds between polymer chains , Crosslinking can increase strength ,durability, and resistance to deformation.[31]

### I.3.8 Applications of Thermoplastic Elastomer in Industrial Fields

There are numerous applications for thermoplastic elastomeric materials. Replacements for artificial and natural rubber, foam making, soft and hard thermal insulation sheets, household and automobile door and window handles, car dash boards, car dash boards knobs, bumpers, CV joint boots, suspension bushings, window & door trim, seals, floor Mats, gear Knobs, flexible grip, mirror case, automotive gaskets, colored interior components and many other body parts, house hold plastic furniture, coat hangers, lacquer ,Toys, plastic eye wear, asphalt modification, personnel hygiene equipment such as razors, shavers, safety equipment, casings for lead acid batteries, document lamination films, packing foam, blister packs of medicines, workshop helmets, lenses for cameras, projectors, and copiers, soft contact lenses for eyesight, vials, monitors, medical devices such as IV sets, blood bags seal, urine bags seal, welding cable insulation, high voltage automobile cable insulation, coil forms and bobbins for transformers, motor parts, aerospace electrical parts, flame retardant insulations for cables and housing for composite high voltage outdoor insulators, substation and transformer

bushings, over molded products, and encapsulation of coils and microelectronic chips, and so on.[32-33]

## Chapter I

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### References

- [1] **Jean-Pierre Pascault, Henri Benoit, and Robert J. J.**"Polyvinyl Chloride: Environmental Aspects and Sustainability" Williams **2002**.
- [2] **R.H. Burgess** (Ed.), *Manufacture and Processing of PVC*, Taylor & Francis, **1991**.
- [3] **L.I. Nass**, *Encyclopedia of PVC*, second ed., vols . 1e4, CRC Press , **1986**.
- [4] **C.E. Wilkes, J.W. Summers, C.A. Daniels** (Eds.), *PVC Handbook*, Hanser Gardner Publications, Inc., Cincinnati, **2005**.
- [5] **Titow, W. V.** *PVC Technology Fourth Edition*. William Andrew Publishing, **1984**.
- [6] **J. O. Osuala**, "The Properties and Applications of PVC" , in *PVC Technology*, edited by S. K. De (John Wiley & Sons, **2013**),pp.70-82.
- [7] **Robert O. Ebeuele** .*Polymer Science and Technology*, CRC Press LLC,**2000**
- [8] **J. O. Osuala**,"Drawbacks and Limitations of PVC", in *PVC Technology*, edited by S. K. De (John Wiley & Sons, **2013**), pp.33-56.
- [9] **K.J Saunders Chapman&Hall**, *Organic polymer chemistry* ,London&new York ,**1988**
- [10] **J.W.Nicholson** *The chemistry of polymer* ,Royal Society of Chemistry Paperbacks,**1991**
- [11] **John Ensley, W.H.**, *Freeman Spektrum, The Consumer's Good Chemical Guide*, Oxford&New York,**1994**.
- [12] **G. AKOVALI**, "Plastic materials: polyvinyl chloride (PVC)", Middle East Technical University (METU), Turkey. Woodhead Publishing Limited, **2012** pp28-32
- [13] **James G. Speight** - *Handbook of Industrial Hydrocarbon Processes*-Gulf Professional Publishing, **2019**.

## Chapter I

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- [14] "Styrene-butadiene rubber." Encyclopædia Britannica. Encyclopædia Britannica, Inc., n.d. Web. 09 Jul. 2021. <https://www.britannica.com/science/styrene-butadiene-rubber>
- [15] Martin-Martinez, J.M. Rubber base adhesives. In Handbook of Adhesion Technology (pp. 491-512). Springer, Cham, 2019
- [16] **R. P. Brown and A. J.** "Styrene-Butadiene Rubber: Its Chemistry and Properties" Sinskey ,2019.
- [17] Transparency Market Research. "Styrene Butadiene Rubber Market - Global Industry Analysis, Size, Share, Growth, Trends, and Forecast 2016 – 2024." Transparency Market Research, 2018, [www.transparencymarketresearch.com/styrene-butadiene-rubtmlber-market.h](http://www.transparencymarketresearch.com/styrene-butadiene-rubtmlber-market.h).
- [18] **R. J.Crowford.** Rubber Technology: Compounding and Testing for Performance. CRC press, 2017.
- [19] **C.A. MIDGLEY,***Handbook of Adhesives 227*, Van Nostrand Reinhold, New York, 1990
- [20] **Hacıoğlu, F.** Degradation of EPDM Via Gamma Irradation and Possible Use of EPDM in Radioactive Waste Management. M. Sc. Thesis, Middle East Technical University, 2010.
- [21] **Jiri George Drobny (editor)**, Handbook of thermoplastic elastomers, Series: Plastics Design Library, Publisher: William Andrew, Year: 2014.
- [22] **J. V. Dawkins and R. A. Pearson** ."Thermoplastic Elastomers: Structure and Properties", published in the Journal of Polymer Science: Polymer Physics Edition in 1984.
- [23] **Minnesota Rubber and QMR Plastics**, Plastic & thermoplastic elastomer materials, online technical report, section 5, 2003.
- [24] **Sadhan K. De and Jim R. White**, Rubber Technologist's Handbook, Rapra Technology Limited Shawbury, Shrewsbury, Shropshire, SY4 4NR, United Kingdom.2001.

## Chapter I

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- [25] **Drobny, J. G.** Handbook of Thermoplastic Elastomers; PDL handbook series; PDL (Plastics Design Library)/William Andrew Pub: Norwich, NY. **2007**.
- [26] **Lu, X., & Lee, L. J.** Thermoplastic elastomers: A comprehensive review on recent advances in materials, processing, and applications. *Polymer Reviews*, **2016**. 56(2), 317-352.
- [27] **N.R. Legge, G. Holden and H.E. Schroeder**, *Thermoplastic elastomers: a Comprehensive Review*, ed. (Carl Hanser Verlag, Munich, vol.80, **1987**), p. 574 .
- [28] **G. Holden, N.P. Lagga, R.P. Qurik and H.E. Schroeder**, *Thermoplastic elastomers, 2nd ed.*, ed. (Hanser&Hanser/ Gardener, Munich, **1996**).
- [29] **E.N. Kresge**, *J. Rubber World* ,217, (**1997**), 30.
- [30] **P. Dreyfuss, L.J. Fetters and D.R. Hansen** , *J. Rubber Chem. Technology* ,53, (**1980**) ,738.
- [31] **J.A. Brydson**. "Thermoplastic Elastomers" , in "Plastics Materials" (8th edition), **2012**.
- [32] **B.M. Walker and C.P. Rader**, *Handbook of thermoplastic elastomers. 2nd ed.*, ed. (Van Nostrand publishers, Reinhold, New York, **1988**).
- [33] **T. Hayashi**, *J. Toyoda Gosei Technical Review, Japan*, 38, (**1996**), 2.

# **CHAPTER II**

## **Thermodynamics of Polymer Blends**

## II.1 General Introduction

Polymer blends are materials formed by the mixing of two polymers or copolymers to make a new material having synergistic properties of each polymer [1-7]. Polymer blending is an interesting method to develop new material for specific applications since it is very cost effective and simple. By blending one can prepare a new material with combined properties of each component. It is a cost-effective method for the preparation of a new material with desired properties other than synthesizing a new one in the lab [1, 2, 4, 8-15]. Polymer blending has many advantages, which involves the following:

- Fabrication of new materials with desired properties.
- Development of new materials in a cost effective manner.
- Better processability of materials.
- Developing materials with combined properties of two or more polymers.
- Tuning of final properties by controlling the morphologies.
- Method of recycling of plastic waste.
- Enhances the product performance to meet the rising customer needs.
- Development of lightweight materials.
- Optimization of composition to suit the requirement.
- Enhances the properties of polymers such as strength, modulus, flame retardancy, and stress cracking resistance, etc.

Polymer blends have great importance in industrial and scientific area. The first polymer blend was prepared by Thomas Hancock and was a mixture of natural rubber with Gutta-percha [7]. Blending of polymers will yield a unique product with combined properties of the individual components. Generally polymer blends can be defined as a physical mixture of two or more structurally different polymers with no covalent bond between them. The expected interactions are only the Vander-Waals forces, dipole interactions, or hydrogen bonding between the components and are useful in making a final product with various property combinations.

Blending can be considered as a cost effective method for the preparation of a material with specific properties required for the applications [4, 7, 12, 16-20].

## II.2 Thermodynamics of binary polymer blend systems

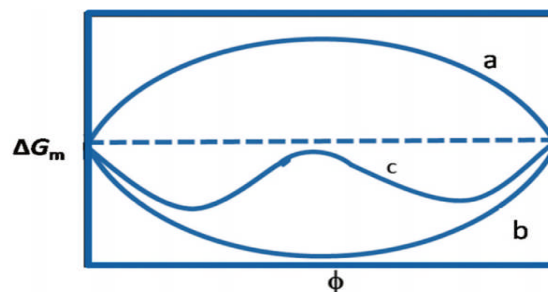
Polymer blend is prepared by mixing two or more polymers or co-polymers to obtain a new material with desired properties. Such blends may be homogeneous or heterogeneous in nature; otherwise it can be termed as miscible or immiscible respectively. Miscibility of polymer blends can be predicted using thermodynamic parameters through the Gibbs free energy of mixing,  $\Delta G_m$ . For miscibility of blends following inequality must be hold for

$$\Delta G_m = \Delta H_m - T\Delta S_m < 0 \quad (\text{II.1})$$

Where,  $\Delta G_m$  is the free energy of mixing per unit volume and  $\Delta H_m$  and  $\Delta S_m$  are enthalpy and entropy of mixing respectively.  $\Delta H_m$  is a measure of energy change. The entropy of mixing for macromolecules is generally very low because of the restricted number of possible molecular configurations and so the negligible entropy of mixing makes  $\Delta G_m$  become more positive due to the major contribution of the positive enthalpy of mixing. The sign of  $\Delta G_m$  depends on the value of the enthalpy of mixing,  $\Delta H_m$  and miscible blends can be formed if the entropic contribution exceeds the enthalpic contribution So, for the negative Gibbs free energy, there should be excellent intermolecular interactions between the components [17].

For miscibility, in addition to a negative value of  $\Delta G_m$ , the following inequality must also hold [18],

$$(\text{II.2}) \quad \left( \frac{\partial^2 \Delta G_m}{\partial \Phi_i^2} \right)_{T, p} > 0$$



**Figure II.1** Free energy of mixing for (a) completely immiscible, (b) completely miscible, and (c) partially miscible [4, 21].

Where  $\phi_i$  represents the volume fraction of component,  $T$  represents the fixed temperature and  $p$  represent fixed pressure.  $\Delta G_m$  for a binary mixture can vary with composition. The phase diagram is shown in **Figure II.1**.

In immiscible polymer blends, Gibbs free energy of mixing is positive and does not satisfy the above two equations, which represents the curve **(a)**. Curve **(b)** represents a miscible system which satisfies the above equation for miscibility and curve **(c)** represents a partially miscible blend system. If two polymers are mixed together, miscible polymer blends show single-phase morphology, immiscible blends show two-phase morphology, and in the case of partially miscible blends, they will show either two-phases or single phase morphology. The miscibility of polymer components depends on several other factors such as polarity of polymer components, composition, molecular weight, processing temperature, pressure, etc.[4].

Miscibility of polymer blends can be explained using a phase diagram shown in **Figure II.2**. There are three different regions and used to explain the degree of miscibility: Phase diagram explains the binodal and spinodal phase separation; spinodal curve and binodal curves are marked in the phase diagram. The position at which Eq. (1.3) satisfies represents the spinodal curve.

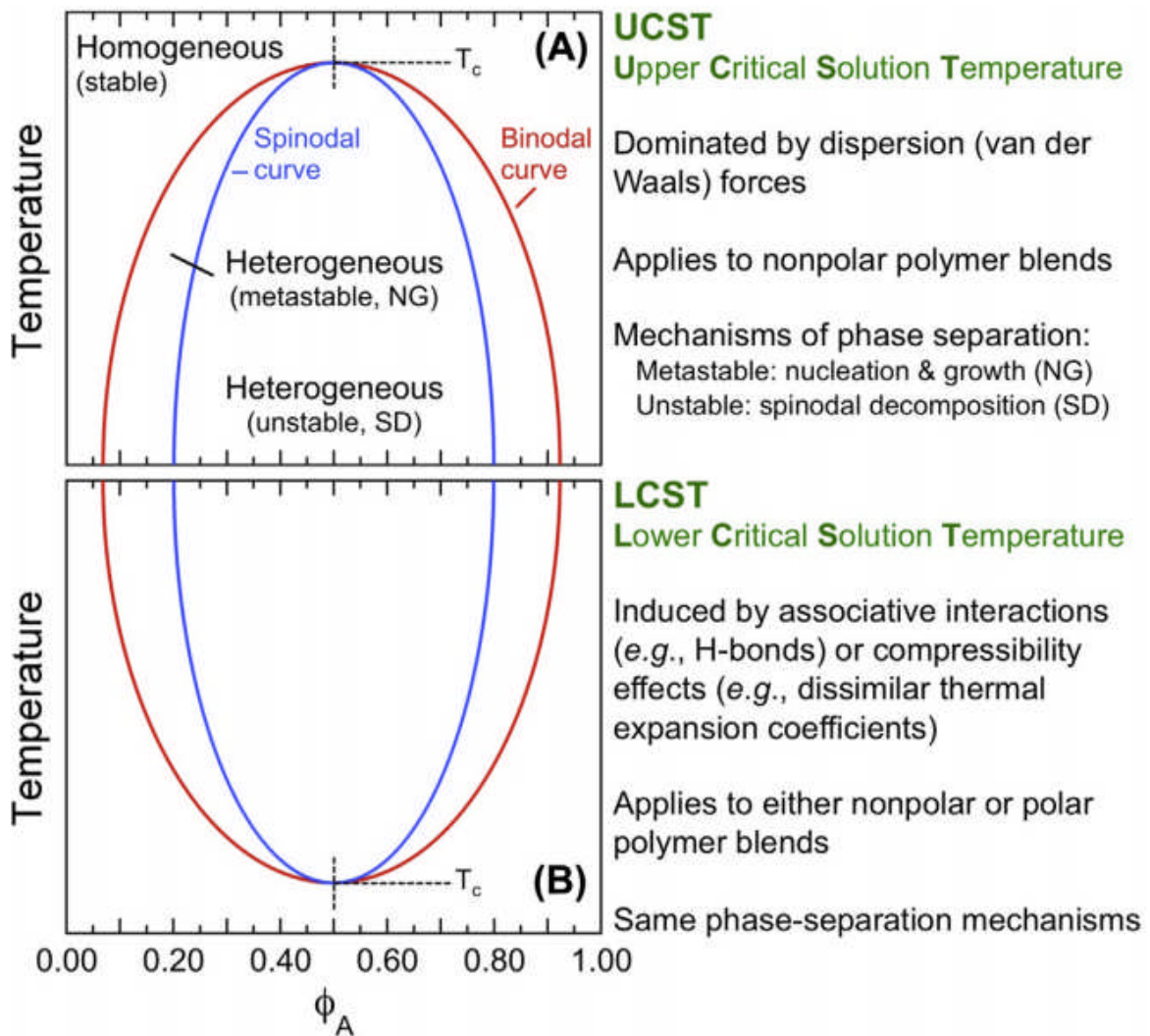
$$(II.3) \quad \text{Spinodal: } \left( \frac{\partial^2 \Delta G_m}{\partial \phi^2} \right)_{P,T} = 0$$

The equilibrium phase boundary between homogeneous and heterogeneous phase (phase separated phase) region represents the binodal curve.

Position of binodal curve can be expressed in terms of chemical potentials ( $\mu$ ) of each polymer components in the binary system.

$$(II.4) \quad \Delta\mu_1^a = \Delta\mu_1^b \quad \Delta\mu_2^a = \Delta\mu_2^b$$

Where 1 and 2 stand for the polymer components and **a, b** denote the phases.



**Figure II.2** Phase diagram showing the performance of polymer blends [18].

The double tangent to the free energy of mixing gives the values of binodal curve. Also at a critical point binodal and spinodal curve intersects and it can be estimated using the equation given below.

$$(II.5) \quad \text{Critical point : } \left( \frac{\partial^2 \Delta G_m}{\partial \phi^2} \right)_{P,T} = \left( \frac{\partial^3 \Delta G_m}{\partial \phi^3} \right)_{P,T} = 0$$

With the help of a phase diagram, degree of miscibility can be explained using spinodals and binodals. Three different regions in the phase diagram can be observed, that is between the two binodals there is single-phase or miscible region (highly miscible system has single phase); between binodals and spinodals there is metastable region: and phase separated or

immiscible region bordered by spinodal curves. Low-molecular-weight substances show two critical points, but in the case of high-molecular-weight substances it can show either lower critical solution temperature (LCST) or upper critical solution temperature (UCST). Polymer blends normally show LCST [18, 22-24].

Flory-Huggins lattice theory is the preliminary one used to explain polymer solutions and blends and is basically an extended concept of normal solutions. According to Flory-Huggins, for binary systems, expression for free energy of mixing can be written as,

$$(II.6) \quad \Delta G_m = RT \left[ \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 + \chi \phi_1 \phi_2 \right]$$

Here  $R$  is the universal gas constant and  $T$  is the absolute temperature.  $\phi_1$  and  $\phi_2$  are the volume fraction of the component 1 and 2, " $r$ " represents the number of polymer segments (proportional to the degree of polymerization) and  $\chi$  is the Flory-Huggins interaction parameter [3, 17, 25, 26].

In the above equation the first two terms are related to the entropy of mixing as,

$$(II.7) \quad \Delta S_m = -R \left[ \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 \right]$$

While the third term represents the enthalpy of mixing, i.e.,

$$(II.8) \quad \Delta H_m = RT \chi \phi_1 \phi_2$$

It is well known that entropy contribution is very small for the infinite molar masses. Hence the miscibility or immiscibility of the system mainly depends on the value of the enthalpy of mixing. If the parameter  $\chi$  is negative, miscibility can be observed for the system ( $\Delta H_m < 0$ ). Miscibility of the system occurs at  $\chi < \chi_{cr}$  where  $\chi_{cr}$  is  $\chi$  parameter at the critical point (function of the molar masses) and it can be expressed as

$$(II.9) \quad \chi_{cr} = \frac{1}{2} \left( \frac{1}{\sqrt{r_1}} + \frac{1}{\sqrt{r_2}} \right)^2$$

### II.3 Classification of polymer blends

Polymer blends are of different types and have different properties. They can be classified into different types on considering the number of phases/morphology, constituents, miscibility, and method of preparation.

#### II.3.1 Classification based on constituents

Based on the constituents, blends can be categorized as rubber/rubber blends, rubber/plastic, and plastic/plastic blends, some examples are listed below in **Table II.1**.

**Table II.1** Examples of polymer blends which are classified based on the constituents.

Plastic/Plastic	Plastic/Rubber	Rubber/Rubber
Polycarbonate/polyethylene(PC/PE) [27]	Natural rubber/high density Polyethylene (NR/HDPE) [28]	Ethylene-propylenediene monomer/butadiene rubber (EPDM/BR) blends [29]
PE/polystyrene (PS) [30]	PE/EPDM[31]	Nitrile-butadiene rubber (NBR)/EPDM [32]
PC/polypropylene (PP) [33]	EPDM/poly vinyl chloride (PVC)[34]	EPDM/ethylenepropylene rubber (EPR)[35]
PP/poly(trimethyleneterephthalate) (PTT) [36]	PVC/NBR[37]	Styrene-butadiene rubber (SBR)/NR [38]
PE/PTT[39]	HDPE/EPDM[40]	NBR/SBR[41]
PP/PE[42]	NR/PP[43]	NR/NBR (nitrile rubber) [44]
Poly (ethylene terephthalate)(PET)/(PP) [45]	Brominated butyl rubber (BIIR)/(EPDM) [46]	EPDM/nitrile-butadiene rubber (NBR) [47]
PS/PP[48]	EPDM/PP[49]	EPDM/NR[50]
Polyamide 6 (PA6)/poly (butylene terephthalate) (PBT) [51]	SBR/PVC[52]	EPDM/epoxidized natural rubber (ENR) [53]
PE/polyethylene oxide blends [54]	NBR/HDPE[55]	EPDM/SBR[56]

### II.3.2 Classification based on the miscibility

According to miscibility polymer blends can be classified into three, which are miscible blends, compatible blends, and immiscible blends.

#### II.3.2.1 Miscible polymer blends

Miscible polymer blends require strong interpolymer interactions, preferably specific interactions such as hydrogen bonding or dipole-dipole forces. The forces must bring the polymers together and overcome the combinatorial entropy that increases with molar mass and the many conformations available to each polymer in the blend. Polymer conformations are restricted compared with small molecules because of the linking of small molecules, the repeat units, in a polymer chain.

Miscible blends exhibit homogeneous morphology with only one glass transition temperature ( $T_g$ ), and is in between the  $T_g$ s of both blend components. In the case of miscible blends,  $\Delta H_m < 0$  due to specific interactions and homogeneity is observed at least on a nanometer scale [5].

As already discussed, for complete miscibility, blend system must satisfy the conditions given as **Eqs. (II.1) and (II.2)**. So it is clear that miscible blends are homogeneous in nature and are associated with a negative value of free energy of mixing. Development of miscible polymer blends depends on many factors which involves chemical nature of the polymers, polarity, viscosity ratio, surface tension, interfacial tension, and exothermic interactions such as dipole-dipole interactions, hydrogen bonding, dispersive forces, acid-base interactions, etc[57].

For example, polystyrene/poly (phenylene oxide) (PS/PPO) blends, poly (styrene-acrylonitrile)/poly (methyl methacrylate) (SAN/PMMA) blends [58].

Measurement of glass transition temperature ( $T_g$ ) can be considered as a general method to judge the miscibility of blends. As already discussed single  $T_g$  of blend represents a miscible blend and two  $T_g$  represents a phase separated blend system. The main experimental techniques which are generally used to measure  $T_g$  of components involve differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA)[59].

### II.3.2.2 Compatible blends

These blends can be referred to as compatible blends since they exhibit fine-phase morphology and better properties. In the case of partially miscible blends, one part of the blend component is dissolved in the other[60].

Both blend phases are homogeneous and have their own  $T_g$  and both the  $T_g$ s are shifted from the values for the pure blend components toward the  $T_g$  of the other blend component. Polycarbonate (PC)/acrylonitrile butadiene-styrene blend is an example for partially miscible blend [61].

### II.3.2.3 Immiscible blends

Most of the polymer blends are immiscible in nature due to the negligible entropy of mixing. Polymers have a high degree of disorder, so the addition of a different polymer does not cause any significant change in entropy. Therefore, the mixing enthalpy has to be negative, to make a polymer spontaneously mix. Immiscible blends have heterogeneous morphology. If two polymers are mixed and are immiscible in nature, it shows two glass transition temperatures ( $T_g$ s) and melting temperatures ( $T_m$ s) corresponding to each polymeric component [5].

Immiscible blends possess sharp interphase and this indicates the absence of strong interactions between the two polymer components. Generally weak interactions like hydrogen bond and van der Waals attraction can be observed in immiscible blends. On the other hand, most of the useful products are made up of immiscible blends.

For example, poly (ethylene terephthalate)/poly (vinyl alcohol) (PET/PVA) blends, polybutadiene/PS blends, poly(propylene) (PP)/PS blends, PP/poly(ethylene) (PE) blends, PC/PP, poly(trimethylene terephthalate) (PTT)/PP [5,33,62].

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**References**

- [1] Blends P, Paul DR, Newman S. NY: Academic Press; **1978**; 2:391.
- [2] Brown SB. Reactive compatibilization of polymer blends. In: Polymer blends handbook. Springer; **2003**. p. 339-415.
- [3] Paul D, Barlow J. Polymer blends. J Macromol Sci Rev Macromol Chem **1980**;18(1):109-68.
- [4] Paul DR. Polymer blends. Elsevier; **2012**.
- [5] Thomas S, Grohens Y, Jyotishkumar P. Characterization of polymer blends: miscibility, morphology and interfaces. John Wiley & Sons; **2014**.
- [6] Utracki LA, Favis B. Polymer alloys and blends. New York: Marcel Dekker; **1989**.
- [7] Utracki LA, Wilkie CA. Polymer blends handbook. Springer; **2002**.
- [8] Bahrami R, Löbbling TI, Schmalz H, Müller AH, Altstädt V. Micromechanics of “raspberry” morphology in PPE/SAN polymer blends compatibilized with linear ABC triblock terpolymers. Polymer **2015**;80:52-63.
- [9] Chiu F-C. Poly (vinylidene fluoride)/polycarbonate blend-based nanocomposites with enhanced rigidityselective localization of carbon nanofillers and organoclay. Polym Test **2017**;62:115-23.
- [10] Otero-Navas I, Arjmand M, Sundararaj U. Carbon nanotube induced double percolation in polymer blends: morphology, rheology and broadband dielectric properties. Polymer **2017**; 114:122-34.

- [11] Wang H, Fu Z, Zhao X, Li Y, Li J. Reactive nanoparticles compatibilized immiscible polymer blends: synthesis of reactive SiO<sub>2</sub> with long poly (methyl methacrylate) chains and the in situ formation of janus SiO<sub>2</sub> nanoparticles anchored exclusively at the interface. ACS Appl Mater Interfaces **2017**;9(16):14358-70.
- [12] Utracki L. Economics of polymer blends. Polym Eng Sci **1982**;22(17):1166-75.
- [13] Roman C, García-Morales M, Gupta J, McNally T. On the phase affinity of multi-walled carbon nanotubes in PMMA: LDPE immiscible polymer blends. Polymer **2017**;118:1-11.
- [14] Jiao Q, Shen J, Ye L, Li Y, Chen H. Poly (oxymethylene)/poly (butylene succinate) blends: Miscibility, crystallization behaviors and mechanical properties. Polymer **2019**;167:40-7.
- [15] Métivier T, Cassagnau P. Compatibilization of silicone/fluorosilicone blends by dynamic crosslinking and fumed silica addition. Polymer **2018**;147:20-9.
- [16] Yu L, Dean K, Li L. Polymer blends and composites from renewable resources. Prog Polym Sci **2006**;31(6):576-602.
- [17] Paul D, Barlow J. A binary interaction model for miscibility of copolymers in blends. Polymer **1984**;25(4):487-94.
- [18] Robeson LM. Polymer blends. Compr Rev **2007**. ISBN-10: 3-446-22569-2 ISBN-13: 978-3-446-22569-5.
- [19] Utracki LA. Compatibilization of polymer blends. Can J Chem Eng **2002**;80(6):1008-16.

- [20] Rostami A, Masoomi M, Fayazi MJ, Vahdati M. Role of multiwalled carbon nanotubes (MWCNTs) on rheological, thermal and electrical properties of PC/ABS blend. *RSC Adv* **2015**;5(41):32880-90.
- [21] Polásková M. Polymer blends with microfibrillar-phase morphology. **2006**.
- [22] Li S, Feng L, Lu H, Feng S. From LCST to UCST: the phase separation behaviour of thermo-responsive polysiloxanes with the solubility parameters of solvents. *New J Chem* **2017**;41(5):1997-2003.
- [23] Yao W, Wang H, Cui G, Li Z, Wang J. Tuning phase behaviour of PEG functionalized ionic liquids from UCST to LCST in alcohol/water mixtures. *Phys Chem Phys* **2016**;18(42):29192-8
- [24] Kuila A, Maity N, Chatterjee DP, Nandi AK. Phase behavior of Poly (vinylidene fluoride)-graft-poly (diethylene glycol methyl ether methacrylate) in alcohol/water system: coexistence of LCST and UCST. *J Phys Chem B* **2016**;120(9):2557-68.
- [25] Ten Brinke G, Karasz FE. Lower critical solution temperature behavior in polymer blends: compressibility and directional-specific interactions. *Macromolecules* **1984**;17(4):815-20.
- [26] Tambasco M, Lipson J, Higgins JS. Blend miscibility and the Flory-Huggins interaction parameter: a critical examination. *Macromolecules* **2006**;39(14):4860-8.
- [27] Wippler C. Dynamic mechanical properties of VAMAS polycarbonate/polyethylene blends. *Polym Eng Sci* **1990**;30(17):1106-13.
- [28] Laokijcharoen P, Coran A. The evolution of morphology in NR/HDPE blends. Part I. Microscopy for unvulcanized blends. *Rubber Chem Technol* **1998**;71(5):966-74.

- [29] Go JH, Ha CS. Rheology and properties of EPDM/BR blends with or without a homogenizing agent or a coupling agent. *J Appl Polym Sci* **1996**;62(3):509-21.
- [30] Brahim B, Ait-Kadi A, Ajji A, Fayt R. Effect of diblock copolymers on dynamic mechanical properties of polyethylene/polystyrene blends. *J Polym Sci B Polym Phys* **1991**;29(8):945-61.
- [31] Ghosh P, Chattopadhyay B, Sen AK. Thermal and oxidative degradation of PEEPDM blends vulcanized differently using sulfur accelerator systems. *Eur Polym J* **1996**;32(8):1015-21.
- [32] Oliveira MG, Soares BG. The effect of the vulcanizing system on cure and mechanical properties of NBR/EPDM blends. *Polym Polym Compos* **2001**;9(7):459-68.
- [33] Arif PM, Sarathchandran C, Narayanan A, Saiter A, Terzano R, Allegretta I, et al. Multi-walled carbon nanotube promotes crystallisation while preserving co-continuous phase morphology of polycarbonate/polypropylene blend. *Polym Test* **2017**;64:1-11.
- [34] Stelescu MD. Physico-mechanical characteristics of some EPDM/plasticized PVC blends. *Macromol Symp* **2008**:70-7. Wiley Online Library.
- [35] Zaharescu T, Mihalcea I. Behaviour of ethylene-propylene elastomers in salt solutions: I. SEM investigation of gamma irradiation effects. *Polym DegradStabil* **1995**;50(1):39-43.
- [36] Ajitha A, Aswathi M, Geethamma VG, Kalarikkal N, Thomas S, Volova TG. An effective EMI shielding material based on poly (trimethylene terephthalate) blend nanocomposites with multiwalled carbon nanotubes. *New Journal of Chemistry* **2018**;42(16):13915-26.
- [37] Li J-X, Chan C-M. Effect of the size of the dispersed NBR phase in PVC/NBR blends on the stability of PVC to electron irradiation. *Polymer* **2001**;42(16):6833-9.

- [38] Le HH, Parsekar M, Ilisch S, Henning S, Das A, Stöckelhuber KW, et al. Effect of non-rubber components of NR on the carbon nanotube (CNT) localization in SBR/ NR blends. *Macromol Mater Eng* **2014**;299(5):569-82.
- [39] Kunjappan AM, Ramachandran AA, Padmanabhan M, Mathew LP, Thomas S. Selective localization of MWCNT in poly (trimethylene terephthalate)/poly ethylene blends: theoretical analysis, morphology, and mechanical properties. *Macromol Symp* **2018**:1800104. Wiley Online Library.
- [40] Chandra R, Mishra S, Parida T. Studies on dynamic behaviour and flow properties of HDPE/EPDM blends by torque rheometer. *Polym Int* **1995**;37(2):141-7.
- [41] Essawy HA, Tawfik ME, El-Sabbagh SH. Rubber nanocomposites based on compatibilized NBR/SBR blends using a series of amphiphilic montmorillonites. *J Elastomers Plast* **2014**;46(2):113-31
- [42] Fel E, Khrouz L, Massardier V, Cassagnau P, Bonneviot L. Comparative study of gamma-irradiated PP and PE polyolefins part 2: properties of PP/PE blends obtained by reactive processing with radicals obtained by high shear or gamma-irradiation. *Polymer* **2016**;82:217-27.
- [43] Nair ST, Vijayan PP, Xavier P, Bose S, George SC, Thomas S. Selective localization of multi walled carbon nanotubes in polypropylene/natural rubber blends to reduce the percolation threshold. *Compos Sci Technol* **2015**;116:9-17.

- [44] Maria HJ, Lyczko N, Nzihou A, Joseph K, Mathew C, Thomas S. Stress relaxation behavior of organically modified montmorillonite filled natural rubber/nitrile rubber nanocomposites. *Appl Clay Sci* **2014**;87:120-8.
- [45] Friedrich K, Evstatiev M, Fakirov S, Evstatiev O, Ishii M, Harrass M. Microfibrillar reinforced composites from PET/PP blends: processing, morphology and mechanical properties. *Compos Sci Technol* **2005**;65(1):107-16.
- [46] Wang J, Pan S, Zhang Y, Guo S. Crosslink network evolution of BIIR/EPDM blends during peroxide vulcanization. *Polym Test* **2017**;59:253-61.
- [47] Ding X, Wang J, Zhang S, Wang J, Li S. Composites based on CB/CF/Ag filled EPDM/NBR rubber blends with high conductivity. *J Appl Polym Sci* **2015**;132(4).
- [48] Ray SS, Pouliot S, Bousmina M, Utracki LA. Role of organically modified layered silicate as an active interfacial modifier in immiscible polystyrene/polypropylene blends. *Polymer* **2004**;45(25):8403-13.
- [49] Uthaipan N, Jarnthong M, Peng Z, Junhasavasdikul B, Nakason C, Thitithammawong A. Effects of crosslinked elastomer particles on heterogeneous nucleation of isotactic PP in dynamically vulcanized EPDM/PP and EOC/PP blends. *J Polym Res* **2017**;24(8):118.
- [50] Gögelein C, Beelen HJH, van Duin M. Morphological explanation of high tear resistance of EPDM/NR rubber blends. *Soft Matter* **2017**;13(23):4241-51.
- [51] Li H, Wang J, Li G, Lu Y, Wang N, Zhang Q, et al. Preparation of core-shell structured particle and its application in toughening PA6/PBT blends. *Polym Adv Technol* **2017**;28(6):699-707.

- [52] Abd-El-Messieh S, Mansour S, El-Nashar D, Ikladios N. Evaluation of polyester resin as a new compatibilizer for SBR/PVC blends. *Can J Chem Eng* **2004**;82(2):358-70.
- [53] Setua D, Nando G. High-performance oil/fuel-resistant blends of ethylene propylene diene monomer (EPDM) and epoxidized natural rubber (ENR). In: *High performance polymers and their nanocomposites*; **2018**. p. 315-46.
- [54] Mural PKS, Madras G, Bose S. Positive temperature coefficient and structural relaxations in selectively localized MWNTs in PE/PEO blends. *RSC Adv* **2014**;4(10):4943-54.
- [55] Ahmed K. Stress-strain and diffusion behavior of industrial waste-filled acrylonitrile-butadiene rubber/high density polyethylene blends. *Chem Lett* **2014**;43(5):690-2.
- [56] El-Nashar D. The compatibilization of EPDM/SBR blends by EPDM-graft-styrene copolymer. *Polym Plast Technol Eng* **2005**;43(5):1425-41.
- [57] Lu X, Weiss R. Relationship between the glass transition temperature and the interaction parameter of miscible binary polymer blends. *Macromolecules* **1992**;25(12):3242-6.
- [58] Brostow W, Chiu R, Kalogeras IM, Vassilikou-Dova A. Prediction of glass transition temperatures: binary blends and copolymers. *Mater Lett* **2008**;62(17e18):3152-5.
- [59] An L, He D, Jing J, Wang Z, Yu D, Jiang B, et al. Effects of molecular weight and interaction parameter on the glass transition temperature of polystyrene mixtures and its blends with polystyrene/poly (2, 6-dimethyl-p-phenylene oxide). *Eur Polym J* **1997**;33(9):1523-8.
- [60] Kalogeras IM, Brostow W. Glass transition temperatures in binary polymer blends. *J Polym Sci B Polym Phys* **2009**;47(1):80-95.

- [61] Tjong S, Meng Y. Effect of reactive compatibilizers on the mechanical properties of polycarbonate/poly (acrylonitrile-butadiene-styrene) blends. *Eur Polym J* **2000**;36(1):123-9.
- [62] Mathew L, Saha P, Kalarikkal N, Thomas S, Strankowski M. Tuning of microstructure in engineered poly (trimethylene terephthalate) based blends with nano inclusion as multifunctional additive. *Polym Test* **2018**;68:395-404.

**CHAPTER III**

**Compatibilization of  
Polymer Blends**

### III.1 General introduction

Blending is an excellent and economic way to enhance the properties of product material. But the blends of polymers usually have coarse phase morphology and poor interfacial adhesion between the blend phases. This may be so, as most polymers are immiscible. When the viscoelastic behavior of polymer blends is observed, the melt viscosity of immiscible polymer blends are found to depend on the interfacial interactions and phase morphology. Hence compatibilization by addition of an interfacial agent is needed to attain synergistic effect for making it most useful. There are several methods for the compatibilization of polymer blends, but the principle of all techniques is the homogenization of mixture of the polymer by adding a compatibilizing agent.

Compatibilizers are macromolecular in nature and bring interfacial activities in heterogeneous polymer blends. The compatibilizer, which can be added directly to the immiscible polymer blend and generated in situ during the blending process, usually has one part miscible with one polymer and the other part miscible with the second polymer. The compatibilizers mainly retard the formation of the Rayleigh disturbances, on the generated threads of polymer 1, which results in decreased interfacial tension. The lower interfacial tension stretches the threads longer, making their diameter also smaller. The smaller size of the generated droplets of polymer 1 helps to bring the average particle size to submicron level. The compatibilizer also prevents the coalescence at the surface of the generated phase. Compatibilizers can thus generate and stabilize finer blend morphology. Several strategies are reported for the compatibilization of polymer blends [1-7].

### III.2 Strategies for compatibilization of polymer blends

Polymer blends can be compatibilized by different methods. Industrial suitability of compatibilization techniques depends on several factors, such as cost, final performance, recyclability, and possible biodegradability.

Some of the general strategies involve the following:

- Adding previously made grafted block copolymers.
- Adding reactive polymers (advantage is the short processing time of a minute or even less).
- Addition of low-molecular-weight chemicals like peroxide activators in inert polyolefins, resulting in the formation of branched copolymers, a functional chemical that forms block

copolymers or a mixture of a peroxide and a functional chemical, all of which leads to the formation of branch/graft copolymers: Lack of chemical selectivity is the problem in this approach although this compatibilization method is quite simple.

➤ Another method used is that of interchange reactions. Here two or more poly-condensates are blended together, resulting in interchange reactions. The type of polymers, nature and concentration of the reactive groups, blending temperature, moisture content, concentration of interchange catalyst, and reaction time will influence this method.

➤ Mechanical mixing is one industrially viable method and requires no chemicals for compatibilization. i.e., no additional polymers or chemicals are added. In this method the polymers are melt processed in kneaders or extruders under high shear forces. Mechano-degradation is advantageous for specific polymer blends.

➤ Addition of selective crosslinking agents is yet another method. This method of specific interactions compatibilization is done by introducing suitable functional groups which can chemically modify the blend components, like a third polymeric or low-molecular-weight material.

Another important strategy for compatibilization of immiscible blends involves the usage of nanofillers. The various chapters in the book discuss the compatibilization of polymer blends by graft copolymers, random copolymers, micro and nanofillers, coupling agents, Janus particles and shear pulverization in a detailed manner. [8]

### III.3 Why do we need compatibilizers?

Even though polymer blends are the combinations of polymers having good properties; its applications are limited due to the immiscibility of most of the polymer blends. Majority of polymer blends are immiscible in nature due to the negligible entropy of mixing, high molar mass, difference in polarity of polymer components, viscosity ratio between components, etc.

The high interfacial tension between the polymer components will offer poor interfacial adhesion between the components and hence shows poor properties inferior to that of individual polymer components. Thus it can be said that un-stabilized morphology, phase separation, poor interfacial adhesion between the polymeric components of immiscible polymer blend will lead to the poor physic-mechanical properties. So, it is necessary to find out

a solution to overcome the disadvantages of immiscible blends, thereby we can enhance the applications of blends into more fields.

Properties of a heterogeneous blend depend mainly on the compatibility between the polymer components. The interface between the phases in a polymer blend system can be characterized by the interfacial tension, which when approaching zero the blend becomes miscible. That is, if there are strong interactions between the polymer components, then the polymer blend will be miscible in nature. Large interfacial tension leads to phase separation and the phase separated particles possibly undergoing coalescence; this will result in large particle size for the dispersed domains. The large interfacial tension between polymer components in polymer blends can be reduced by the addition of interfacial agents known as compatibilizers; these are generally molecules that can be aligned along the interfaces between the two polymer phases, reducing the interfacial tension and thereby increasing the compatibility of the polymer blends.

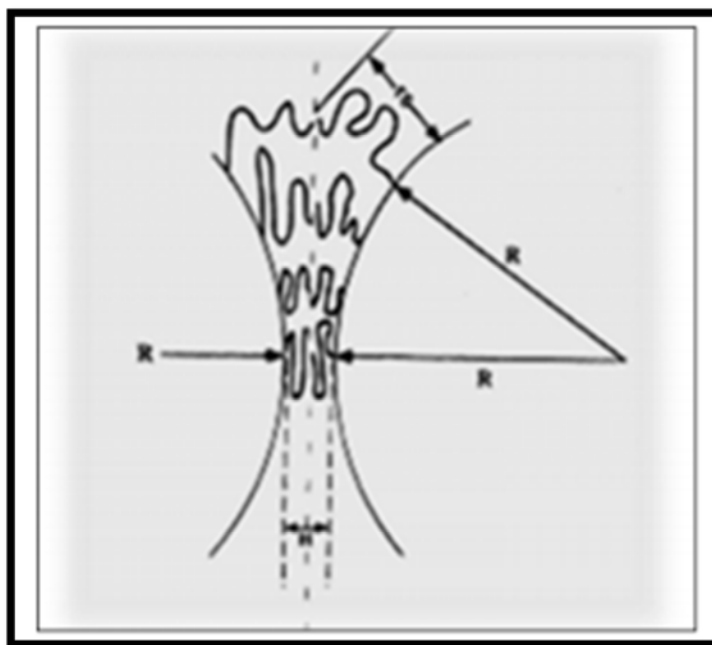
Compatibilizers play a key role to improve the interfacial adhesion between the components and to reduce the interfacial tension between the components. They exhibit interfacial activities in heterogeneous polymer blends. The interfacial activities of compatibilizers help to stabilize the morphology by enhancing interfacial adhesion. Compatibilizers resist the coalescence of dispersed phases, thereby reducing the interfacial tension and the size of the dispersed domains which results in an increase of adhesion at the interface and improved properties of the final product. Commonly used compatibilizers are block, graft, or random copolymers consisting of dissimilar blocks [9,10].

The high interfacial tension between the polymer components will offer poor interfacial adhesion between the components, thereby polymer blends become immiscible in nature and show poor properties inferior to that of individual polymer components. Thus compatibilizers can be helpful for the conversion of immiscible polymer blends into useful polymeric products with improved properties. By adding compatibilizers into immiscible polymer blends one can increase the application of immiscible blends in an industrial level. The overall action of compatibilizers involves the improvement in the compatibility between the components by enhancing the interaction between the components, reducing the interfacial tension between the components, improving the interfacial adhesion between the components, etc. and the compatibilizing action of compatibilizers is similar to that of an emulsifier [11-13].

#### III.4 Theoretical aspects of compatibilisation

A good compatibilizer should migrate to the interface and reduce the interfacial tension coefficient, decreasing the dispersed phase dimensions, thereby stabilizing the blend morphology and enhancing the adhesion between phases in the solid-state. Compatibilizing agents often provide additional morphology stabilization by acting as a surfactant and decreasing the interfacial surface tension. In general, the added compatibilizers, if compatible with both phases, segregate preferentially at the interface and ensure strong interfacial adhesion [14, 15]

A successfully compatibilized blend of moderate composition (up to 30 wt% minority component) exhibits spherical dispersed phases with consistent diameters, averaging on the micron and submicron scale. Such consistent morphologies can be achieved when the compatibilizing agent provides a steric hindrance to the dispersed phase coalescence. Compatibilizers which provide steric hindrances act as anchors for minority phase droplets in the matrix, (Figure 3.1) and also serve as repulsive “springs” when two droplets are in proximity.



**Figure III.1** Steric hinderence by compatibilizers. Compatibilizers acting as both anchors and repulsive springs ensuring the stability and prevention to coalescence[16].

From a commercial point of view, it can say that compatibilization is the method of converting a multiphase polymer mixture into a commercially useful product. In principle, a molecule can act as a compatibilizer if it has a segment that is miscible in one phase and another segment

that is miscible in the other phase. And this will lead to the positioning of the compatibilizer across the interface.

So a good compatibilizer will

- Reduce interfacial tension between components,
- Permit finer dispersion during mixing,
- Provide a measure of stability against gross separation,
- Produce ultimate product, and
- Results in improved interfacial adhesion.

### **III.5 Blending with a compatibilizer, a third component**

#### **III.5.1 Compatibilizer immiscible in both blended polymers**

When two polymers are to be blended, but they are incompatible, then a third component or additive can be added to make the blend compatible. The compatibilizer will form at surfaces or provide an interphase. A compatibilizer is analogous to a surfactant. A surfactant can emulsify or compatibilize oil and water dispersions by stabilizing interfaces in the micellar mechanism. Compatibilizers function in the same way; they can, however, form an interphase containing some of each component. A compatibilizer can be a small molecule or a polymer. If the compatibilizer is immiscible, but compatible with both polymers of a blend, then it will tend to reside at the interface. An inclusion of filler particles, particularly nanoparticles with their large surface area to volume ratio, can be a compatibilizer between two blended polymers [17].

Nanoparticles that interact with both polymers of an incompatible blend tend to align at the blend interface to minimize surface energy. This organization of nanoparticles along an interface can be used to create nanoparticles alignment and emphasizes the properties contributed by the nanoparticles. Graphene has been oriented in blends to enhance conductivity by providing continuous pathways along the graphene even when the graphene is at low concentration; the percolation threshold is lowered. PLA and poly-caprolactone blends have been prepared with graphene trapped at the interface to obtain massive enhancement of thermal conductivity at volume fraction of graphene as low as 0.53% [18]. PP blends

with poly(ethylene terephthalate) (PET) have been prepared with graphene mostly in the PET phase of the co-continuous or double percolated blend that exhibited increased electrical conductivity and electromotive force shielding in the GHz frequency range [19].

### III.5.2 Compatibilizer mutually miscible

When the compatibilizer is mutually miscible with both blended polymers then it can form an interphase. The interphase is a region of finite thickness between the two blended polymers. The interphase is a composition or structure gradient between the two blended polymers and it may provide a functional mechanical gradient to the properties. An example is a blend of PVC with a poly(alkyl acrylate) where a plasticizer such as di-octyl phthalate has been added; this ester will be miscible in both phases and function as a plasticizer for the PVC. The poly(alkyl acrylate) may also be plasticized by the ester, but regardless it can be a toughening agent for PVC. Toughening is performed by a separate phase of a deformable polymer, not a miscible phase that gives plasticization that decreases the modulus and strength overall. PVC has been shown to be miscible with some ester and ether repeat unit polymers, such as poly(methyl methacrylate) and poly(oxyethylene) due to donor-acceptor interactions between chlorines and ester or ether oxygens [20]. Plasticizers such as dioctyl phthalate or poly(ethylene adipate), are miscible with the host PVC and also with blended polymers used for toughening PVC, such as poly(alkyl acrylate)s or poly(alkyl methacrylate).

### III.5.3 Compatibilizer miscible with one of the blended polymers

If there is miscibility with one of the blended polymers, then the compatibilizer can provide a secondary modification as a plasticizer for instance.

Since the blended polymers are incompatible, the compatibilizer can migrate from the polymer within which it is miscible to the interface. The driving force for this migration will be to reduce the interfacial energy, which will occur when the compatibilizer develops at least a monolayer at the interface. In each situation where the interfacial energy is minimized, there is opportunity for dispersed particle size reduction, which involves creation of a greater interfacial area. A greater interfacial area is thermodynamically stable when the interfacial energy is minimized.

### III.6 Role of compatibilizers in blending processes

Compatibilizers are macromolecular species exhibiting interfacial activities in heterogeneous polymer blends. Usually the chains of a compatibilizer have a blocky structure, with one constitutive block miscible with one blend component and a second block miscible with the other blend component. These blocky structures can be pre-made and added to the immiscible polymer blend, but they can also be generated in-situ during the blending process. The latter procedure is called reactive compatibilization, and mutual reactivity of both blend components is required.

The role of compatibilizers in the blending process is firstly to retard the formation of the Rayleigh disturbances on the generated threads of polymer, as the result of a decreased interfacial tension.

The lower the interfacial tension, the longer the deformation tension exceeds the interfacial tension, the longer the stretching of the thread will proceed, the smaller the diameter of the resulting thread will become, and, consequently, the smaller the size of the generated droplets of polymer will be. Usually, an average particle size in the sub-micron range can be achieved. In addition, the presence of compatibilizer molecules at the surface of the small generated particles prevents coalescence from occurring during subsequent processing. Compatibilizers are thus able to generate and to stabilize a finer morphology.

Finally, provided that each block of a poly(A-b-B) compatibilizer penetrates the parent phase (A and B, respectively) deeply enough to be entangled with the constitutive chains, the interfacial adhesion is enhanced. Good interfacial adhesion is essential for stress transfer from one phase to the other one to be efficient and for cracks initiated at the interface to be prevented from growth until catastrophic failure occurs. Refinement and stabilization of the phase morphology and the enhancement of the interfacial adhesion usually upgrade an inferior and useless immiscible polymer blend to an interesting material.[21]

### III.7 Properties of polymer blends influenced by compatibilization

Most polymer systems are thermodynamically immiscible. The enthalpy of mixture of molten polymer mixtures takes a positive value, much more than the negligible amount of entropy, which is the characteristic of macromolecules. Correspondingly, high interfacial tension among dispersed and matrix components in a polymer blend leads to immiscibility[22]. The use of a compatibilizer strengthens the interfacial adhesion between blend components. Commercially available compatibilizers are block or graft copolymers that can be added to a polymer blend prior to or during the mixing process. In general, the presence of compatibilizer

promotes miscibility through the interfacial adhesion improvement, which is responsible for change in mechanical, rheological, thermal, and morphological characteristics of polymer blends [23-27]. Addition of compatibilizer to a polymer blend allows for interfacial tension reduction, while above a critical concentration it may cause interfacial saturation [28]. Therefore, there were attempts to explain structure-property interrelation in binary [29] and ternary [30] polymer blends in terms of interfacial phenomena.

### III.8 New challenges in compatibilized blends

When we think about the polymer blends, ease of handling, new mixing technologies, stability of blend morphology, suitability for advanced applications, and recycling are the major concerns. Compatibilization opens new windows to polymer technology and applications. Two polymers having good intrinsic properties, but are immiscible and incompatible or nonreactive can be utilized by converting them to blends using compatibilizers. As mentioned in the above sections, thermodynamic miscibility parameters play an inevitable role in compatibilization. It is demanding to select most favorite pair of polymers and ease to handle compatibilizing agents. Conventionally single compatibilizing agents have been utilized, but a mixture of more than one or a hybrid compatibilizer can be an interesting in this field. Interestingly nano-hybrids are creating a trend nowadays. New types of homogeneous compatibilizing agents will enhance the scope of the study. The interface modifiers which are added to the blend system may get inserted into the interface region and get broken down to extremely small size. This type of breaking up leads to the development of nano-structured morphology in the blends. Generally compatibilizers are selected depending on the polymer mixture and compatibilization is somewhat a selective process. Not all the compatibilizing agents are suitable for all blend systems.

All-in-one compatibilizing agents are still a mirage in polymer research. A compatibilizing agent that suits different pairs of polymers is a challenge in development. It is most of the times the localization of the compatibilizing agent in a binary or ternary blend system is unpredictable. Tuning the localization to a particular phase is another challenge. Development of compatibilizers that can be recycled and reused is a necessary situation. Exploring new materials, technology, methods, and characterization in blending invites the researchers to hit new horizons.

### III.9 Application of compatibilized polymer blends in biomedical fields

Life expectancy among people increases along technology progression level. The future ahead of such technological advances in various fields underlines the need for new and innovative tools in accordance to people's comfort. Health is the most important issue worldwide and scientists endeavor to enhance the level of people's health, so various strategies have been developed so far to meet health requirements. Nowadays polymers are known as the building blocks of both commodity and modern stuff ranging from general purpose to sophisticated applications. In particular, polymers have been vital elements of advanced materials and systems in medical landscapes [31].

As a general term, medicine is a vast field in which a proper therapy or treatment method depends on early-stage diagnosis of disease. Biomedical engineering can bridge between engineering and biology, seeking new methods and materials to enhance the health level of life, and then getting prepared for advanced health-care treatment such as therapy, diagnosis, and monitoring. The tunable microstructure of polymers paves the way for targeted design of biomedical materials and systems. Application of polymers as diagnostic system like fluorescent loaded polymeric nano-particle, as therapeutic system like drug carrier, and as regenerative scaffold in tissue engineering has been the subject of several reports [32,33].

Biocompatibility is the first requirement of a polymer to be utilized in biomedical applications. Polymers used in biomedical engineering can be categorized into two main groups including synthetic and natural polymers. Each group has some pros and cons, for instance, natural polymers like chitosan exhibit appropriate biocompatibility, but their mechanical properties are not acceptable, unless one makes them blend with polymers.

Polycaprolactone (PCL) is known as a biocompatible synthetic polymer widely used in tissue engineering, but unsurprisingly hydrophobic properties of PCL deteriorates efficacy of cell attachment emphasizing the need for blending PCL with other polymers in the quest of hydrophilicity. Various methods have been proposed to enhance PCL performance, among which grafting and blending are the most promising methods. For the sake of simplicity and affordability, blending is preferable [34,35].

Miscibility is an important factor in blending polymer pairs. Immiscible polymers are prone to phase separation which affects even the surface topology of blends, thereby governing the cell activity. A scaffold having uniform topology results in monotonic cellular growth. There is

agreement that polymer blends are hardly miscible, but they can be partially miscible by using compatibilizers. Immiscibility of polymer blends leads to non-uniform activity of cells and disintegrated cells. The use of a layer of natural polymer as compatibilizer is responsible for insufficient biocompatibility in immiscible polymer systems [36]. Various compatibilizers have been added to polymer blends to enhance the miscibility. Naffakh et al. employed polylactic acid (PLA)/polypropylene (PP) blends containing tungsten disulphide as a candidate for biomedical applications, but phase separation led to unsuitable properties. To overcome this drawback, PP grafted maleic anhydride (PP-g-MAH) was used as a compatibilizer [37].

Calandrelli et al. blended PLA with PCL to fabricate artificial liver. Addition of lactic acid-caprolactone copolymer as a compatibilizer enhanced the miscibility of PLDA and PCL in their blends, so that cell proliferation enhanced due to restricted phase separation [38]. It should be noticed that high concentration of the compatibilizer sometimes results in toxicity, signifying the need for optimizing compatibilizer content.

Various types of biocompatible polymer blends have been fabricated so far and utilized in biomedical applications. It is always required for bio-based polymer blends to be processed appropriately. Typically, blends are fabricated using various methods such as electro-spinning, gelation, and casting, but the final application determines the polymer blends and fabrication methods to be selected. For example, fabrication of injectable interpenetrating polymer networks has been recognized as a noninvasive method to regenerate damaged tissues. Since cells can proliferate properly on the aligned scaffold rather than random morphology, electro spinning driven nanostructures are promising to enhance cellular activity. For instance, electrospun nanofibers have been utilized in bio-sensing applications and enhanced material performance [39,40]. All in all, it can be concluded that there is need for profound knowledge about biocompatible polymers to select proper blends for biomedical applications.

Human health care was the main driving force behind several sorts of research and market developments in the past decades. Having this in mind, biomedical engineering received ever increasing attention and several technologies were developed to enhance the human health level. Macromolecular design/engineering enabled production of a vast variety of biomaterials for biomedical uses. Natural and synthetic polymers have been utilized in various applications such as tissue engineering, biosensors, and drug delivery pursuing such developments. Natural polymers due to their inferior mechanical properties required to be reinforced through blending with other polymers to receive credit from mechanical

properties perspective. Meanwhile, due to their acceptable mechanical characteristics, synthetic polymers were used in the form of blend with natural ones having good cellular attachment. In general, natural polymers could mimic ECM properties, while synthetic polymers could in principal enhance the mechanical properties. In this regard, fine-tuning the microstructure of bio-based polymer blends was centered to the focus and hot challenges. Though there was some evidence that natural and synthetic polymers could in the form of blend provide synergistic properties, very limited miscibility window of such blends when melted was the reason for using appropriate compatibilizer. Based on final applications, precise choice of biopolymers for blending together with a proper compatibilizer required for interfacial adhesion toward high performance encouraged having this chapter written.

**References**

- [1] Utracki LA, Favis B. Polymer alloys and blends. New York: Marcel Dekker; **1989**.
- [2] Blends P, Paul DR, Newman S, vol. 2. NY: Academic Press; **1978**. p.391.
- [3] Xanthos M. Interfacial agents for multiphase polymer systems: recent advances. *PolymEng Sci* **1988**;28(21):1392-400.
- [4] Lambla M, Yu R, Lorek S. Coreactive polymer alloys. In: *Multiphase polymers: blends and ionomers*; **1988**. p. 67-83.
- [5] Saleem M, Baker W. In situ reactive compatibilization in polymer blends: effects of functional group concentrations. *J Appl Polym Sci* **1990**;39(3):655-78.
- [6] Xanthos M, Dagli S. Compatibilization of polymer blends by reactive processing. *Polym Eng Sci* **1991**;31(13):929-35.
- [7] Liu N, Baker W. Reactive polymers for blend compatibilization. *Adv Polym Technol* **1992**;11(4):249-62.
- [8] Cor Koning, Martin Van Duin, Christophe Pagnoulle', Robert Jerome, Strategies for compatibilization of polymer blends, *Progress in Polymer Science* Volume 23, Issue 4, **1998**, Pages 707-757
- [9] Bharati A, Wübbenhorst M, Moldenaers P, Cardinaels R. Dielectric properties of phase-separated blends containing a micro-capacitor network of carbon nanotubes: compatibilization by a random or block copolymer. *Macromolecules* **2017**;50(10):3855-67.
- [10] Van der Donck T, Wübbenhorst M, Moldenaers PP. Tuning the phase separated morphology and resulting electrical conductivity of carbon nano-tube-filled PAMSAN/PMMA blends by compatibilization with a random or block copolymer. *Polymer* **2017**;108:483-92.

- [11] Saleem M, Baker W. In situ reactive compatibilization in polymer blends: effects of functional group concentrations. *J Appl Polym Sci* **1990**;39(3):655-78.
- [12] Sinha Ray S, Bousmina M. Compatibilization efficiency of organoclay in immiscible polycarbonate/poly (methyl methacrylate) blend. *Macromol Rapid Commun* **2005**;26(6):450-5.
- [13] Yoon KH, Lee HW, Park OO. Properties of poly (ethylene terephthalate) and maleic anhydride-grafted polypropylene blends by reactive processing. *J Appl Polym Sci* **1998**;70(2):389-95.
- [14] Ajitha A.R., Sabu Thomas, *Compatibilization of Polymer Blends: Micro and Nano Scale Phase Morphologies, Interphase Characterization and Properties*, Book **2020**, 640 Pages
- [15] Utracki LA. *Commercial Polymer Blends*. Chapman & Hall, London; New York. 1998
- [16] Macosko, C. W., Guegan, P., Khandpur, A. K., Nakayama, A., Marechal, P., Inoue, T. *Macromolecules* **1996**, 29, 5590-5598
- [17] Salzano de Luna M, Filippone G. Effects of nanoparticles on the morphology of immiscible polymer blends: challenges and opportunities. *Eur Polym J* **2016**;79:198-218.
- [18] Huang J, Yutian Z, Lina X, Jianwen C, Wei J, Xiaonan N. Massive enhancement in the thermal conductivity of polymer composites by trapping graphene at the interface of a polymer blend. *Compos Sci Technol* **2016**;129:160-5
- [19] Sadeghi A, Yeganeh MR, Khademzadeh J. Highly conductive PP/PET polymer blends with high electromagnetic interference shielding performances in the presence of thermally reduced graphene nanosheets prepared through melt compounding. *Polym Compos* **2019**.

- [20] Subramaniam RT, Yahaya AH, Arof AK. Miscibility studies of PVC blends (PVC/PMMA and PVC/PEO) based polymer electrolytes. *Solid State Ionics* **2002**;148(3):483-6.
- [21] Koning Cor, Van Duin Martin, Pagnouille Christophe, Jérôme Robert, Strategies For Compatibilization Of Polymer Blends, *Progress in polymer science* **1998**, vol. 23, iss. 4, pp. 707-757
- [22] Anastasiadis SH, Gancarz I, Koberstein JT. Interfacial tension of immiscible polymer blends: temperature and molecular weight dependence. *Macromolecules* **1988**;21(10):2980-7.
- [23] Majumdar B, Keskkula H, Paul D, Harvey N. Control of the morphology of polyamide/styrene-acrylonitrile copolymer blends via reactive compatibilizers. *Polymer* **1994**:4263-79.
- [24] Koning C, Van Duin M, Pagnouille C, Jerome R. Strategies for compatibilization of polymer blends. *Prog Polym Sci* **1998**;23(4):707-57.
- [25] Van Puyvelde P, Velankar S, Moldenaers P. Rheology and morphology of compatibilized polymer blends. *Curr Opin Colloid Interface Sci* **2001**;6(5e6):457-63.
- [26] La Mantia FP, Ceraulo M, Mistretta MC, Botta L, Morreale M. Compatibilization of polypropylene/polyamide 6 blend fibers using photo-oxidized polypropylene. *Materials* **2018**;12(1):81.
- [27] Rigoussen A, Raquez J-M, Dubois P, Verge P. A dual approach to compatibilize PLA/ABS immiscible blends with epoxidized cardanol derivatives. *Eur Polym J* **2019**;114:118-26.
- [28] Rastin H, Saeb MR, Jafari SH, Khonakdar HA, Kritschmar B, Wagenknecht U. Reactive compatibilization of ternary polymer blends with core-shell type morphology. *Macromol Mater Eng* **2015**;300(1):86-98.

- [29] Kim S, Kim JK, Park C. Effect of molecular architecture of in situ reactive compatibilizer on the morphology and interfacial activity of an immiscible polyolefin/polystyrene blend. *Polymer* **1997**;38(8):1809-15.
- [30] Jazani OM, Arefazar A, Peymanfar MR, Saeb MR, Talaei A, Bahadori B. The influence of NBR-g-GMA compatibilizer on the morphology and mechanical properties of poly (ethylene terephthalate)/polycarbonate/NBR ternary blends. *Polym Plast Technol Eng* **2013**;52(13):1295-302.
- [31] Bakhshandeh B, Zarrintaj P, Oftadeh MO, Keramati F, Fouladiha H, Sohrabijahromi S, et al. Tissue engineering; strategies, tissues, and biomaterials. *Biotechnol Genet Eng Rev* **2017**;33:144-72.
- [32] Zarrintaj P, Moghaddam AS, Manouchehri S, Atoufi Z, Amiri A, Amirkhani MA, et al. Can regenerative medicine and nanotechnology combine to heal wounds? The search for the ideal wound dressing. *Nanomedicine* **2017**;12:2403-22.
- [33] Nilforoushzadeh MA, Amirkhani MA, Zarrintaj P, Salehi Moghaddam A, Mehrabi T, Alavi S, et al. Skin care and rejuvenation by cosmeceutical facial mask. *J Cosmet Dermatol* **2018**;17(5):693-702.
- [34] Nilforoushzadeh MA, Zare M, Zarrintaj P, Alizadeh E, Taghiabadi E, Heidari Kharaji M, et al. Engineering the niche for hair regeneration-a critical review. *Nanomed Nanotechnol Biol Med* **2018**;15(1):70-85.
- [35] Tariverdian T, Zarrintaj P, Milan PB, Saeb MR, Kargozar S, Sefat F, et al. Nanoengineered biomaterials for kidney regeneration. In: *Nano-engineered biomaterials for regenerative medicine*. Elsevier; **2019**. p. 325-44
- [36] Diban N, Stamatialis D. Polymeric hollow fiber membranes for bioartificial organs and tissue engineering applications. *J Chem Technol Biotechnol* **2014**;89:633-43.

- [37] Naffakh M, Díez-Pascual AM, Marco C. Polymer blend nanocomposites based on poly (l-lactic acid), polypropylene and WS2 inorganic nanotubes. *RSC Adv* **2016**;6:40033-44.
- [38] Calandrelli L, Calarco A, Laurienzo P, Malinconico M, Petillo O, Peluso G. Compatibilized polymer blends based on PDLLA and PCL for application in bioartificial liver. *Biomacromolecules* **2008**;9:1527-34.
- [39] Przybysz M, Zedler Ł, Saeb MR, Formela K. Structure-property relationships in peroxide-assisted blends of poly ( $\epsilon$ -caprolactone) and poly (3-hydroxybutyrate). *React Funct Polym* **2018**;127:113-22.
- [40] HassanpourAsl F, Saeb MR, Jafari SH, Khonakdar HA, Rastin H, Pötschke P, et al. Looking back to interfacial tension prediction in the compatibilized polymer blends: discrepancies between theories and experiments. *J Appl Polym Sci* **2018**;135:46144.

**CHAPTER IV**  
**Literature Review**

## II.1 Literature Review

In this part and for the sake of illustration, a brief presentation of some and **few** of the works that have been published and which covered different aspects of the subject, will be made. These studies are presented in a chronological order.

For example, **S.H.Zhu et al [1]** have studied the compatibilization of Poly(vinyl chloride)/Styrene-Butadiene Rubber (PVC/SBR) thermoplastic elastomer blends using nitrile rubber (NBR) as a compatibilizing agent. The dynamic vulcanization was used also as a technological compatibilization for PVC/SBR TPE systems. Three types of NBR and two ABSs-NBR-18 were also reported. Sulfur and Dicumyl peroxide (DCP) were chosen as the two different curing agents for the blends. The effects of compatibilizers as well as dynamic vulcanization on the mechanical properties of PVC/SBR system were also investigated by means of tensile test. They have found that the tensile strength, young's modulus increased by the addition of compatibilizers and the elongation at break decreased for the PVC/SBR thermoplastic vulcanizates (TPVs) samples. This could be attributed to enhance and improve the interfacial adhesion and reduce the interfacial tension between the two polymer phases. (i.e: PVC, and SBR).

In another publication, the interfacial adhesion of the compatibilized 50/40/10 PVC/SBR/NBR thermoplastic elastomer was reported by **S.H.Zhu et al [2]**. To investigate the effect of compatibilizing agent in the PVC/SBR TPE system, morphological properties were carried out by means of transmission electron microscopy (TEM). TEM results show the best dispersion of the minor phase in the major phase which is imparted by the compatibilizing agent. This is due to the development of the interactions between the component systems which are explained by the stabilizing effect of the higher rubber concentration in the interfacial regions between PVC and SBR.

**Shuihan Zhu and Chi-Ming Chan [3]** have investigated the effect of crosslinking agent as well as compatibilizer on the interfacial interaction of compatibilized PVC/SBR thermoplastic elastomer blends. Blends of 50 wt% of poly(vinyl chloride) (PVC) and 40 wt% of styrene butadiene rubber (SBR) with 10 wt% of acrylonitrile butadiene rubber (NBR) as the compatibilizer were prepared in a Haake mixer. An inversion of phase continuity was observed when the sulfur concentration was changed from 0.0 to 2.0 parts per hundred parts of resins (phr) in the blends containing an NBR with an acrylonitrile content of 29.5 wt% (NBR-29). The SBR phase, which is continuous in the unvulcanized blend, changes

progressively into the dispersed phase as sulfur concentration increases. This is explained by the viscosity increase of the rubber caused by crosslinking. There is no phase inversion as a result of increasing sulfur concentration when the compatibilizer NBR-29 was replaced by an NBR with an acrylonitrile content of 40 wt% (NBR-40). The SBR phase is discrete in the unvulcanized blend with NBR-40 as the compatibilizer. A change in phase continuity occurs during processing of the vulcanized PVC/NBR-29/SBR (50/10/40) blends. A torque peak in the torque curve during processing is correlated to the transition of the PVC phase continuity. There is a gradual increase in the torque curve after the torque peak. The rubber particle size decreases as a result of such a post-peak increase in the torque. The torque peak and the post-peak increase in the torque are absent in the case of the binary blends (PVC/NBR and PVC/SBR). The post-peak increase in the torque is attributed to the interfacial reaction between SBR and NBR that resides in the PVC phase. A novel method developed recently was applied to study the interface development during processing. An interface with a higher rubber concentration develops during processing of the compatibilized blends. These effects could be attributed to enhanced and improvement of the interfacial adhesion and reduced the interfacial tension between the two polymer phases (PVC, and SBR) imparted by both Dynamic vulcanization as well as compatibilizing agent.

In another publication, **Shuihan Zhu and Chi-Ming Chan [4]**. The mechanical properties of poly(vinyl chloride) (WC)/styrene-butadiene rubber (SBR) blends compatibilized by acrylonitrile-butadiene rubber (NBR) were studied by means of tensile test. A sulfur curing system was employed to crosslink the rubber of the blends. In the case of the blends without any curing agents, an increase in NBR content did not improve the tensile strength and elongation-at-break. However, a significant improvement in the mechanical properties was observed when NBR was added as a compatibilizer and the blend was vulcanized. In the WC/NBR/SBR (50/10/40) blends, the tensile strength and elongation-at-break increased with an increase in sulfur concentration. This improvement was attributed to co-vulcanization between NBR and SBR.

In another study, S.L. Abd-El-Messieh et al [5] have studied the Evolution of Polyester Resin as a New Compatibilizer for SBR/PVC Thermoplastic Elastomer Blends. A polyester (PE) based on the glycolized products of PET was prepared and added in different concentrations to a series of SBR/PVC blends. The addition of the polyester showed that all properties of SBR/PVC blends were improved by incorporation of PE. Highest mechanical strength values were obtained at a polyester concentration of 7.5 phr. Thermal

analysis as well as dynamic mechanical properties of SBR/PVC blends after the addition of 7.5 and 10 phr polyester indicated one single glass transition temperature.

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**References**

- [1] Zhu, S.-H.; Chan, C.-M.; Zhang, Y.X. Poly (Vinyl Chloride)/Styrene-Butadiene Rubber Blends Prepared by Dynamic Vulcanization with Nitrile Rubber as the Compatibilizer. *J. Appl. Polym. Sci.* **1995**, 58, 621–631, [doi:10.1002/app.1995.070580317](https://doi.org/10.1002/app.1995.070580317).
- [2] Zhu, S.-H.; Cheung, M.K.; Chan, C.-M. Interfacial Characterization of Compatibilized PVC/SBR Blends by Solid-State NMR and TEM. *Polymer* **1998**, 39, 6099–6108, [doi:10.1016/S0032-3861\(98\)00039-1](https://doi.org/10.1016/S0032-3861(98)00039-1).
- [3] Zhu, S.; Chan, C.-M. Transition of Phase Continuity Induced by Crosslinking and Interfacial Reaction during Reactive Processing of Compatibilized PVC/SBR Blends. *Polymer* **1998**, 39, 7023–7032, [doi:10.1016/S0032-3861\(98\)00176-1](https://doi.org/10.1016/S0032-3861(98)00176-1).
- [4] Zhu, S.-H.; Chan, C.-M.; Wong, S.C.; Mai, Y.-W. Mechanical Properties of PVC/SBR Blends Compatibilized by Acrylonitrile-Butadiene Rubber and Covulcanization. *Polym. Eng. Sci.* **1999**, 39, 1998–2006, [doi:10.1002/pen.11593](https://doi.org/10.1002/pen.11593).
- [5] Abd-El-Messieh, S.L.; Mansour, S.H.; El-Nashar, D.; Ikladios, N.E. Evaluation of Polyester Resin as a New Compatibilizer for SBR/PVC Blends. *Can. J. Chem. Eng.* **2008**, 82, 358–370, [doi:10.1002/cjce.5450820217](https://doi.org/10.1002/cjce.5450820217).

# Conclusion

# Conclusion

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## Conclusion

Polymer blends expand and diversify properties available from individual polymers. Blends should be compatible without being miscible so that properties of component polymers are retained instead of averaged; we may say they are truly a novelty to the world. A blend will usually consist of a matrix and dispersed phase, though various composition-dependent continuous morphologies can be formed. The polymers for blends can be chosen from compatible polymers, separate compatibilizer additives included, or various reaction strategies used to enhance compatibility.

Compatibility facilitates the dispersion process, stabilizes the dispersion, and increases the strength of the interface between the blended polymers. Interfacial strength is enhanced by interactions between the constitutive polymers as measured by the interaction parameter; however, macromolecular conformation and confinement as denoted by entropy of mixing is significant and may exceed specific interactions. Such polymer blends are never thermodynamically stable; the metastable morphology is maintained by interfacial interactions and solidification of the blend. Polymer blending is particularly favorable to broaden the properties and applications of commodity polymers. Creation of new materials by combining existing polymers is often more appealing than synthesis of new copolymers; hence obtaining the required combination of characteristics and properties from each polymer.

The blending process of compatibilized PVC/SBR blends involves the combination of polyvinyl chloride (PVC) and styrene-butadiene rubber (SBR) to create a material with improved properties compared to the individual components. Interfacial interactions between PVC and SBR play a crucial role in determining the rheological, mechanical, dynamic mechanical, thermal, and morphological development of the blends. Here are the effects of interfacial interactions on each of these aspects:

1-Rheological properties: Interfacial interactions affect the viscosity, melt flow behavior, and processing characteristics of the blends. Strong interfacial interactions can enhance the blend's melt strength, reduce melt viscosity, and improve processability. This can result in improved blend homogeneity and ease of processing during molding or extrusion.

2-Mechanical properties: Interfacial interactions influence the mechanical performance of the blends, including tensile strength, elongation at break, and impact resistance. Strong interfacial interactions can lead to improved mechanical properties by enhancing the

# Conclusion

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compatibility between PVC and SBR. It promotes better stress transfer between the phases and improves the overall toughness of the blend.

3-Dynamic mechanical properties: Interfacial interactions affect the viscoelastic behavior of the blends as a function of temperature and frequency. Enhanced interfacial interactions can lead to increased glass transition temperatures ( $T_g$ ) of the blend, indicating improved compatibility. The presence of strong interfacial interactions can also affect the storage modulus, loss modulus, and damping properties of the blend, influencing its dynamic mechanical response.

4-Thermal properties: Interfacial interactions can influence the thermal stability, thermal transitions, and heat resistance of the blends. Improved interfacial interactions can increase the thermal stability of the blend by reducing the mobility of the polymer chains and inhibiting thermal degradation. Additionally, interfacial interactions can affect the melting and crystallization behavior of the blend, leading to changes in its thermal transitions.

5-Morphological development: Interfacial interactions play a critical role in determining the morphology and phase distribution of the blends. Effective interfacial interactions promote interfacial adhesion between PVC and SBR, leading to reduced phase separation and the formation of a finer and more uniform morphology. This can result in improved blend compatibility, reduced void formation, and enhanced dispersion of the rubber phase within the PVC matrix.

Overall, strong interfacial interactions in the blending process of compatibilized PVC/SBR blends can lead to improved rheological properties, enhanced mechanical performance, increased thermal stability, and better morphological development. These effects are crucial for achieving desired properties in the final blend and optimizing its application potential.

## Abstract

### Abstract

When PVC (polyvinyl chloride) and SBR (styrene-butadiene rubber) are blended together, they are considered immiscible due to their different chemical compositions and polarities. This Immiscible polymer blends exhibit phase separation, where PVC and SBR tend to separate into distinct domains within the blend. The immiscibility of PVC/SBR blends can lead to several challenges and limitations in terms of their properties. However, the compatibilization strategies play a crucial role in improving the properties of PVC/SBR systems. These strategies aim to enhance the compatibility between the immiscible components, resulting in improved mechanical, thermal, and morphological properties.

**Keywords:** Polyvinyl chloride, Styrene-Butadiene Rubber, Thermoplastic Elastomer, Immiscible Blends, Compatibilization.

### Résumé

Lorsque le PVC (chlorure de polyvinyle) et le SBR (caoutchouc styrène-butadiène) sont mélangés ensemble, ils sont considérés comme non miscibles en raison de leurs différentes compositions chimiques et polarités. Ces mélanges de polymères non miscibles présentent une séparation de phase, où le PVC et le SBR ont tendance à se séparer en domaines distincts dans le mélange. L'immiscibilité des mélanges PVC/SBR peut conduire à plusieurs défis et limites en termes de propriétés. Cependant, les stratégies de compatibilisation jouent un rôle crucial dans l'amélioration des propriétés des systèmes PVC/SBR. Ces stratégies visent à améliorer la compatibilité entre les composants non miscibles, ce qui améliore les propriétés mécaniques, thermiques et morphologiques.

**Mots Clés:** Chlorure de Polyvinyle, Caoutchouc Styrène-Butadiène, Elastomère Thermoplastique, Mélanges Non Miscibles, Compatibilité.

### ملخص

عندما يتم مزج كلوريد البولي فينيل ومطاط الستايرين-بوتادين معًا، فإنهما يعتبران غير قابلين للمزج بسبب تركيباتهما الكيميائية المختلفة واستقطابتهما. يمزج هذا البوليمر غير القابل للانقسام فصل الطور، حيث تميل كلوريد البولي فينيل ومطاط الستايرين-بوتادين إلى الانفصال إلى مجالات مميزة داخل المزيج. يمكن أن تؤدي عدم قابلية خلطات كلوريد البولي فينيل ومطاط الستايرين-بوتادين إلى العديد من التحديات والقيود من حيث خصائصها. ومع ذلك، تلعب استراتيجيات التوافق دورًا حاسمًا في تحسين خصائص أنظمة كلوريد البولي فينيل ومطاط الستايرين-بوتادين. تهدف هذه الاستراتيجيات إلى تعزيز التوافق بين المكونات غير القابلة للفصل، مما يؤدي إلى تحسين الخصائص الميكانيكية والحرارية والمورفولوجية.

### الكلمات المفتاحية

كلوريد البولي فينيل ، مطاط ستايرين بوتادين ، مطاط حراري ، خلاط غير قابلة للامتزاج ، موازنة.