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Assessment of Compatibilization Efficiency by using Compatibilizers in Immiscible Binary Polymers based on Polypropylene/Polystyrene (PP/PS) Blends.

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

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Chapter II

Thermodynamics of polymer blends

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List of Notations and Abbreviations

Abbreviations	**Description**
ASTM	American Society for Testing and Materials
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared
AFM	Atomic force microscopy
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimeter
DTG	Derivative thermogravimetry
DCP	Dicumyl peroxide
FTIR	Fourier transform infrared
^{1}H-NMR	Proton nuclear magnetic resonance
iPP	Isotactic polypropylene
ISO	International Standards Organization
MA	Maleic anhydride
MA-g-PP	Maleic anhydride grafted polypropylene
Mn	Number average molecular weight
Mw	Mass average molecular weight
NMR	Nuclear magnetic resonance
PP	Polypropylene
PS	Polystyrene
Ph-PP	Phenolic modified polypropylene
SEBS	Styrene Ethylene/Butylene Styrene
SEBS-g-MA	Styrene-ethylene-butylene-styrene-graft-maleic anhydride
SEM	Scanning electron microscope
TEM	Transmission electron microscope
TGA	Thermogravimetric Analysis

List of Notations and Abbreviations

Symbols	Description
E	Young’s modulus
E’	Storage modulus
E’’	Loss modulus
ΔHm	Melting enthalpy of sample
ΔH_0	Theoretical enthalpy for 100 % crystalline
Tan δ	Loss tangent
Tc	Crystallization temperature
Tm	Melting temperature
Tg	Glass transition temperature
t	Time
ρ	Density
TS	Tensile strength
m	Mass
Ɛb	Elongation at break
T	Temperature
σ	Tensile strength
ε	Strain
ml	Milliliter
mm	Millimeter
min	Minute
µm	Micrometer
N	Newton
MPa	Megapascal
ºC	Degree Celsius
h	Hour
J	Joule
%	Percent
wt%	Percent by weight
η	Viscosity

General Introduction

Introduction

Polymer blending is an effective and facile way to achieve plastic materials with modified properties at low cost as compared to the development of new polymeric material. Main purpose of polymer blending is to combine the advantages and overcome the disadvantages of individual polymers **[1-6]**. Among them, polypropylene (PP) is extensively used polymer in industry due to its superior chemical resistant, processability, low density and better thermal properties; however its poor impact strength and stiffness limits the use in electrostatic discharge (ESD) protection and electronic packaging applications **[7-9]**. The rigid polymers like and polystyrene (PS) are used to reinforce PP matrix to achieve a new polymer blending with modified properties. PS has many advantages such as low mold shrinkage, wide thermal processing window and marvelous printability which enables the slight degradation during melt blending with PP. PP and PS are the commodity thermoplastic materials having high consumption in all over the world and can mixed easily with slight degradation during melt blending **[10].**

Nevertheless, PP/PS blend is a familiar binary immiscible system, which generally shows poor mechanical and electrical properties due to fragile interfacial adhesion between PP and PS phases. Fortunately, compatibilization can improve the adhesion/interaction between polymer phases by reducing the droplet size and suppresses the coalescence of dispersed phase in polymer blend systems. Compatibilization increase the miscibility between different homopolymers consequently improves the electrical and mechanical properties of resultant blend **[11-14].**

This Master Thesis is composed of four chapters. The first presents a theoretical background of Polypropylene and Polystyrene, their properties as well as their applications in industrial fields. The second chapter presents the thermodynamics principles of polymer blends, the morphology and properties of polymer blends, and the third chapter presents the strategies for compatibilization of polymer blends. The fourth chapters present a brief presentation of some 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.

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Chapter I

Theoretical Background

I.1 Introduction

Polymer blends have been the subject of intense study during the last two decades. Attention has been paid both to the theoretical investigation of the rules governing the blending process and the possibilities of match the market demands. Unfortunately, most polymers are immiscible from a thermodynamic point of view because the entropy contribution to the Gibbs energy of mixing is negligible. Therefore, mixing of two homopolymers often leads to a coarse heterogeneous phase structure with a low adhesion between the phases. A method for improving interfacial interactions in polymer blends includes the use of a suitable modifier, the addition of which plays an important role in lowering the interfacial tension and in promoting adhesion between the two homopolymer phases. These interfacial agents are usually block or graft copolymers whose segments are at least partially miscible with the particular components of the system, that is, they are either chemically identical or similar to the blend components.

In this chapter we present an overview of the polymers involved in this study.

I.2 Polypropylene

I.2.1 Synthesis method of polypropylene

The synthetic approach for polypropylene is much the same as that for the production of HDPE by the Ziegler process. The same reactor can be used to polymerize ethylene, propylene or other a-olefins with some modifications, if necessary. For propylene, the reaction condition should be so chosen as to overwhelmingly favor formation of the isotactic polymer. The catalyst may be prepared from TiCpl, and aluminium triethyl combination dispersed in naphtha. Propylene is charged into the reactor under pressure. Nearly 80-85% conversion is achieved in 8-10 h at 60°C. The reaction variables are molar ratio of catalyst components, catalyst concentration, and reaction temperature and monomer pressure. Hydrogen may be used as a chain terminating or transfer agent for control of molecular weight. About 8-15% atactic polymer is also formed along with the formation of the isotactic polymer in the main. After the reaction reaches 80-85% conversion stage, the ingredients are transferred into a flash drum to purge off the unreacted monomer which is then recycled. The atactic product is soluble in the solvent naphtha. The solution is decanted off after centrifugation whereby most of the atactic material is removed. The residue is then treated with methanol acidified with traces of HCI to decompose and dissolve the catalyst. The polymer is then centrifuged washed, dried and collected. **[1]**

I.2.2 Chemical Structure of polypropylene

Polypropylene is a tough, rigid and semi crystalline thermoplastic produced from propene (or propylene) monomer. It is a linear hydrocarbon resin. The chemical formula of polypropylene is (C_3H_6) n. Polypropylene is a vinyl polymer in which every carbon atom is attached to a methyl group and can be expressed as shown in **Figure I.1.**

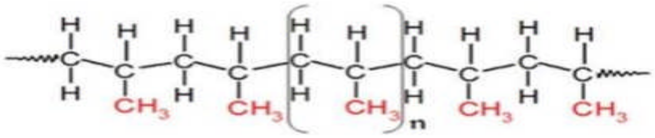
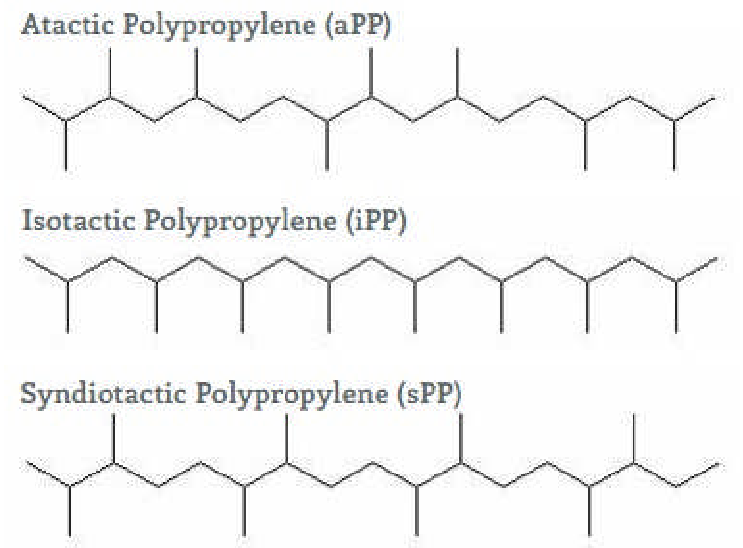


Figure I.1 Chemical structure of polypropylene.

Polypropylene is made from polymerization of propene monomer by: Ziegler-Natta polymerization or Metallocene catalysis polymerization. Upon polymerization, PP can form three basic chain structures depending on the position of the methyl groups (**Figure I.2**)

1-Atactic (aPP) - Irregular methyl group (CH_3) arrangement, 2-Isotactic (iPP) – Methyl groups (CH_3) arranged on one side of the carbon chain. 3- Syndiotactic (sPP) - Alternating methyl group (CH_3) arrangement **[2-3]**



Atactic Polypropylene (aPP)

Isotactic Polypropylene (iPP)

Syndiotactic Polypropylene (sPP)

Figure I.2: The Ziegler-Natta catalytic polymerization of propene with three different stereoregular structures

I.2.3 Properties of polypropylene

Polypropylene is a thermoplastic polymer that has many useful properties. Some of the main properties of polypropylene include:

High melting point: Polypropylene has a high melting point, typically ranging from 160°C to 170°C. This makes it suitable for applications that require high temperature resistance.

Good chemical resistance: Polypropylene is highly resistant to a wide range of chemicals, including acids, bases, and solvents. This makes it suitable for use in chemical processing and storage applications.

Lightweight: Polypropylene has a low density, which makes it a lightweight material. This property is beneficial in applications where weight is a critical factor, such as in the automotive and aerospace industries.

Good stiffness and toughness: Polypropylene is a stiff and tough material, with good resistance to impacts and abrasion. This makes it suitable for use in a variety of structural applications.

Low moisture absorption: Polypropylene is hydrophobic, which means it has a low affinity for water. This property makes it resistant to water absorption and moisture-related degradation.

High electrical insulation: Polypropylene is an excellent electrical insulator, with low dielectric loss and high dielectric strength. This property makes it suitable for use in electrical and electronic applications.

Good processability: Polypropylene is easy to process using various methods, including injection molding, extrusion, and blow molding. This makes it suitable for high-volume manufacturing.

Overall, the combination of properties makes polypropylene a versatile material that is used in a wide range of applications, including packaging, textiles, automotive parts, medical devices, and construction materials **[4]**

I.2.4 Major advantages of polypropylene

Polypropylene has many benefits which have made it such a popular material for manufacturers who can apply it to many uses. See what the main advantages of the material are below.

- Polypropylene’s chemical properties mean it does not react with acids which make it the ideal material for containers made to hold acidic liquids such as cleaning agents.
- Polypropylene is also highly resistant to corrosion and chemical leaking, making it the choice material for piping systems. The plastic resists to freezing well too, so climate conditions are also not an issue for polypropylene pipes.
- Polypropylene will turn to liquid at its melting point, and in this form, it can be moulded into any desired shape, and this can be done several times without much degradation to the plastic. Polypropylene is used in injection moulding because of how it responds to heat
- Polypropylene does not conduct electricity well, and so is classed as an insulator. This has made it an excellent material for manufacturing to be used with electronic components such as cables and audio equipment.
- Polypropylene is malleable, which means it can be made into a living hinge; a piece of material which can bend without breaking even after repetitive bending.
- Polypropylene has a high tensile strength, which means it is a useful material for heavy loads, as it can withstand 4800 psi.
- Polypropylene is also low density when compared to other plastics, so for manufacturers, they have the benefit of saving money from low weight**.[5]**

I.2.5 Disadvantages of polypropylene

Like all manufactured materials, polypropylene has some drawbacks which users and manufacturers should be aware of before they apply the plastic material.

- Polypropylene is often affected by UV degradation, making it not suitable for use in high altitude or places where UV penetration is high.
- Polypropylene has limited use in high temperatures as it suffers from chain degradation which can lead to oxidization. This result in cracks appearing in the polypropylene but can be fixed with polymer stabilizers.

- Polypropylene has poor bonding properties, which makes it a hard material to paint. One solution for this is to treat the surface to enhance the adhesive strength of paints and inks which can color the polypropylene.
- Polypropylene is extremely flammable and will melt when exposed to heat. The flash point, the temperature at which a liquid produces flammable vapour to form a mixture which can be ignited when contacted with a spark or flame, is just 260 degrees Celsius.

I.2.6 Applications of polypropylene

Polypropylene is widely used in various applications due to its good chemical resistance and weldability. Some common uses of polypropylene include:

1. **Packaging Applications**

   Good barrier properties, high strength, good surface finish, and low cost make polypropylene ideal for several packaging applications.

   a. **Flexible packaging**. PP films' excellent optical clarity and low moisture-vapor transmission make it suitable for use in food packaging. Other markets include shrinkfilm overwrap, electronic industry films, graphic arts applications, and disposable diaper tabs and closures. PP film is available either as cast film or bi-axially orientated PP (BOPP).

   b. **Rigid packaging.** PP is blow molded to produce crates, bottles, and pots. PP thin walled containers are commonly used for food packaging

2. **Consumer goods.**

   Polypropylene is used in several household products and consumer goods applications, including translucent parts, house wares, furniture, appliances, luggage, and toys.

3. **Automotive applications**

   . Due to its low cost, outstanding mechanical properties, and moldability, polypropylene is widely used in automotive parts. Main applications include battery cases and trays, bumpers, fender liners, interior trim, instrumental panels, and door trims. Other key features of automotive applications of PP include low coefficient of linear thermal expansion and specific gravity, high chemical resistance and good weatherability, processability, and impact/stiffness balance.

4. **Fibers and Fabrics.**

   A large volume of PP utilized in the market segment known as fibers and fabrics. PP fiber is utilized in a host of applications including raffia/slit-film, tape, strapping, bulk continuous filament, staple fibers, spun bond and continuous filament. PP rope and twine are very strong and moisture resistant very suitable for marine applications.

5. **Medical Applications.**

   Polypropylene is used in various medical applications due to its high chemical and bacterial resistance. Also, the medical grade PP exhibits good resistance to steam sterilization. Disposable syringes are the most common medical application of polypropylene. Other applications include medical vials, diagnostic devices, petri dishes, intravenous bottles, specimen bottles, food trays, pans, pill containers [**6]**

I.2.7 Manufacturing Processes of polypropylene

The process technology for PP manufacture has kept pace with catalyst advances and the development of new product applications and markets. In particular, the Characteristics of Polypropylene relationship between process and catalyst technology was clearly symbiotic and that of a partnership. Advances in one technology had always exerted a strong push–pull effect on the other to improve its performance. The progress in process technology has resulted in process simplification, investment cost and manufacturing cost reductions, improvement in plant constructability, operability, and broader process capabilities to produce a wider product mix.

The simplified block diagrams in **Figures.I.3–I.5** serve to illustrate the advances in PP process technology from a complex process in **Figure I.3** to one that is simpler in **Figure I.5.** The slurry process technology as illustrated in **Figure I.3** is typical of manufacturing units built in the 1960s and 1970s. This technology was designed for catalysts of the first and second generations. It required a solvent such as butane, heptane, hexane, or even heavier is oparaffins. The solvent served as the medium for dispersion of the polymer produced in the reactors and for dissolving the high level of atactic byproducts for removal downstream. The use of a solvent also facilitated the catalyst deactivation and extraction (or deashing) step, which required contacting the reactor product with alcohol and caustic solutions. Plants based on this technology required a large amount of equipment, a great deal of space, and complicated plot plans. They were high in both capital and operating costs, labor intensive, and energy inefficient. Moreover, there were environmental and safety issues associated with the handling of a large volume of solvent and the disposal of the amorphous atactic byproducts, and a large wastewater stream containing residual catalyst components. With the advent of third- and fourth-generation catalysts, many of these older slurry plants stayed viable by cost reduction aided by the higher catalyst activities and lower atactic production. They also benefitted from plant capacity creeps and debottlenecking.

The slurry process technology evolved into the more advanced slurry process **(Figure. I.4)** in the late 1970s to take advantage of the higher performing third generation catalysts initially and later the even better fourth-generation catalysts. The improved slurry processes were commonly referred to as the bulk (slurry) process. One major change from the older slurry technology was the substitution of liquid propylene in place of the solvent system. This became possible because catalyst de-ashing and atactic removal were no longer needed to produce acceptable PP resins. With very few exceptions, virtually all slurry plants built over the last two decades were based on bulk process technology. Montell's Spheripol process represents technology of this type, using pipe loop reactors operated liquid full, with a PP slurry in liquid propylene. Additionally, a fluidized bed reactor is used by Spheripol downstream of the bulk pipe loop reactors when impact copolymers are in the product slate.

The emergence of gas-phase process technology for PP occurred about the same time as the bulk processes. Gas-phase technology was revolutionary in that it completely avoided the need for a solvent or liquid medium to disperse the reactants and reactor product. This process eliminates the separation and recovery of large quantities of solvents or liquid propylene required in slurry or bulk reactors. The PP products from the gas-phase reactors are essentially dry, requiring only deactivation of the very low level of catalyst residues before the incorporation of additives and pelletization. Thus, this process technology reduced the manufacturing of PP to the bare essential steps. Representatives of commercial gas-phase process technology include Amoco, Union Carbide (Unipol), and BASF (Novolen). Amoco's technology features a horizontal stirred bed reactor system that uses mild mechanical agitation for reactor mixing and temperature control. The heat of polymerization is removed by the use of quench cooling or evaporative cooling using a spray of liquid propylene. The Unipol process is based on a gas fluidization principle that relies on a large volume of fluidizing gas for reactor mixing, polymerization heat removal, and temperature control. According to trade literature, Unipol has claimed that the gas cooling can now be supplemented by some amount of liquid evaporation in the fluidized bed, referred to as the ‘‘condensing’’ mode cooling. The BASF gas-phase reactor is a vertical stirred bed reactor in which the polymerization heat is removed by vaporization of liquid propylene in the bed. In the above three gas-phase processes, a second reactor of a similar design as the first reactor is added for the production of impact copolymers. A sketch of the reactor systems associated with the four types of commercial PP process technology described above—Amoco, Spheripol, BASF, Unipol—is shown in **Figure. I.6.**The Amoco gas-phase process technology is more completely depicted in **Figure. I.7** In summary, over four decades, PP process technology has never stopped creating value for the resin customers through both incremental and generational changes. The changes came about through a partnership with advancements in catalysts to result in better manufacturing economics and simpler plants, making them easier to operate and at higher efficiencies. At the same time, the improved process technology has also added enhancements to many product properties and expanded the product applications.

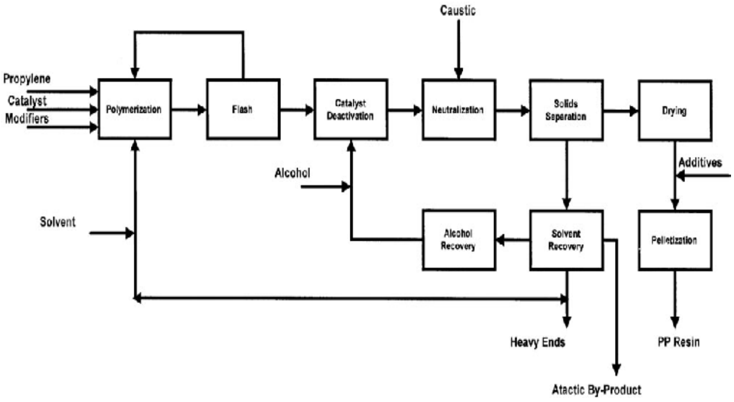


Figure I.3 Early slurry process technology.

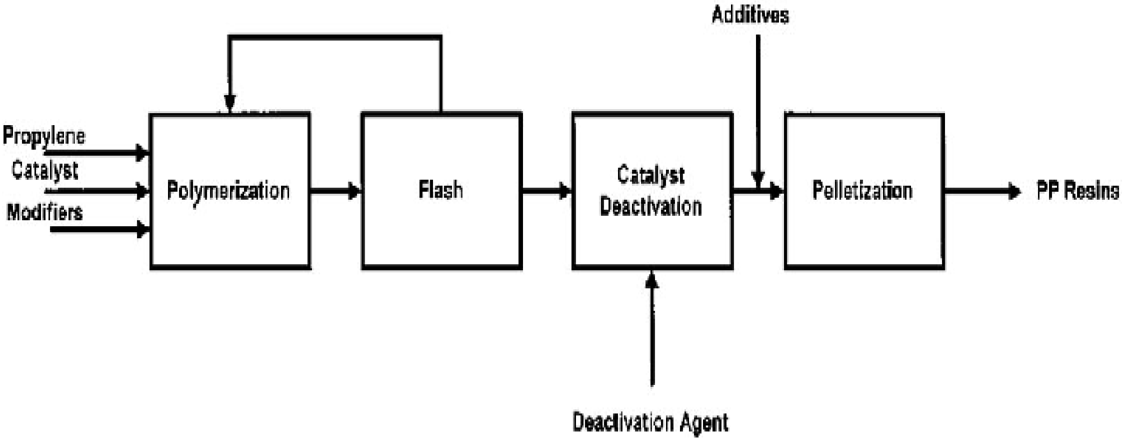


Figure I.4 Bulk (slurry) process technology.

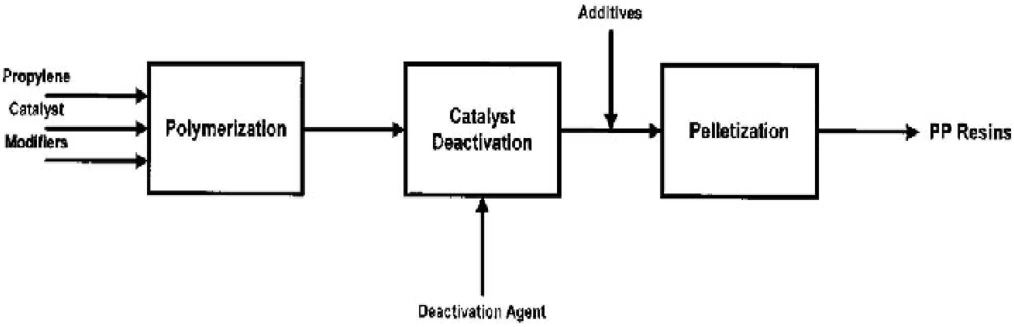


Figure I.5 Gas-phase process technology.

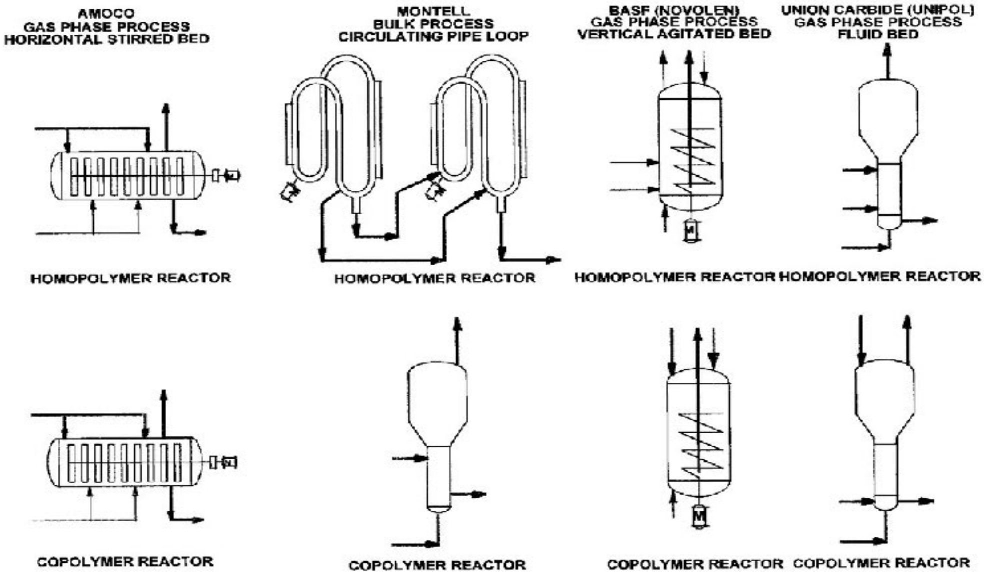


Figure I.6 Reactor systems in polypropylene technologies.

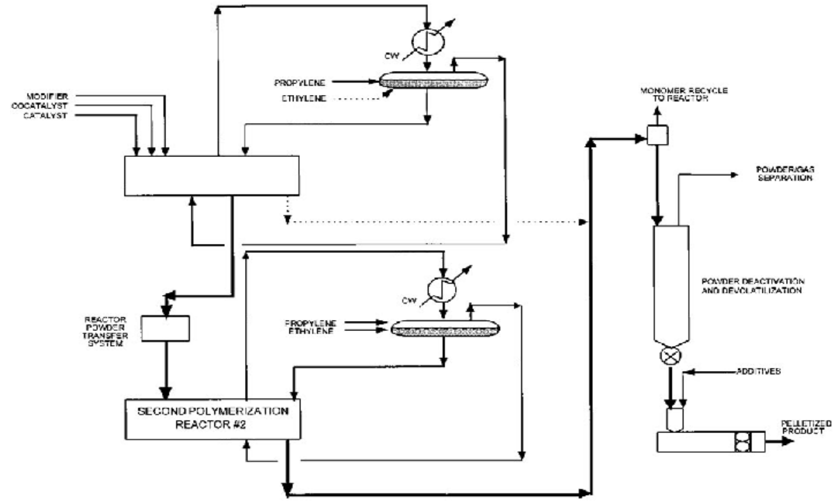


Figure I.7 Amoco gas-phase process technology.

I.3 Polystyrene

I.3.1 Synthesis method of polystyrene

Polystyrene is produced by the polymerization of monomer–styrene, as it is shown in **Figure I.8** General-purpose PS can be considered as a linear polyethylene chain, which has laterally attached phenyl groups. Isotactic PS, where all phenyl groups are on the same side, is an isomer of PS which is not commercially produced. Namely, although isotactic PS is a semi-crystalline polymer with a melting point of around 240 °C, its crystallization rate is too slow to be used in injection molding. SPS, where phenyl groups are placed on alternating sides of the polymer chain, has a much faster crystallization rate than that isotactic PS. Atactic PS which has randomly distributed phenyl groups on both sides of the hydrocarbon backbone and consequently no crystallinity, is the most commercially significant isomer of PS.

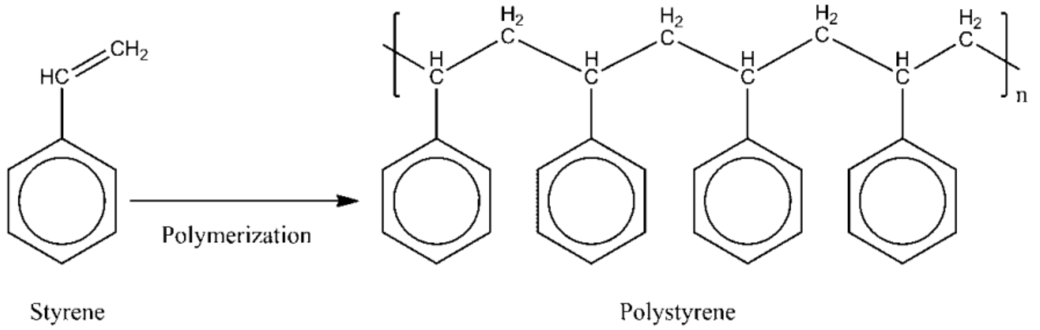


Figure I.8 The reaction scheme for the synthesis of PS from monomer – styrene.

Because C-C double bond of styrene can act either as electron donating or as electron withdrawing center, the low polarity of the styrene and resonance stabilization of the growing polystyryl species in the transition state, synthesis of PS can be performed by free radical, anionic and cationic polymerization of styrene and using metal catalyzed conditions. Depending on the applied method for the synthesis, molecular structure of PS can be linear, branched, star- and comb-like or dendritic. As an example, the mechanism of the free radical polymerization of styrene, using benzoyl peroxide as initiator, is presented in (**Figure I.9)** and (**Figure I.10)** Beside peroxides, other initiators, such as redox systems, azo components, etc. can be used to start the polymerization of styrene. Also, the reaction can be started thermally, without application of chemical initiator.

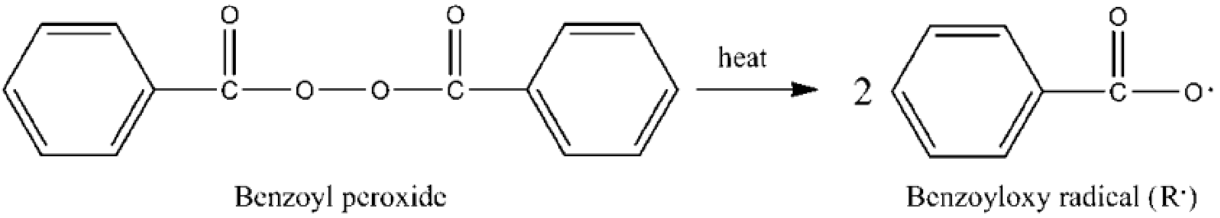


Figure I.9 The reaction scheme for the formation of the radical initiator from benzoyl peroxide.

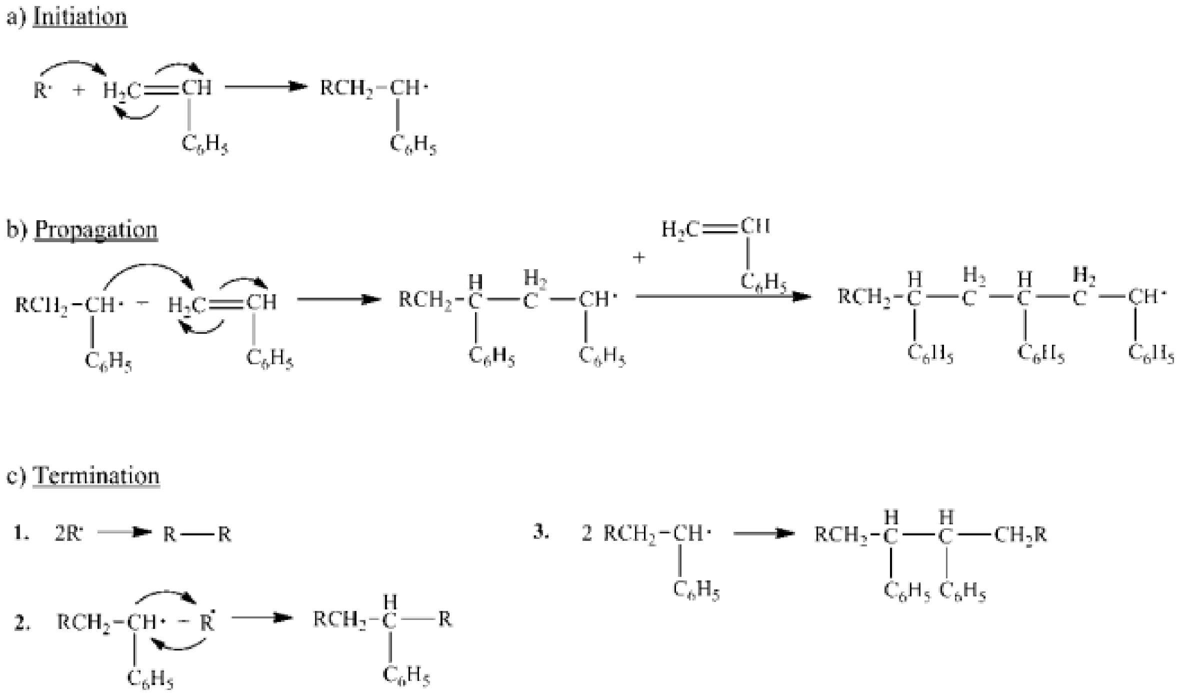


Figure I.10 The reaction scheme for the free radical polymerization of styrene.

After formation of benzoyloxy radical (R•) from benzoyl peroxide, as shown in (**Figure I.10)** R• reacts with styrene and forms an active center **(Figure I.10.a).** In the propagation step, presented in **(Figure I.10.b),** chain continues to grow until termination **(Figure I.10.c).** Besides termination, transfer reaction to other components of the polymerization reaction also occurs. Chain transfer agents can be the initiator, monomer, solvent, polymer or an added chemical agent. The transfer reactions have no effect on the polymerization rate, but can decrease the average molecular weight. By adequate use of transfer agent, such as mercaptanes, molecular weight of PS can be controlled. Generally, it is very hard to control molecular weight, molecular weight distribution and molecular structure of the PS synthesized using free radical polymerization process. These disadvantages of radical polymerization reactions can be overcome by applying the substances called iniferters (initiatior-transfer agent-termination), which act as initiators, transfer agents and termination agents. Iniferters react with growing macromolecular radicals and form temporarily hidden species, minimizing in this manner termination by recombination and disproportionation. Also, the presence of iniferters increases the concentration of reactive polymer chains in comparison to the concentration of free radicals, which lowers polymerization rate.

Free-radical PS can be prepared either by bulk, solution, suspension or emulsion technique. For the synthesis of PS by bulk process, pure styrene must be applied and as a result polymer with high clarity is obtained. Due to its poor control, this process is not used commercially. For the solution polymerization, styrene is dissolved in adequate solvent, which makes temperature control easier. However, the presence of solvents reduces molecular weight and polymerization rate. Both processes can be carried out in batch or continuously. The advantages of these kinds of PS synthesis are production of more uniform product and low volatile levels. In suspension polymerization, the polymerization system is composed of monomer suspended in water, stabilizing agents and initiators to speed polymerization. The advantages of suspension polymerization are easy heat control and removal of the final product. In emulsion polymerization water is used as carrier with emulsifying agents. This type of polymerization technique produces extremely small particles and it is usually used for the production of ABS copolymers**.** Today the majority of general purpose PS is prepared using solution polymerization of styrene in a continuous process with heat removal by evaporation of styrene and solvent. Due to the consistent temperature, high product quality can be obtained with a narrow molecular weight distribution (Mw/Mn = 2.2 - 2.4) and high transparency. Depending of the synthetic procedure, three grades of general purpose PS are commercially produced: easy flow, medium flow and high heat. Easy and medium flow PS are used for injection molding, while high heat for the extrusion applications **[8]**

I.3.2 Chemical Structure of polystyrene

Polystyrene is a synthetic polymer made up of repeating units of the monomer styrene. Its chemical formula is $(C_8H_8)n$, where n is the number of repeating units in the polymer chain. The structure of polystyrene is depicted below (**Figure I.11**):

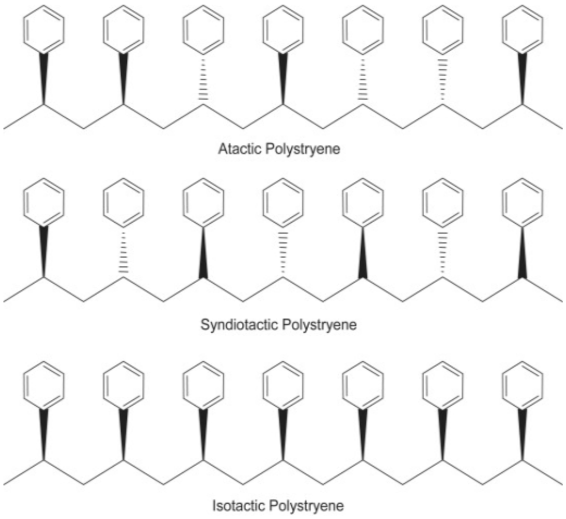


Figure I.11: Different chemical structures of polystyrene according to their tacticity **[9]**

I.3.3 Properties of polystyrene

- Polystyrene exists in an amorphous state because of the presence of bulky phenyl groups, packing of polystyrene chains is not efficient.
- Polystyrene is non-polar in nature.
- The polystyrene melting point is 240 degrees Celsius.
- Polystyrene density is 1.05 g/cm^3
- The polystyrene boiling point is 430 degrees Celsius.
- Polystyrene thermal conductivity is 0.003 W/m.K.
- Polystyrene-specific gravity is 1.054.
- Polystyrene has a good optical property like it is a transparent polymer allowing high transmission of all wavelengths. Moreover, its high refractive index gives it a particularly high brilliance.
- Due to the chain stiffening effect of the benzene ring, polystyrene is hard but brittle. It emits a characteristic metallic sound when dropped.
- Being a non-polar amorphous polymer, its softening temperature is low. It can not with-stand the temperature of boiling water.

- Polystyrene has a low tendency for moisture absorption. Moreover, it has good electrical insulation characteristics. Therefore, it is used in making polystyrene insulation products.

- Polystyrene has reasonable chemical resistance but mediocre oil resistance**.[10]**

I.3.4 Major Advantages of polystyrene

Polystyrene is a widely used thermoplastic polymer that offers several advantages, including:

Lightweight: Polystyrene is a lightweight material, making it ideal for applications where weight is a concern, such as in packaging and insulation.

Good insulation properties: Polystyrene has excellent thermal insulation properties, making it useful for insulation applications in the construction industry, such as for walls, roofs, and floors.

Versatility: Polystyrene can be easily molded into different shapes and sizes, making it suitable for a wide range of applications, including packaging, disposable cutlery, toys, and insulation.

Affordable: Polystyrene is a cost-effective material, making it an excellent choice for many applications, particularly those that require large quantities.

Chemical resistance: Polystyrene is resistant to many chemicals, making it ideal for packaging and storage applications where chemical resistance is required.

Transparency: Polystyrene is a clear and transparent material, making it useful in applications where visibility is required, such as in packaging and display cases.

Recyclability: Polystyrene can be recycled, making it an environmentally friendly material.

Overall, polystyrene is a versatile and cost-effective material with a wide range of applications in industries such as packaging, construction, and consumer goods. Its lightweight, insulation properties, and versatility make it an excellent choice for many applications, while its affordability and recyclability make it a popular choice for many industries**.[11]**

I.3.5 Disadvantages of polystyrene

Polystyrene is a synthetic polymer made from styrene monomers, which is widely used in many industries due to its lightweight, insulating, and versatile properties. However, there are several disadvantages associated with polystyrene, including:

Environmental impact: Polystyrene is not biodegradable, which means that it can persist in the environment for hundreds of years. It is also difficult to recycle due to its low density and contamination by food and other materials.

Health risks: The production and disposal of polystyrene can release hazardous chemicals, such as styrene, which have been linked to various health issues, including respiratory problems, nervous system disorders, and cancer.

Flammability: Polystyrene is highly flammable, and when it burns, it releases toxic fumes, such as carbon monoxide, which can be harmful to human

Health Brittleness: Polystyrene can be brittle and easily breakable, which can make it unsuitable for certain applications.

Poor heat resistance: Polystyrene has a low melting point, which means that it can melt or deform when exposed to high temperatures, making it unsuitable for some applications that require high heat resistance.

Not suitable for hot liquids: Polystyrene foam cups and plates are not suitable for hot liquids as they can release toxic chemicals into the food or drink. Overall, the use of polystyrene should be carefully considered, and alternatives should be explored wherever possible to reduce its negative impact on the environment and human health**.[12]**

I.3.6 Applications of polystyrene

(1) PS in Electronics

The electronic industry uses PS in the manufacturing of telivions and in computers as different types of emerging trends which follows the norms for its use such as combination of function, form and aesthetics and a high performance as well as cost ratio. With the advancement of disposable cutlery, the life of individual has become very easy and comfortable as the sheet or moulded form of PS is serving and the enormous utility in the production of plastic cutlery which is once used and thrown away. It is also the preferred choice now a days as media enclosures, cassette tape and jewellery boxes for protecting CD‘s and DVD cases and many devices that are used in the information technology sector. PS is fit for manufacturing various household appliances like blenders, air conditioners, refrigerators, hot air and microwave ovens, hand-held vacuum cleaners. The increased uses of PS in the industrial sector is due to its easy production processing, capability of imparting an easy and clear cut end of the appliances while meeting almost all the end product requirements. The consumer goods such as kitchen and bathroom accessories, lawn accessories are found to be produced by inculcating PS in the process of synthesis and manufacture. The availability of PS in economical prices compared with many other polymers and convenient to processing into desired shapes and sizes are especially making it to use in toys and other playing accessories, injection-molding, extrusion, thermoforming and smoke detecting alarms when the fire flares up.

(2) PS in Automotives

PS in automotives are quiet randomly used for various purposes by making of use of its characteristics such as thermal stability at a broader temperature range, high mechanical strength along with other elements, conductivity when used in ionic form, economical, recyclable, moisture free, etc. The commonly manufactured products in the automobile industry includes the bumper cores, boot in-fills, void fillers, roof liners, head rests, head impact, knee bolsters, side-impact protection, car seating, sun visors, car air conditioning liners, under bonnet battery liners, under bonnet sound deadening and material handling dunnage.

(3) **PS in Food Packaging**

PS is used as an insulator and food protector in the food packing process. The various food items like meat, fish, eggs, dairy products, salads, cold drink carry out meals can be prevented from decomposition/spoiling by packing it in PS material and is an easy and less expensive way of preserving food. Only because of PS role in packaging industry in terms of the goods packaging, refrigeration and transportation in developed countries ensured that only a 2% of food is that gets spoiled when compared with developing or underdeveloped countries where PS revolution has not started. The PS packaging materials are versatile and can serve as disposables for food having rigid packing and are recyclable. To transport other consumer goods and health care products (pharmaceuticals, neutraceuticals, etc) across the countries, they are packed in boxes along with PS as a supporting materials and also to provide insulation and protection from various external factors like moisture, air and temperature by maintaining its properties at all conditions

(4) PS in Construction

PS resin, a long chain hydrocarbon has an excellent insulation capacity and so it can be used in building and construction industry as for insulating the ceilings, walls, floors, roofing, siding, panels, bath and shower units, in addition to lighting and plumbing fixtures to get rid of external temperature differences and humidity. The PS resin of chemical compound are mainly required for lighting and plumbing fixtures, panels and slidings used during the construction purposes. The polymers also find its utility in soundproofing walls of buildings 278 Tanvir Arfin, Faruq Mohammad and Nor Azah Yusof due to its properties of good processing ability and excellent performances at all climatic conditions

(5) PS in Medical Sector

PS has a wide range of utility in medical field. The use of PS advances the technology to the patient and physician as its versatility had made it to be more suitable for use in the medical field. It is highly preferable for making medical equipments due to its excellent clarity which helps in good visibility and outstanding sterilization process. PS resins are used in the manufacturing of disposable medical appliances which includes the tissue culture plates, trays for conducting test, petri dishes, test tubes and kits for housing test which is involved in biomedical research. Many diagnostic test equipments and components made up of PS such as medical cups, medical keyboards, plastic boxes, vaginal dilator speculum are also under every day use.

(6) PS in Crafts

PS uses are also highly influencing the art and crafts sector. Extruded PS or Styrofoam is a special form of the polymer having closed cell which is used for art and craft projects. The material or the equipments are easily cut into various shapes and sizes for ornamenting it to amazing craft pieces which is of excellent beauty. Craft materials such as candle holders and ornaments for decorating christmas tree are generally made of Styrofoam. For making and manufacturing the model of architectural designs, PS is mainly used which can be replace in convenience for corrugated cardboards**.[13]**

I.3.7 Manufacturing processes of polystyrene

Polystyrene is easily manufactured by the free radical polymerization of styrene using free-radical initiators **(Figure I.12).** Styrene with or without diluents is mixed with a free radical initiator like dibenzoyl peroxide and heated to a temperature of 120°C. Several stages of polymerization results in a polymer dissolved in the monomer or the diluent solution. The unreacted monomer and diluent are flashed off under vacuum leaving the high molecular weight polystyrene.

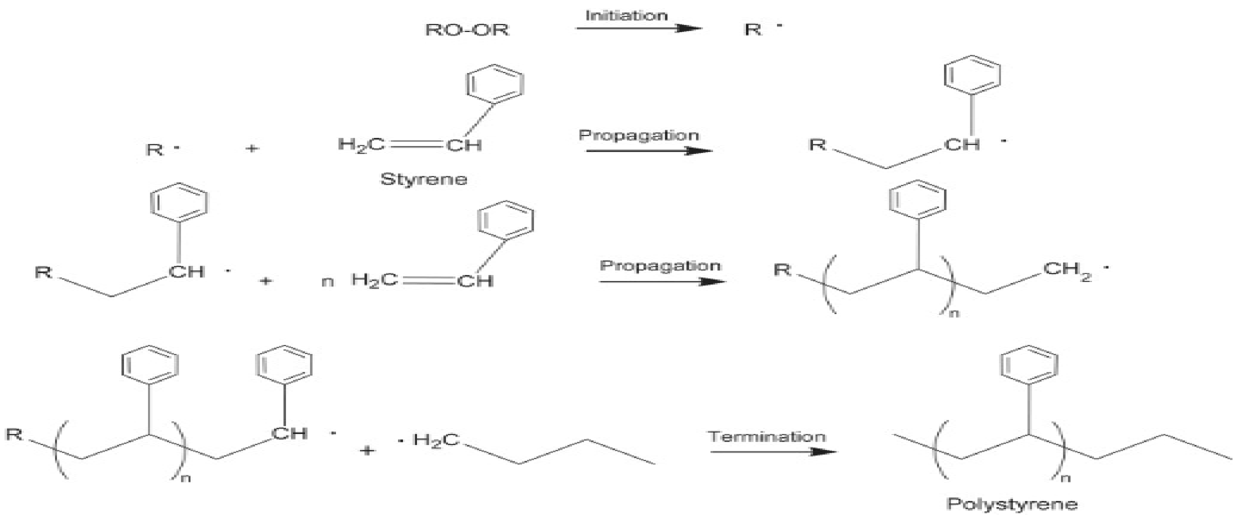


Figure I.12 Free radical polymerization of polystyrene.

High impact polystyrene is manufactured by the inclusion of a rubber like polybutadiene during polymerization. During polymerization, the polybutadiene is encapsulated into the polystyrene. Grafts and partial cross-linking of the butadiene can also take place affecting the final polymer's properties.

Syndiotactic polystyrene (sPS) was first commercialized by Idemitsu Petrochemical Company, Ltd. of Japan and developed jointly with Dow in 1988. Syndiotactic polystyrene is a new semicrystalline engineering polymer and is produced by a continuous polymerization process using metallocene catalysts similar to those used for polyolefins.Like conventional amorphous polystyrene, sPS is brittle but can be reinforced with glass or alloyed with other polymers to improve toughness. sPS is extremely chemically resistant and has a high melting point (270 °C) and very low dielectric constant. Its high flow and processing ease make it an excellent candidate for thin wall applications.**[14]**

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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, ΔGm. For miscibility of blends following inequality must be hold for

$$\Delta Gm = \Delta Hm - T\Delta Sm < 0 \qquad \textbf{(II.1)}$$

Where, ΔGm is the free energy of mixing per unit volume and ΔHm and ΔSm are enthalpy and entropy of mixing respectively. ΔHm 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 ΔGm become more positive due to the major contribution of the positive enthalpy of mixing. The sign of ΔGm depends on the value of the enthalpy of mixing, ΔHm 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 ΔGm, the following inequality must also hold **[18],**

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

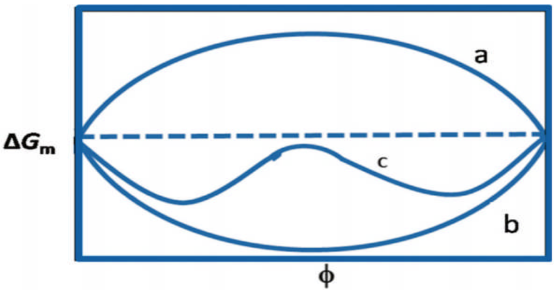


Figure II.1 Free energy of mixing for **(a)** completely immiscible, **(b)** completely miscible, and **(c)** partially miscible **[4, 21].**

Where **ϕi** represents the volume fraction of component, **T** represents the fixed temperature and **p** represent fixed pressure. ΔGm 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.

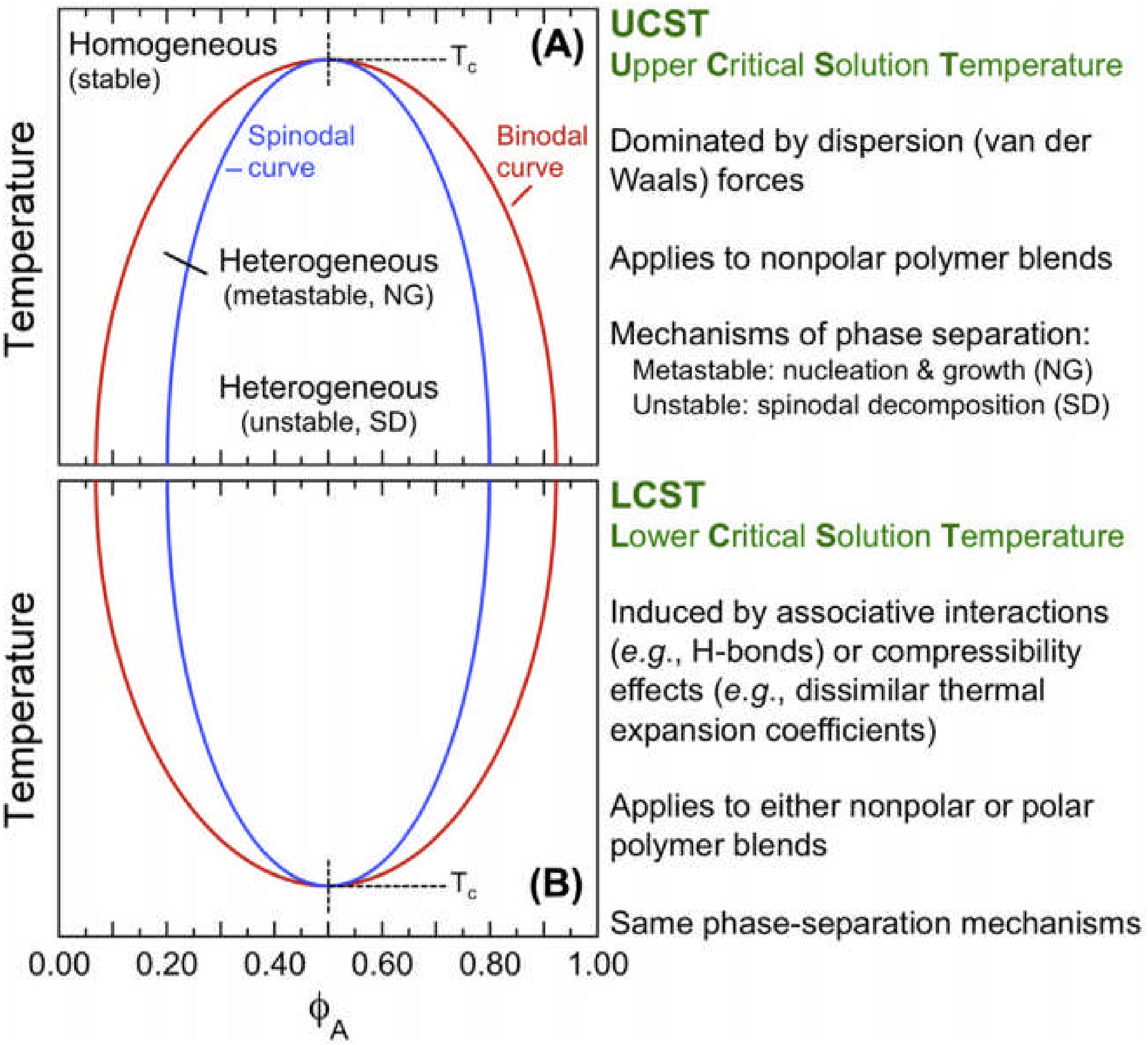
$$\text{Spinodal:}\ \left(\frac{\partial^2 \Delta G_{\mathrm{m}}}{\partial \phi^2}\right)_{P,T} = 0 \qquad \textbf{(II.3)}$$

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 (μ) of each polymer components in the binary system.

$$\Delta\mu_1^a = \Delta\mu_1^b \quad \Delta\mu_2^a = \Delta\mu_2^b \qquad \textbf{(II.4)}$$

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



Dominated by dispersion (van der Waals) forces

Applies to nonpolar polymer blends

Mechanisms of phase separation:
Metastable: nucleation & growth (NG)
Unstable: spinodal decomposition (SD)

Induced by associative interactions (*e.g.*, H-bonds) or compressibility effects (*e.g.*, dissimilar thermal expansion coefficients)

Applies to either nonpolar or polar polymer blends

Same phase-separation mechanisms

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.

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

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,

$$\Delta G_{\mathrm{m}} = RT\left[\frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \chi\phi_1\phi_2\right] \qquad \textbf{(II.6)}$$

Here **R** is the universal gas constant and **T** is the absolute temperature. Ø1and Ø 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 χ 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,

$$\Delta S_{\mathrm{m}} = -R\left[\frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2\right] \qquad \textbf{(II.7)}$$

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

$$\Delta H_{\mathrm{m}} = RT\chi\phi_1\phi_2 \qquad \textbf{(II.8)}$$

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 χ is negative, miscibility can be observed for the system (ΔHm<0). Miscibility of the system occurs at $\chi<\chi_{cr}$ where χ_{cr} is χ parameter at the critical point (function of the molar masses) and it can be expressed as

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

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 (Tg), and is in between the Tgs of both blend components. In the case of miscible blends, $\Delta Hm<0$ 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 (Tg) can be considered as a general method to judge the miscibility of blends. As already discussed single Tg of blend represents a miscible blend and two Tg represents a phase separated blend system. The main experimental techniques which are generally used to measure Tg 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 Tg and both the Tgs are shifted from the values for the pure blend components toward the Tg 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 (Tgs) and melting temperatures (Tms) 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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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 activate 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 discusses 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 the 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.

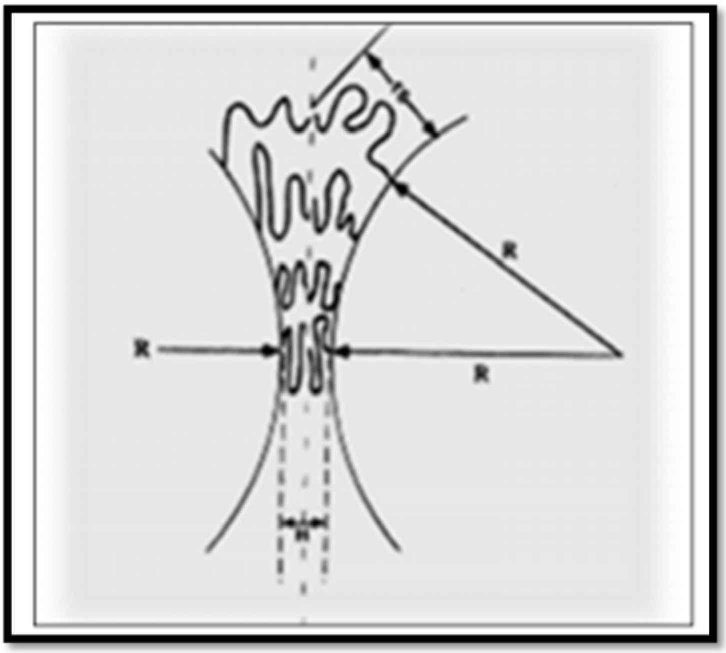

Figure III.1 Steric hinderence by compatibilizers. Compatibilizers acting as both anchors and repulsive springs ensuring the stability and prevention to coalescence **[16].**

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 booming 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 donoreacceptor 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 acide-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 synthetics polymers have been utilized in various applications such as tissue engineering, biosensors, and drug delivery pursuing such developments. Natural polymers due to the 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.

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CHAPTER IV

Literature Review

IV.1 Literature Review

In this section and for the sake of illustration, a brief presentation of the some of the works has been published to cover all aspects of the subject. The following research works are presented in the chronological order.

For example; **Guangxue Xu and Shangan Lin [1]**, have studied the effect of 50/50 diblock isotactic polystyrene-isotactic polypropylene (iPS-b-iPP) as a compatibilising agent in isotactic polystyrene / isotactic polypropylene (iPS/iPP) blends. The morphological as well as mechanical properties were also investigated by means of scanning electron microscopy (SEM), and tensile measurements. The morphological examination of the iPS/iPP system pairs unambiguously support the interfacial activity of the iPS-b-iPP diblock copolymer as both that of a dispersant and an 'anchoring' compatibilizer. The addition of less than 10 wt % of this diblock copolymer to an iPS/iPP blend has a large compatibilizing effect on its morphological properties, showing the importance of the interfacial adhesion between the two components of a incompatible iPS/iPP blend. Not only is the phase size dramatically reduced but also the phase dispersion and the interphase interactions are significantly increased when the compatibilizer is added. Improvements in the mechanical properties of iPS/iPP blends containing compatibilizers have been noted. The addition of the diblock copolymer significantly promotes an enhancement of the tensile strength, elongation at break as well as Izod impact strength of the control iPS/iPP systems.

In another study, **L. D'orazio et al [2]** have studied the effects of the addition of a graft copolymer of Propylene with Styrene (PP-g-PS) as a compatibilizer in the morphological and Thermal behavior of Isotactic Polypropylene/Polystyrene Blends. Morphological examinations as well as thermal properties were investigated by means of Optical Microscopy, and Differential Scanning Calorimetry (DSC), respectively. They have found that the presence of the PP-g-PS copolymer affects the interfacial interaction and interfacial tension between the iPP and aPS phases in the melt state, with the aPS particle size and the particle-size distribution being, in fact, strongly modified. Their results indicated that, relevant thermodynamic parameters of the iPP phase, such as the equilibrium melting temperature (Tm) and the folding surface free energy (σe) of the lamellar crystals were found to be influenced by the presence of the PP-g-PS copolymer. A linear decrease of the melting temperature (Tm) and σe values with increasing PP-g-PS content was, in fact, observed. Such results have been accounted for by an increase of the presence of defects along the iPP crystallizable sequences and by the very irregular and perturbed surface of the crystals with increasing copolymer content. The observed decrease in melting temperature values revealed, moreover, that, in the iPP/aPS/PP-g-PS blends.

G. Radonjic and coworkers [3] have investigated the effects of the poly(styrene-b-butadiene-b-styrene) (SBS) as a compatibilizing agent in the morphological and mechanical properties of immiscible polypropylene/polystyrene (PP/PS) thermoplastic polymer blends. Blends with three different weight ratios of PP and PS were prepared by an internal mixer at temperature of 200°C, and a rotor speed of 50 rpm for 6 minutes, and three different concentrations of SBS were used for investigations of its compatibilizing effects. From their results, Scanning electron microscopy (SEM) showed that SBS reduced the diameter of the PS-dispersed particles as well as improved the interfacial adhesion between the matrix and the dispersed phase (i.e: PP matrix, and PS). The mechanical properties in terms of tensile strength, Young's modulus, and elongation at break, shows a trend of increased tensile strength and modulus and a decrease of the elongation at break. This means that the addition of SBS increased the capacity of the blends to withstand the tensile load and therefore led to an enhanced mechanical resistance. This could be attributed to a reduction of the interfacial tension and an enhanced the interphase interactions imparted by the SBS compatibilizer.

In another publication, Compatibilizing effects of styrene/rubber block copolymers poly(styrene-b-butadiene-b-styrene) (SBS), poly(styrene-b-ethylene-co-propylene) (SEP), and two types of poly(styrene-b-ethylene-co-butylene-b-styrene) (SEBS), which differ in their molecular weights on morphological properties of immiscible polypropylene/polystyrene (PP/PS) 70/30 blend were investigated by **G. Radonjic [4].** Three different concentrations of styrene/rubber block copolymers were used (2.5, 5, and 10 wt %). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to examine the phase morphology of blends. The SEM analysis revealed that the size of the dispersed particles decreases as the content of the compatibilizer increases. The SEM analysis confirmed improved interfacial adhesion between matrix and dispersed phase. The TEM micrographs showed that SBS, SEP, and low-molecular weight SEBS enveloped and joined pure PS particles into complex dispersed aggregates.

In another study, **P.H.P. Macau´bas, and N.R. Demarquette [5]** have reported the compatibilization of immiscible polypropylene/ polystyrene (90/10) blends using styrene–butadiene–styrene (SBS) as well as styrene–ethylene/butylene–styrene (SEBS) triblock copolymer as compatibilizers. The possibility of inferring the interfacial tension between the two polymer phases (i.e: PP and PS) as a function of amount of triblock copolymer added to the blend using the morphological measurements was investigated. The concentration of compatibilizers ranged from 0 to 25% relative to the weight of the dispersed phase (PS). They have found the addition of compatibilizers resulted in a reduction of the size of the dispersed PS phase particles in the PP matrix. The addition of compatibilizers to the PP/PS blend resulted in a reduction of interfacial tension and improves the interfacial adhesion. The morphological and interfacial tension results showed that SEBS is a better compatibilizer for the PP/PS blend compared to those of SBS.

J.Kim and co-workers [6] have studied the compatibilization of PP/PS thermoplastic polymer blends using PE-g-PS as a compatibilizing agent. The effects of PE-g-PS on the morphological and thermal properties of the PP/PS blend were investigated. The thermal properties as well as the morphological examinations of the PP/PS samples were also reported by means of DSC analysis and SEM microscopy, respectively. They have found that the crystallization temperature of the PP in the PP/PS decreased with increasing the PE-g-PP contents. The addition of PE-g-PS has led to the decrease in the degree of crystallinity and crystallization temperature, due to the lack of mobility of PP chains in the PP/PS systems. In the presence of the compatibilizer, PP chains have difficulty in forming crystals due to the developed interactions with PP/PE-g-PS/PS. Morphologies of the PP/PE-g-PS/PS showed much better dispersion of minor phase in the major phase especially for higher PE-g-PP concentrations.

In another article, **J.Pionteck et al [7]** have studied the morphological properties of the reactive blending of PP/PS system. The morphological examination was investigated by means of Scanning Electron Microscopy (SEM). To investigated the reactive compatibilization of PP/PS, main chain and functionalized of both polymers (i.e: PP, and PS) have been synthesized by different methods of grafting with Hyperbranched polymer (HBP). The morphological results indicated a finer phase dispersion of minor phase in the major phase for the compatibilized blends compared to those of the uncompatibilized ones. This could be attributed to develop of the interfacial interactions between the two phases imparted by the functional groups grafting in the polymer chains.

Yu Zhang et al [8] have reported the crystallization behavior and dynamic mechanical properties of Polypropylene/Polystyrene PP/PS blends modified with maleic anhydride and styrene. Polypropylene (PP)/polystyrene (PS) blends modified with reactive monomers, such as maleic anhydride (MAH) and styrene (St), and in situ formed PP/PS blends were prepared by melting extrusion. The structure of the grafted copolymer, the crystallization, melting behavior and the dynamic mechanical properties of the PP/PS blends were investigated with Fourier transform infrared, differential scanning calorimetry, and dynamic mechanical analysis, respectively. The FTIR results indicated that MA-g-PS was formed in PP/PS blends modified by MAH. However, the formation of MA-g-PP was observed in PP/PS blends modified by MAH and St Co-monomers. In PP modified by the co-monomer, the formation of MA-g-PP was more significant. The thermal results indicated that the addition of MAH hardly influenced the crystallization temperature of PP in the blends, but the addition of MAH and St increased the crystallization temperature of PP in its blends. The blends showed no remarkable variety for the melting temperature, but the shapes of the melting peaks were influenced by the addition of the reactive monomers. In addition, a significant increase in the storage and loss moduli of all the modified PP/PS blends was observed. They have also found that the addition of PS to PP hardly changed the crystallization and melting behavior of PP, just like the addition of MAH to PP/PS blends. However, MAH could significantly increase the storage modulus and loss modulus of the blends. Moreover, the blends modified with MAH shifted Tg of PP to a lower temperature region. It was suggested by IR results that MA-g-PS was the main grafting product in the blends.

To understand more the effect of reactive compatibilization in the PS/PP thermoplastic polymer system; A novel reactive compatibilization strategy on immiscible PP/PS was investigated by **C.Hung and co-workers [9].** PP and PS are immiscible and incompatible blends. Since both PP and PS components possess no reactive functional group, reactive compatibilization of a PP/PS blend is impossible unless certain reactive functional groups are imparted to either PP or PS. In their study, they provide a simple approach to reactively compatibilize the PP/PS blend system by chemically functionalizing PP and PS with the addition of maleic anhydride grafted PP (PP-g-MA) and styrene maleic anhydride random copolymer (SMA), respectively. An epoxy monomer, serving as a coupler and possessing four epoxy groups able to react with the maleic anhydride of PP-g-MA and SMA, was then added during melt blending. The morphological as well as mechanical properties of the PP/PS blends were reported by means of SEM, tensile and flexural tests, respectively. They have found that the PS domain size is significantly reduced for those compatibilized PP/PS blends from the SEM graphs. The tensile strength and flexural modulus of the compatibilized PP/PS blends are substantially improved compared to those of the uncompatibilized systems.

In another publication, **A.Abd Aziz et al [10]** have investigated the effect of multiple compatibilizers on the impact properties of Polypropylene/Polystyrene (PP/PS) blend. Effects of compatibilizers on impact properties of polypropylene/ polystyrene (PP/PS) blends were studied and carried out through melt blending using co-rotating twin-screw extruder. A combination of two compatibilizers, maleic anhydride grafted polypropylene (PP-g-MA) and styrene maleic anhydride (SMA) was applied into PP/PS blends. The mechanical as well as the morphological properties were investigated for the uncompatibilized and compatibilized blends by means of impact strength test, and scanning electron microscopy. The results from the Izod impact strengths, SEM observations and contact angle measurements in 50/50 PP/PS blends indicated a better compatibilization effect with the use of dual compatibilizers. This was most probably due to improved adhesion between phases in PP/PS blend systems. The use of dual compatibilizers in the blend compositions produced higher impact properties in the PP/PS blend systems compared to single compatibilizer system.

In another study, **Na Wang et al [11]** have studied the Compatibilizing Effects of MCM-41 and PP-g-MAH on the Mechanical and Thermal Analyzer of PP/PS Blends. The effects of the MCM-41 and PP-g-MAH on the mechanical and crystallization properties of PP/PS composites were investigated by means of tensile test, impact strength, and dynamic mechanical thermal analysis (DMTA),respectively. The results of mechanical tests showed that the co-incorporation of MCM-41 filler and PP-g-MAH gave rise to much better tensile and impact strength than adding of MCM-41 and PP-g-MAH respectively due to different interfacial structure between the fillers and the matrix. DMA attested that the good adhesion between PP/PS blend was obtained by addingMCM-41 and PP-g-MAH fillers.

In another article; the effects of polypropylene-graft-maleic anhydride on the morphology and dynamic mechanical properties of polypropylene/polystyrene blends have reported by **J.r Parameswaranpillai et al [12].** Polypropylene (PP) and polystyrene (PS) blends were prepared by melt processing in a Haake at 180 °C. PP/PS blends are immiscible and the blend morphologies were characterized by scanning electron microscopy. The viscoelastic properties were characterized using dynamic mechanical analysis (DMA) with reference to blend ratio.

The blend morphologies such as matrix droplet and phase inverted morphologies were observed. The storage modulus of the blends increased with increase in PS content and the value was maximum for neat PS. DMA showed changes in the polystyrene glass transition temperatures (Tg) over the entire composition range. There was a sharp increase in the Tg of PS with increasing PP content in the blend and a 12°C elevation in Tg was observed. The increase in Tg was explained by proposing a new model based on the physical interaction between the blend components. It is assumed that the different effects by the PP phase resulted in the formation of constrained PS chains leading to high Tg values. The addition of PP-g-MAH has a positive effect on the morphology, and increases the storage modulus of the compatibilized PP/PS systems.

The Compatibilization Effects of Alkylated-grafted-Graphene Oxide on Polypropylene/Polystyrene Blends were investigated by **Y.Hao and co-workers [13].** Modified graphene oxide (GO) was synthesized by covalently grafted alkylated chains on GO sheets and their compatibilization effects on the morphologies and mechanical properties of immiscible polypropylene/polystyrene (PP/PS) blends were studied. Alkylated-grafted-GO/PP/PS batches were fabricated by melt-mixing approach and displayed different morphologies with various modified GO loadings. When the content of alkylated-grafted-GO is 0.2 wt%, the tensile strength of obtained composite could reach 17.97 MPa, showing a 36.3% enhancement compared to that of pristine PP/PS, indicating the positive compatibilization of modified GO in polymer blends. Moreover, the mixing order also plays an important role in achieving the desired improvement in properties. Due to the preferential location of modified GO in PP phase, a favorable “transition zone” could be formed at the interfacial region of two polymers when alkylated-grafted-GO was premixed with PS and subsequently mixed with PP, leading to an improvement of compatibilization between two polymers and an enhancement of mechanical properties. However, serious phase separation and declined tensile strength were obtained with a reversed mixing sequence.

F. B. de Mello et al [14] have investigated the effects of compatibilization on the mechanical behavior, morphological examination, and rheological properties of PP/HIPS blends using styrene–ethylene–butylene–styrene (SEBS) block copolymer, styrene–butadiene–styrene (SBS), and ethylene vinyl acetate as a compatibilizers (From 2.5 to 7.5 wt%). The mechanical, morphological, as well as rheological properties were also evaluated by means of tensile, impact strength, SEM micrographs, and Melt flow index, respectively. They have found that the blend containing SBS and 7.5 wt% of SEBS showed a positive effect regarding impact strength, although with a decrease in Young’s modulus and tensile strength. However, the use of EVA as compatibilizer did not prove effective. Compression-molded samples of the SBS and SEBS compatibilized blends showed improved mechanical properties compared to the uncompatibilized blend, mainly regarding impact strength, although some domains were dispersed in the matrix. However, due to the coarse morphology formed during mixing, blends compatibilized with EVA did not show a positive effect on mechanical properties compared with the blend without compatibilizer. It is possible also to observe that the addition of SBS and SEBS decreased the size of the dispersed particles, showing an interesting compatibilizing effect. As for the rheological characteristics, the blends compatibilized with SBS and SEBS showed greater viscosities at low shear rates compared to the uncompatibilized blend or the blend compatibilized with EVA due to the interfacial adhesion.

Z. Starý et cowerkers [15] have studied a new multicomponent compatibilization system for Polyolefin/Polystyrene blends. An efficient compatibilization system based on a combination of styrene-butadiene block copolymer (SBS) with ethane-propene random copolymer (EPM) has been developed for polyolefin/polystyrene blends. Model blends of polypropylene and polystyrene have been taken for compatibilization studies. Concentration of combined compatibilizer in all studied blends was 5 or 10 wt. %. The ratio of EPM/SBS in the compatibilizers was varied from 4/1 to 1/4. Tensile impact strength was used as the main criterion of compatibilization efficiency. Besides mechanical properties, basic morphological investigation of the prepared blends was carried out. The compatibilization efficiency of the EPM/SBS system in PS/PP blends depends on the type of blend matrix. Generally, the use of EPM/SBS leads to better or comparable mechanical properties of final polystyrene/polypropylene blends compared with those using common SBS compatibilizers.

It can be stated that combination of EPM and SBS is an efficient compatibilizer for PS/PP blends. Localization of the compatibilization system in the blend depends on its composition and also on the matrix type. Synergic activity of EPM and SBS was found for the blends with PS matrix. In the case of PS/PP 75/25 and 50/50 blends, EPM and SBS are concentrated at the interface in the form of double-layer, which shows a higher compatibilization efficiency than the simple SBS compatibilizer. In the blends with polypropylene matrix, EPM was not clearly identifiable at the interface and also toughness was practically the same as in the blends compatibilized with simple SBS compatibilizer. Hence, EPM is scattered in the PP matrix and therefore it is inactive as a compatibilizer. In these blends, SBS is located not only at the

PS/PP interface but forms partitions in PS particles. Application of the EPM/SBS compatibilization system leads to an increase in elongation at break and tensile strength together with a drop of Young’s modulus. Generally, the use of the EPM/SBS system results in better or the same mechanical properties of polystyrene/polypropylene blends in comparison with usual SBS compatibilizers in spite of the fact that neat EPM does not act as a compatibilizer in the studied blends.

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Conclusion

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 co-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.

Melt-blending of different polymers is a more effective and less expensive method of producing multiphase new materials. Polypropylene (PP), polystyrene (PS) and their blends are the most widely used polymeric materials for making variety of commercial and industrial products, since both PS and PP are very cheap and are easily processable. Plethora of studies has been reported for PP/PS system, mainly focused on the morphology, rheology, and mechanical, crystallization, and viscoelastic properties. However, PP/PS blends are immiscible due to the semi-crystallinity of PP phase and make these polymer pairs chemically and mechanically incompatible. This incompatibility between the blend components leads to extensive phase separation with poor interfacial adhesion. PS is one of the most brittle engineering plastic materials, blending PS with PP leads to relatively poor mechanical properties. The incompatibility of PP/PS blends can be reduced by the incorporation of block and graft copolymer compatibilizing agents such as styrene-butadiene (SB), styrene-butadiene-styrene (SBS), styrene–ethylene-butylene–styrene (SEBS), polyethylene-graft-polystyrene (PE-g-PS), polypropylene-graft-polystyrene (PP-g-PS) ,and polypropylene-graft-maleic anhydride (PP-g-MAH). Besides, adding these agents directly, compatibilizer can be produced by in-situ reaction. It is important to mention that, the reactive compatibilization is preferred over simple addition of compatibilizer over the blend components. In both routes, compatibilizer forms an interfacial layer at the interface between the two polymers and reduces the interfacial energy of the phases, stabilizes the morphology against coalescence and improves the interfacial adhesion between the phases, leading to better properties.

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.

Abstract

Abstract

This Master Thesis aims to investigate the effects of various compatibilizers on the Rheological, Mechanical and Morphology properties of polypropylene (PP) and polystyrene (PS) blends. PP and PS are immiscible polymers, resulting in poor interfacial adhesion between them, which leads to inferior mechanical properties of the resulting blends. To improve the compatibility between PP and PS, different compatibilizers, including maleic anhydride grafted PP (PP-g-MAH) and styrene-maleic anhydride copolymer (SMA), were used.

The effect of different compatibilizers on the morphology and mechanical properties of the PP/PS blends was investigated. The results showed that the addition of compatibilizers improved the interfacial adhesion between PP and PS, resulting in enhanced mechanical properties of the blends. Furthermore, the morphology of the blends was also improved, as evidenced by the reduction in the size of minor phase dispersed in the major matrix.

The findings of this research can have potential applications in various industries, including packaging, automotive, and construction, where PP/PS blends are commonly used.

Keywords: Polypropylene, Polystyrene, Immiscible Blends, Compatibilizers,

Résumé

Ce Mémoire de Master vise à étudier les effets des différentes compatibilisateur sur les propriétés rhéologiques, mécaniques et morphologiques des mélanges de polypropylène (PP) et de polystyrène (PS). Le PP et le PS sont des polymères non miscibles, ce qui entraîne une mauvaise adhérence interfaciale entre eux, ce qui entraîne des propriétés mécaniques inférieures des mélanges résultants. Pour améliorer la compatibilité entre PP et PS, différents compatibilisateurs, y compris le PP greffé à l'anhydride maléique (PP-g-MAH) et le copolymère styrène-anhydride maléique (SMA), ont été utilisés.

L'effet de différents compatibilisateurs sur la morphologie et les propriétés mécaniques des mélanges PP/PS a été étudié. Les résultats ont montré que l'ajout de compatibilisateurs a amélioré l'adhérence interfaciale entre PP et PS, ce qui a amélioré les propriétés mécaniques des mélanges. En outre, la morphologie des mélanges a également été améliorée, comme en témoigne la réduction de la taille de la phase mineure dispersée dans la matrice majeure.

Les résultats de cette recherche peuvent avoir des applications potentielles dans diverses industries, y compris l'emballage, l'automobile et la construction, où les mélanges PP/PS sont couramment utilisés.

Mots clés: Polypropylène, Polystyrène, Mélange Non-Miscibles, Agent de Compatibilization

ملخص

تهدف هذه الرسالة الرئيسية إلى التحقيق في تأثيرات الموافقات المختلفة على الخصائص الريولوجية والميكانيكية والمورفولوجية لمزيج البولي بروبيلين (PP) والبوليسترين (PS). PP و PS هي بوليمرات غير قابلة للخلط، مما يؤدي إلى ضعف الالتصاق البيني بينهما، مما يؤدي إلى خصائص ميكانيكية أدنى للخلطات الناتجة. لتحسين التوافق بين PP و PS، تم استخدام موافقات مختلفة، بما في ذلك أنهيدريد الماليك المطعم PP (PP-g-MAH) والستيرين الماليك أنهيدريد البوليمر المشترك.(SMA)

تم فحص تأثير معاملات التوافق المختلفة على التشكل والخصائص الميكانيكية لخلطات PP/PS ، حيث أظهرت النتائج أن إضافة أجهزة التوافق حسنت الالتصاق البيني بين PP وPS ، مما أدى إلى تحسين الخصائص الميكانيكية للخلطات. علاوة على ذلك، تم أيضًا تحسين مورفولوجيا الخلائط، كما يتضح من انخفاض حجم المرحلة الثانوية المنتشرة في المصفوفة الرئيسية.

يمكن أن يكون لنتائج هذا البحث تطبيقات محتملة في صناعات مختلفة، بما في ذلك التغليف والسيارات والبناء، حيث يتم استخدام مزيج PP/PS بشكل شائع.

الكلمات المفتاحية:

البولي بروبيلين ،البوليسترين ، بوليمرات غير قابلة للخلط، معاملات التوافق.