REPUBLIQUE ALGERIENNE DEMOCRATIQUE ET POPULAIRE

MINISTERE DE L'ENSEIGNEMENT SUPERIEUR ET DE LA RECHERCHE SCIENTIFIQUE

UNIVERSITE DE20AOUT 1955 SKIKDA

FACULTE DE TECHNOLOGIE

DEPARTEMENT DE GENIE DES PROCEDES

Mémoire

En vue de l'obtention du diplôme de

Master

Filière : Génie des Procédés

Spécialité : Génie des Polymères

Compatibilization Of High Density Polyethylene and Poly (Ethylene Terephthalate) (HDPE/PET) Immiscible Thermoplastic Polymer Blends for Enhancing Their Rheological, Mechanical, Morphological Properties and Sustainable Development of Thermoplastic Blend Materials.

Soutenu le **26 Juin2023**

Réalisé par :

1-DJEGHIOUR Maria

2-RAMDANE Wissal

3-BOUIDIOUA Maroua

Encadré par :

Dr. BELHAOUES Abderrahmane

Année Universitaire **2022- 2023**

Dedication

Dedications

We would like to dedicate our Master-thesis:

- To our family especially our parents whose unbelievable endurance, unconditional love, and untouchable devotion have been monumental;

-To all our brothers and sisters;

-To those who will be happy with this new goal in our study career;

-To all our best friends;

- To anyone who has ever taught us anything.

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

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

Acknowledgements

Acknowledgements

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

All praises to Allah the Almighty for giving us the strengths, guidance, and patience in completing this Master-thesis. With His blessing, this Master-thesis is finally accomplished.

First of all, there are a lot of people that helped us significantly throughout these years to reach the end of this beautiful journey. All those people were very influential and supportive, and we would like to thank them and show our appreciation for what they did.

We would like to take this opportunity, first and foremost, to express our heartiest thanks and deep gratitude to our supervisor, *Dr. Belhaoues Abderrahmane* for his helpful guidance, valuable discussions, and support throughout this bibliographic research.

We wish to express our gratitude to *Dr. Krid Ferial* the Head of the Process Engineering Department, Faculty of Technology, Skikda University, for all kinds of official help, and for offering facilities and support to carry out this bibliographic research.

We would like also to place on record our great appreciation to all our teachers at Skikda-University, where we have studied a Polymer Engineering specialty.

These acknowledgments would not be complete without thought to our family. We want to especially express our deep gratitude to our dearest parents for their endless support. They have always been there for us during all these years of study and encouraged us to finish our Master's studies.

Last but not the least; we would like to thank each and every member of our family, who spurred our efforts with their love and affection, inspiration, and care.

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

Table of Contents

Table of contents

Contents **Page**

Chapter I

Theoretical background

Chapter II

Thermodynamics of Polymer Blends

Chapter III

Compatibilization of Polymer Blends

Chapter IV

Literature Review

List of Figures

List of Figures

List of Figures **Page**

Chapter I Theoretical Background

List of Figures

Chapter II Thermodynamics of Polymer Blends

Chapter III Compatibilization of Polymer Blends

List of Tables

List of Tables **Page**

Chapter I

Theoretical Background

Chapter II

Thermodynamics of Polymer Blends

List
Of
Notations
and
Abbreviations

List of Notations and Abbreviations

Abbreviations	Description
BR	Butadiene Rubber
BHI	Blocked Isocyanate
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimeter
ENR	Epoxidized Natural Rubber
EPDM	Ethylene propylene diene rubber
EVA	Ethylene vinyl acetate
EPR	Ethylene propylene rubber
EBAGMA	Ethylene–Butyl Acrylate–Glycidyl Methacrylate
E /EA /GMA	ethylene/ethyl acrylate/glycidyl methacrylate
E-GMA	ethylene/glycidyl methacrylate
EPDM	Etheylene –propylene- diene monomer
EPDM-M	Etheylene –propylene- diene monomer masterbatch
FTIR	Fourier transform infrared
GMA	Glycidyl methacrylate
HDPE	High density polyethylene
HDPE-g-BHI	High-density polyethylene grafted with the blocked isocyanate
HDPE-g-MA	High density polyethylene grafted with the Maleic anhydride
HI	Isocyanate
LPE	Linear polyethylene
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
MA	Maleic anhydride
NBR	Acrylonitrile butadiene rubber
NR	Natural rubber
PE	Polyethylene
PLA	Polylactide
PMMA	Poly(methyl methacrylate)
PET	polyethylene terephthalate
PEAA	Poly(ethylene –co-acrylic)
POE-g-GMA	Polyoxyethylene-grafted- glycidyl methacrylate
PP-MAH	Polypropylene grafted with the Maleic anhydride

List of Notations and Abbreviations

PP	Polypropylene
PVC	Polyvinyl Chloride
PS	Polystyrene
SBR	Styrene Butadiene Rubber
SBS-g-GMA	Styrene Butadiene Styrene grafted with the glycidyl methacrylate
SAN	Styrene-acrylonitrile
SEM	Scanning electron microscope
Tg	Glass transition temperature
r-PET	Recycled polyethylene terephthalate
XLPE	Cross-linked polyethylene
VLDPE	Very Low Density Polyethylene

Symbols	**Description**
E	Young's modulus
E'	Storage modulus
E''	Loss modulus
ΔHm	Melting enthalpy of sample
ΔH_0	Theoretical enthalpy for 100 % crystalline
Tc	Crystallization temperature
Tg	Glass transition temperature
ρ	Density
TS	Tensile strength
m	Mass
Ɛb	Elongation at break
T	Temperature
σ	Tensile strength
ε	Strain
mm	Millimeter
ºC	Degree Celsius
%	Percent
wt%	Percent by weight
η	Viscosity

General Introduction

I. General Introduction

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

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

Interest in the development of polymer blends stems from theeconomic and environmental advantages in producing improved polymericmaterials through the blending of existing polymers, rather than throughdevelopment of new synthetic polymers. Blending may be used to combinethe attractive properties of two polymers and/or to improve the deficientproperties of a given polymer. Imparting solvent resistance to an amorphousmaterial through addition of a crystalline phase and improving the impactresistance of brittle materials through incorporation of a dispersion of rubberparticles are examples of improvements which may be made throughblending of polymers.

While some pairs of polymers exhibit complete miscibility over allranges of temperature and blend composition, the majority of polymer pairsdo not. Most polymer pairs are thermodynamically incompatible due to thesmall mixing entropy in mixtures of long chain molecules. Typical usefulblends are usually mixtures of two (or more) immiscible or partially misciblepolymers, and exhibit a microscopically inhomogeneous structure. Theproperties of immiscible blends are strongly dependent on the size anddistribution of phases and the strength of the interphase interface(s). Thedevelopment of many useful blends depends on the control of two importantaspects of their structure. First, a stable dispersion of one polymer in the othermust be realized, and second, the interface between the two polymericcomponents of the blend must be strong enough to support load transfer. Thetypical approach to managing this problem is to add block copolymer'compatibilizers' to the mixture. This technique involves adding a blockcopolymer of the type A-B to a mixture of polymers A and B. The copolymerssegregate to the A/B interfaces and act as an emulsifier thereby lowering theA/B interfacial tension, improving the resistance to particle coalescence, andstabilizing the dispersion. If the blocks of the A-B copolymers are sufficientlylong then they can extend into the homopolymer phases and entangle causingmechanical linking which leads to a strong A/B interface. The drawbacks totraditional compatibilization are: 1) separate fabrication of A-B copolymers isrequired, which is prohibitively expensive in most cases, 2) it is difficult toproperly disperse the block copolymers during processing so that they arepositioned at the interfaces, and 3) the amount of compatibilizer which may beadded is limited to low concentrations by the formation of copolymermicelles.

A novel approach to the modification of interfaces in incompatibleblends which has been recently receiving much attention is reactivecompatibilization, in which compatibilizers are formed in-situ at theinterfaces. Homopolymer blend components which have reactive groups incorporated along the chains are utilized. Functional pendant or end groupsare inherent to many types of polymers and may be added to others thoughrelatively cost efficient processes such as small-molecule grafting, conversionof existing moieties or copolymerization. The functional groups come incontact during mixing of the two polymers and react, forming bonds betweenthe homopolymers at the interfaces. Recent studies have concentrated on thecontrol of blend morphology which may be achieved through this type ofreactive compatibilization scheme. It has been demonstrated that thedispersion of the minor polymer blend component decreases in average sizewith increasing concentration of functional groups, and that a homogenousmaterial may be achieved at sufficiently high functional group concentrations.

We have chosen high-density polyethylene (HDPE) and poly(ethy1ene terephthalate) (PET) as blend components for this study. HDPE and PET are not miscible with each other. PET is widely used as an engineering thermoplastic for packaging, electronics, and other applications. When blended with other polymers, it may offer an attractive balance of mechanical and barrier properties. HDPE is also used extensivelyin packaging of consumer and industrial products. Mixtures of these two polymers constitute a significant portion of post-consumer waste, compatibilizing this pair successfully could help efforts to recycle post-consumer household waste.

Overall; This Master Thesis is composed of four chapters. The first presents atheoretical background of Polyethylene (PE), and Polyethylene terepthalate (PET); The second chapterpresents thethermodynamicsprinciples of polymer blends, , and the third chapter presents the different strategies for compatibilization of polymer blends.The fourthchapter illustratesa 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.

References

[1] Paul, D.R. Control of phase structure in polymer blends, in Functional polymers (eds D.E. Bergbreiter and C.R. Martin), Plenum Press, New York, **1989**, p. 1–18.

[2] Scobbo, J.J, Jr and Goettler, L.A. Applications of polymer alloys and blends, in Polymer Blends Handbook(ed. L.A. Utracki), Kluwer Academic Publishers, **2003**, pp. 951–976.

[3] White, J.L. and Bumm, S.H. Polymer blend compounding and processing, in Encyclopedia of Polymer Blends(eds A.I. Isayev and S. Palsule), Wiley-VCH, Weinheim, **2011** , pp. 1–26.

Chapter I

Theoretical Background

I.1 Polyethylene

I.1.1 Synthesis Methods of Polyethylene

Among industrial processes for production of polyethylene, free radical polymerizations are conducted under the most severe conditions, typically employing temperatures of >200 °C and pressures of 15,000 to 45,000 psig. Free radical polymerizations are conducted adiabatically in thick-walled autoclaves or tubing. At such high temperatures, polymerization of ethylene occurs in "solution" of polymer in excess monomer. Diluents (solvents) are not needed. Polyethylene particles precipitate from excess monomer when the reaction mix cools. Except for the reactor zones, autoclave and tubular processes are very similar. Peripherals in both cases are designed pre-reactor to ramp pressures and temperatures to very high levels and post-reactor to reduce temperatures and lower pressures to near ambient conditions to enable product isolation. Simplified process flow diagrams for the autoclave and tubular processes are shown in **Figures I.1** and **Figures I.2**, respectively. ExxonMobil has produced LDPE by both high pressure processes since the late 1960s. Schuster and Kaus have described the workings and advantages of ExxonMobil high pressure processes for LDPE **[1]**

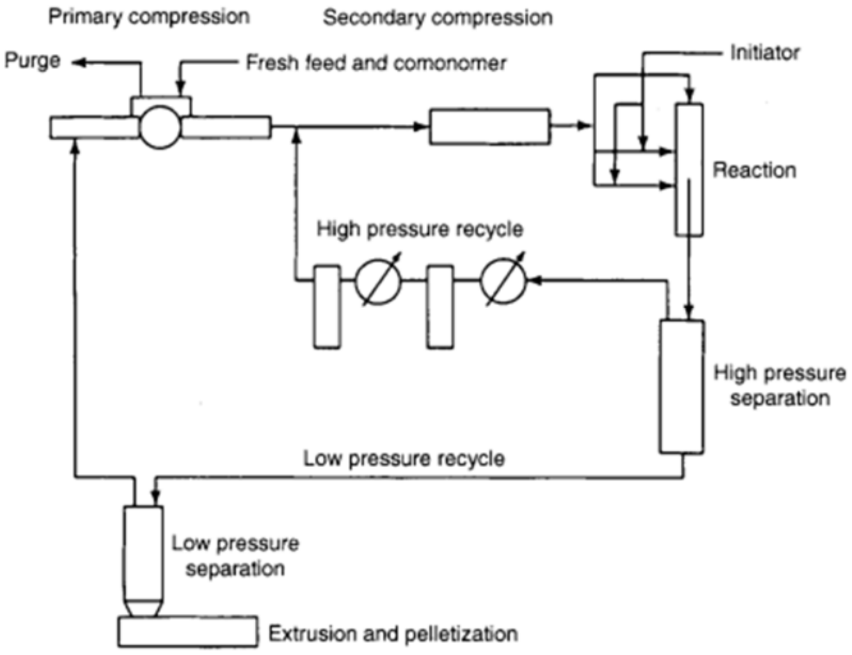


Figure I.1: Schematic process flow diagram for autoclave high pressure process for production of low density polyethylene.

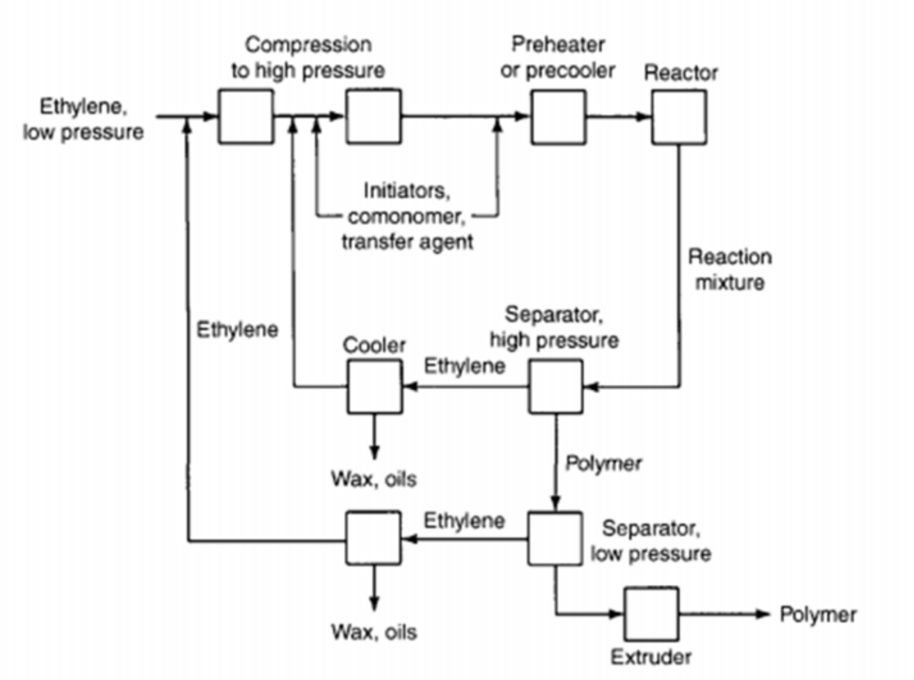


Figure I.2: Schematic process flow diagram for tubular high pressure process for production of low density polyethylene.

I.1.1.1 Autoclave Process

The original process for high pressure polyethylene was based on use of a high pressure autoclave and used air to introduce free radicals sufficient to initiate polymerization of ethylene. Principal features of the autoclave process are summarized in **Table I.1**

Use of air has been largely supplanted by organic peroxides. Organic peroxides are injected at several points in the autoclave and initiates free radical polymerization by chemistry discussed.Reactor residence**. [1]**

Table I.1 Typical operating features of autoclave processes for LDPE.

Operating Temp:	• 180-300°C
Operating Pressure:	• 15,000-30,000 psig
Features:	- Continuous stirred tank reactors with agitators are used - Multiple reactor zones typically used - Polymerization takes place in "solution"

I.1.1.2 Tubular Process

The tubular process for LDPE may be considered to be a plug flow reactor. As in the autoclave process, organic peroxide initiator is injected at several points along the length of the tube. The tubes are typically 1000-2000 m long with an internal diameter of 25-50 mm (0.1—0.2 in). Product from the tubular process is typically higher in molecular weight and has more short chain branches than LDPE from the autoclave process. Key operating features of the tubular process are summarized in **Table I.2 [1]**

Table I.2: Typical operating features of tubular processes for LDPE.

Operating Temp	• 150-300°C
Features:	-Polymerization takes place in "solution" - tube is 1000-2000 m long and internal diameter of 25-50 mm (0.1-0.2 in) - Organic peroxides typically used as initiators - Polymer chain-length usually longer than product from autoclave process, but with relatively short branches

Times are very short (seconds or even fractions of a second). Excess ethylene is used to aid in heat removal . In general, purification of ethylene monomer is not necessary for high pressure processes. Unlike processes that use transition metal catalysts, high pressure processes are tolerant of trace amounts of water.

I.1.1.3 Slurry (Suspension) Process

Polymerizations may be conducted in diluents in which polyethylene is insoluble at the process temperature. Such processes are termed slurry (or suspension) processes. Diluents must be inert toward the catalyst system and are usually saturated hydrocarbons such as propane, isobutane and hexane. Slurry processes typically operate at temperatures from about 80 to 110 °C and pressures of 200-500 psig. Polyethylene precipitates as formed resulting in a suspension of polymer in diluent. The catalysts most commonly used in slurry processes are chromiumon-silica or supported Ziegler-Natta catalysts. Polymerizations that use supported chromium (Phillips) catalysts are conducted predominantly in slurry processes (though a small portion employs the gas phase process, see below). The historical development of the Phillips process has been expertly reviewed by Hogan and Mc Daniel .The slurry process originally developed by Phillips Petroleum (now Chevron Phillips) has been called the' "particle form loop slurry process" and the "slurry loop reactor process" for production of HDPE and LLDPE . Hexene-1 is most often used as co-monomer for LLDPE in the Phillips process. A simplified process flow diagram for the Phillips loop-slurry reactor process is shown in **Figure I.3** and key operating features are summarized in **Table I.3**. Another well-known slurry (suspension) process was developed by what was then Hoechst in Germany in the mid-1950s. Hoechst was the first licensee to use the catalyst and process developed by Karl Ziegler for producing low pressure **[1]**

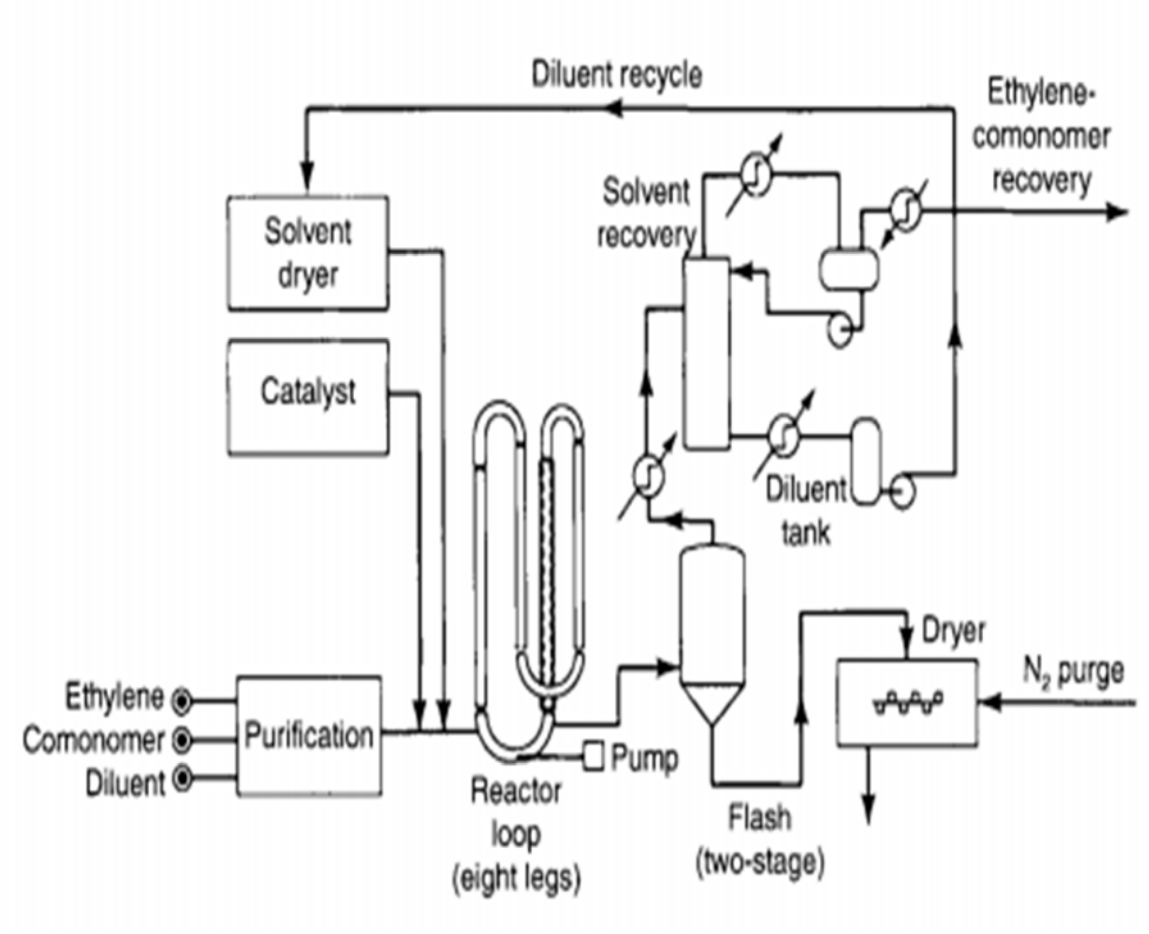


Figure I.3: Schematic process flow diagram for Chevron Phillips loop slurry process for production of linear low density polyethylene.Linear polyethylene in 1955. Hoechst was eventually absorbed into the company that is known today as LyondellBasell. The Hoechst slurry process was improved over the years and has evolved into what is now called the Hostalen process. Hostalen is a slurry-cascade process that is capable of producing a wide range of molecular weight distributions of HDPE. The modern Hostalen process employs 2 continuous stirred tank reactors that can be run in series or in parallel to produce unimodal and bimodal HDPE **.[1]**

Table I.3 Typical operating features of slurry/suspension processes for LLDPE and HDPE.

Operating temp:	• 80-110 °c
Operating pressure:	• 150-450 psig
Features:	- Particles of growing polymer form as suspension in Hydrocarbon diluent - Catalyst residence time ~ 1 hour for phillips loop slurry Process - Morphology and psd of catalyst are important - Wide range of comonomers may be used

I.1.1.4 Gas Phase Process

Gas phase ethylene polymerizations are typically conducted in fluidized beds at pressures of 200-500 psig and temperatures of 80-110 °C. Gas phase processes for polyethylene were developed originally by Union Carbide (now Dow) and later by Naphtachimie (now INEOS). These processes are called the Unipol and Innovene processes, respectively. The predominant catalyst used in each process is of the supported Ziegler-Natta type, though the catalysts are produced by completely different chemistries. The Unipol process is now licensed through Univation Technologies, a joint venture of Dow and ExxonMobil. Historically, the Unipol process has dominated licenses for gas phase processes for linear polyethylene, but Innovene has attracted a significant number of licensees in recent years. Most of the polyethylene made in gas phase processes employs Ziegler-Natta catalysts. There are, however, a few instances where supported chromium and single site catalysts are used. A simplified process flow diagram for the Unipol gas phase reactor process is shown in **Figure I.4**. Principal operating features of the gas phase process are summarized in **Table I.4 [1]**

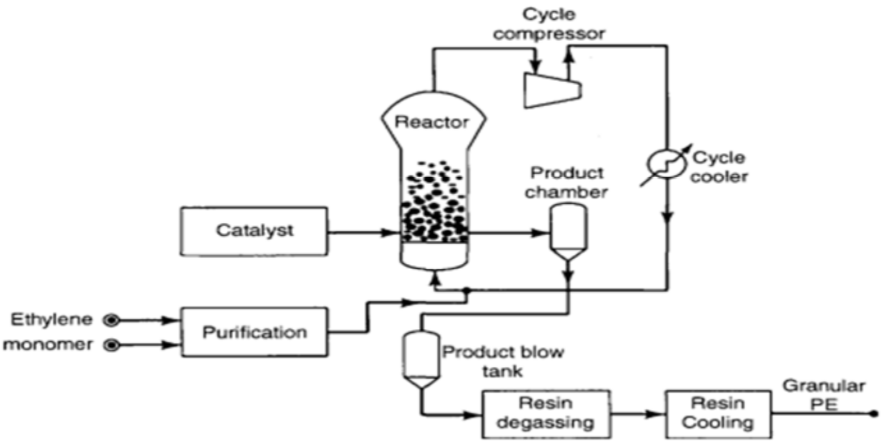


Figure I.4. Schematic process flow diagram for Unipol gas phase process for linear low density polyethylene.

Table I.4 Typical operating features of gas phase processes for HDPE and LLDPE.

Operating Temp:	• 80-110°C
Operating Pressure:	• ~ 300 psig
Features:	- Particles of growing polymer form in fluidized bed - Catalyst residence time 2-4 hours - Morphology and psd of catalyst are important - Previously (pre-1990s) restricted in range of comonomer that could be used; because of emergence of "condensed" mode operation, a wide range of comonomers may now be used

In the 1990s, an improvement for the gas phase process was developed called "condensed mode" operation of Unipol reactors. This technique greatly expanded capacity of gas phase reactors and product capability by making it more practical to use higher alpha-olefin comonomers such as octene-1.

I.1.1.5 Solution Process

In 1960, DuPont-Canada (now Nova) commercialized what has become known as the "solution process" using Ziegler-Natta catalysts based on titanium and vanadium compounds.DSM (Stamicarbon) and Dow also developed highly successful solution processes for polyethylene. These processes employ mostly Ziegler-Natta catalysts. Solution processes operate at 160-220 °C and pressures of 500-5000 psig. Under such conditions, the polymer is dissolved in the solvent, typically cyclohexane or C8 aliphatic hydrocarbons. Polymerization is homogeneous, occurring in solution at temperatures well above the melting range of polyethylene. A simplified process flow diagram for the Nova solution process is shown in **Figure I.5**. Key operating features for the solution process are summarized in **Table I.5.**

Dual continuous stirred tank reactors are used in the modern version of the DuPont-Canada/Nova solution process which is called "Advanced SCLAIRTECH" technology. Both Ziegler-Natta and single site catalysts may be used in Advanced SCLAIRTECH technology. The process is capable of producing a wide range of molecular weight distributions and densities ranging from VLDPE to HDPE. The SCLAIRTECH process for polyethylene has been described by Wiseman.**[1]**

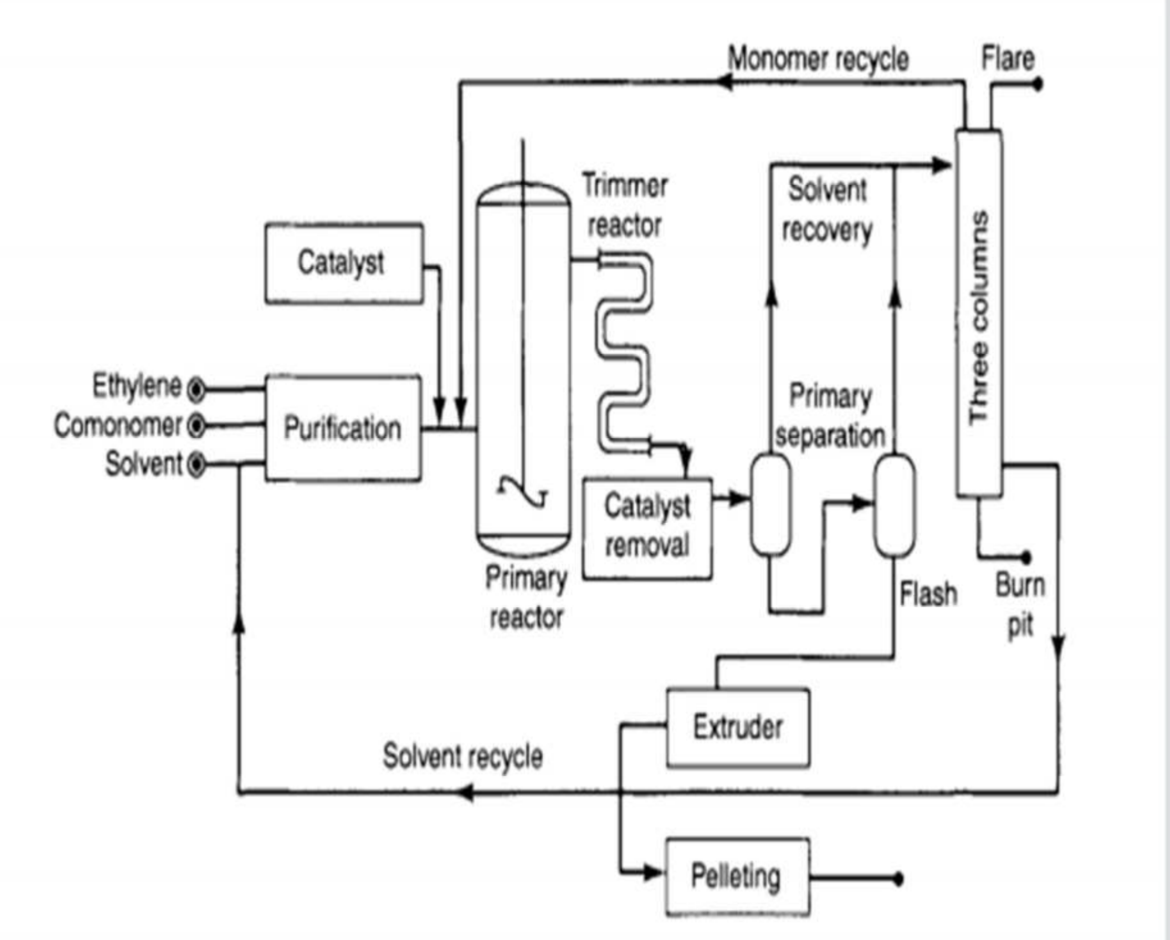


Figure I.5: Schematic process flow diagram for DuPont-Canada (now Nova) solution process for production of polyethylene.

Table I.5: Typical operating features of solution processes for LLDPE and HDPE.

Operating Temp:	• 160-220°C
Operating Pressure:	• 500-5000
Features:	- Polymerization takes place in "solution" - Catalyst residence time short (minutes) - Catalyst and co-catalyst must show reasonably good high temperature stability - Morphology and psd of catalyst are less important than in other processes. - Wide range of comonomers may be used

I.1.1.6 Combined Processes

As mentioned in section 1, technologies have been developed in recent years wherein combinations of processes are used to produce polyethylene. A case in point is the Borstar process developed by Borealis and started up in 1995.

Borstar is capable of producing the entire range of polyethylenes from LLDPE to HDPE . The Borstar process employs a small loop prepolymerization reactor (see section 3.6 for a discussion of the advantages of prepolymerization). Ziegler-Natta catalysts and triethylaluminum cocatalyst are commonly used but the process is capable of using single site catalysts . Borstar also uses a large-scale loop slurry polymerization reactor and a gas phase polymerization reactor in series and is capable of producing bimodal polyethylene. The loop slurry reactor produces low molecular weight fractions and the gas phase reactor produces higher molecular weight produc**t.[1]**

I.1.2 Chemical Structure of Polyethylene

In its simplest form a polyethylene molecule consists of a long backbone of an even number of covalently linked carbon atoms with a pair of hydrogen atoms attached to each carbon; chain ends are terminated by methyl groups. This structure is shown schematically in **Figure I.6.** Chemically pure polyethylene resins consist of alkanes with the formula C_2H_4, where n is the degree of polymerization, i.e., the number of ethylene monomers polymerized to form the chain. Unlike conventional organic materials, polyethylene does not consist of identical molecules. Polyethylene resins comprise chains with a range of backbone lengths. Typically the degree of polymerization is well in excess of 100 and can be as high as 250,000 or more, equating to molecular weights varying from 1400 to more than 3,500,000. Low molecular weight polyethylenes (oligomers) with a degree of polymerization between 8 and 100 are waxy solids that do not possess the properties generally associated with a plastic. When the degree of polymerization is less than 8, alkanes are gases or liquids at ordinary temperatures and pressures. Polyethylene molecules can be branched to various degrees and contain small amounts of unsaturation.**[2]**

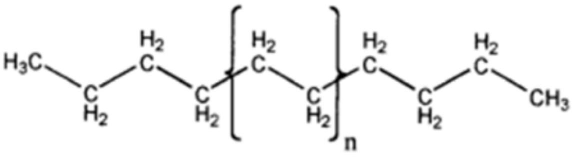


Figure I.6 Chemical structure of polyethylene.

Variations on Theme Many types of polyethylene exist, all having essentially the same backbone of covalently linked carbon atoms with pendant hydrogens; variations arise chiefly from branches that modify the nature of the material. There are many types of branches, ranging from simple alkyl groups to acid and ester functionalities. To a lesser extent, variations arise from defects in the polymer backbone; these consist principally of vinyl groups, which are often associated with chain ends. In the solid state, branches and other defects in the regular chain structure limit a sample's crystallinity level. Chains that have few defects have a higher degree of crystallinity than those that have many. As the packing of crystalline regions is better than that of non-crystalline regions, the overall density of a polyethylene resin will increase as the degree of crystallinity rises. Generally, the higher the concentration of branches, the lower the density of the solid. The principal classes of polyethylene are illustrated schematically in **Figure I.7.a.** High Density Polyethylene. High density polyethylene (HDPE) is chemically the closest in structure to pure polyethylene. It consists primarily of unbranched molecules with very few flaws to mar its linearity. The general form of high density polyethylene is shown in **Figure I.7.a**. With an extremely low level of defects to hinder organization, a high degree of crystallinity can be achieved, resulting in resins that have a high density (relative to other types of polyethylene). Some resins of this type are copolymerized with a very small concentration of 1-alkenes in order to reduce the crystallinity level slightly. High density polyethylene resins typically have densities falling in the range of approximately 0.94–0.97 g/cm3. Due to its very low level of branching, high density polyethylene is sometimes referred to as linear polyethylene (LPE). b. Low Density Polyethylene. Low density polyethylene (LDPE) is so named because such polymers contain substantial concentrations of branches that hinder the crystallization process, resulting in relatively low densities. The branches primarily consist of ethyl and butyl groups together with some long-chain branches. A simplified representation of the structure of low density polyethylene is shown in **Figure I.7.b.** Due to the nature of the high pressure polymerization process by which low density polyethylene is produced, the ethyl and butyl branches are frequently clustered together, separated by lengthy runs of un-branched backbone. Long-chain branches occur at random intervals along the length of the main chain. The long-chain branches can themselves in turn be branched. The mechanisms involved in the production of branches are discussed in. The numerous branches characteristic of low density polyethylene molecules inhibit their ability to crystallize, reducing resin density relative to high density polyethylene. Low density polyethylene resins typically have density polyethylene. The result is a density range of approximately 0.90–0.94 g/cm^3.

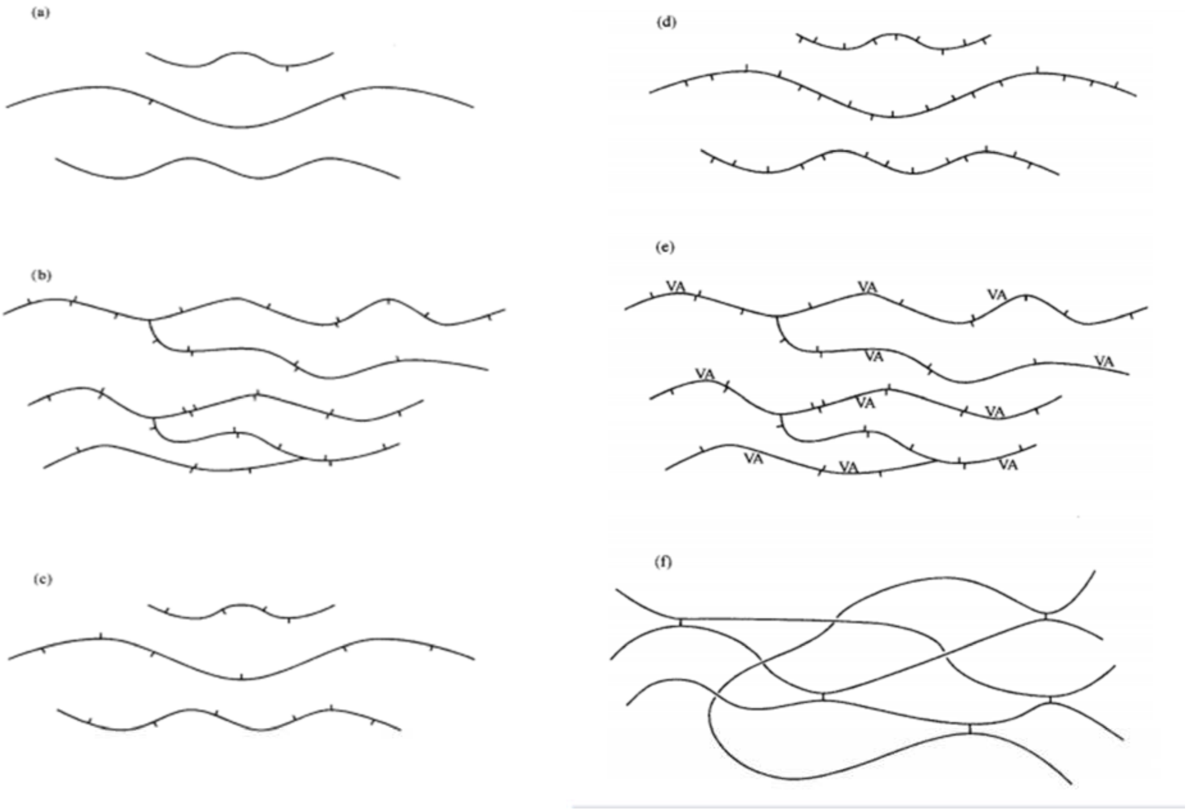


Figure I.7 Schematic representations of the different classes of polyethylene. (a) High density polyethylene; (b) low density polyethylene; (c) linear low density polyethylene; (d) very low density polyethylene; (e) ethylene-vinyl acetate copolymer; (f) cross-linked polyethylene. f. Ionomers. Ionomers are copolymers of ethylene and acrylic acids that have been neutralized (wholly or partially) to form metal salts.

By far the most commonly encountered ethylene-vinyl ester copolymer is ethylene-vinyl acetate (EVA). These copolymers are made by the same high pressure process as low density polyethylene and therefore contain both short- and long-chain branches in addition to acetate groups. The general structure of ethylene-vinyl acetate resins is shown schematically in **Figure I.7.e** (in which ‘‘VA’’ indicates an acetate group). The acetate groups interact with one another via dispersive forces, tending to cluster. The inclusion of polar groups endows such copolymers with greater chemical reactivity than high density, low density, or linear low density polyethylene. The acetate branches hinder crystallization in proportion to their incorporation level; at low levels these copolymers have physical properties similar to those of low density polyethylene, but at high levels of incorporation they are elastomeric. Due to the incorporation of oxygen, ethylene-vinyl acetate copolymers exhibit higher densities at a given crystallinity level than polyethylene resins comprising only carbon and hydrogen.**[2]**

The copolymerization of these molecules takes place under conditions similar to those under which low density polyethylene is made; thus, in addition to polar groups, ionomers contain all the branches normally associated with low density polyethylene. The neutralized acid functionalities from adjacent chains interact with the associated metal cations to form clusters that bind neighboring chains together. A two-dimensional representation of an ionomers cluster is shown in **Figure I.8**.

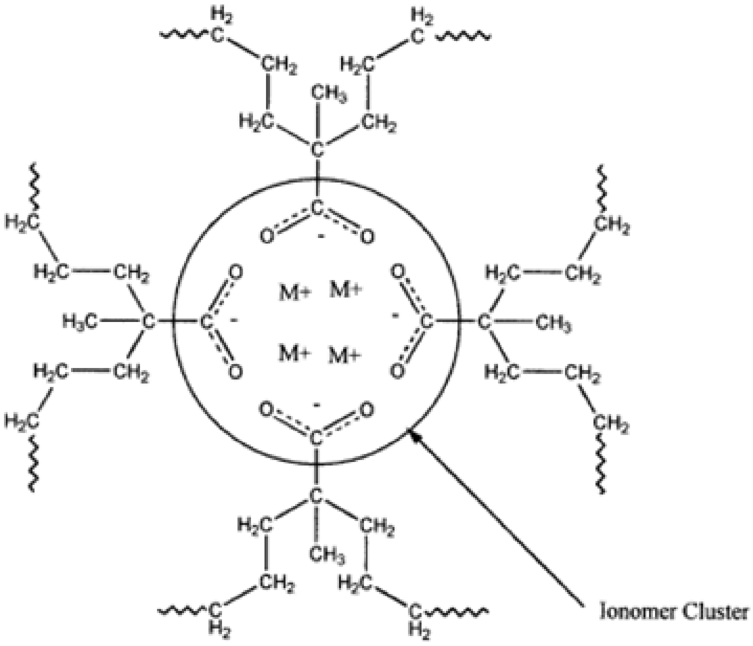


Figure I.8 Schematic representation of an ionomer cluster.

The complex branching structure of ionomers and the existence of polar clusters drastically reduce their ability to crystallize. Despite their low levels of crystallinity, the density of ionomers is normally the highest of all polyethylenes due to the relatively high atomic weight of the oxygen and metal atoms in the ionic clusters. g. Cross-Linked Polyethylene. Cross-linked polyethylene (XLPE) consists of polyethylene that has been chemically modified to covalently link adjacent chains. A schematic representation of cross-linked polyethylene is shows.

In **Figure I.7.f;** Cross-links may comprise either direct carbon–carbon bonds or bridging species such as siloxanes. Cross-links occur at random intervals along chains; the concentration can vary widely, from an average of only one per several thousand carbon atoms to one per few dozen carbon atoms. The effect of crosslinking is to create a gel-like network of interconnected chains. The network is essentially insoluble, although it can be swollen by various organic solvents. This is in direct contrast to the non-cross-linked varieties of polyethylene that are soluble in appropriate solvents at high temperature. Cross-links greatly hinder crystallization, limiting the free movement of chains required to organize into crystallites. Thus the density of a cross-linked polyethylene is lower than that of the polyethylene resin on which it is based **[2]**

I.1.3 Properties of Polyethylene

I.1.3.1 Chemical Properties

Polyethylene has good properties such as high chemical resistance due to its hydrophobic nature, excellent chemical resistance and low water vapor permeability. It is unusual in its insolubility and inertness to chemical reagents.

Certain aliphatic and aromatic hydrocarbons have a more pronounced effect. For example, gasoline, lubricating oil, carbon tetrachloride, and trichloro benzene show definite swelling action. The low moisture permeability and good water resistance indicate its suitability for the coating of cloth, paper, wood, brick, and concrete, for the fabrication of containers (for milk and other liquids), and for packaging in general. For packaging purposes the plastic can be employed either as sheeting or an impregnate for paper**.[3]**

I.1.3.2 Mechanical Properties

The presence of a crystalline phase enables PE to retain its mechanical strength over a large temperature range, despite the relatively low Tg. Probably the most important and significant single mechanical measurement to be made on PE is the determination of elastic modulus or 'stiffness'. The stiffness of PE increases linearly with density **(Figure I.9)** and depends on temperatur**e (Figure I.10)**.It is evident from Figure 3.11 that the decrease in modulus of highly branched PE with increasing temperature follows a curve quite different from that of more dense linear polymers.

Yield strength, tensile strength, and elongation at break are mechanical properties that are particularly important in terms of practical applications. They represent the maximum elastic strength, the ultimate strength, and the amount that the PE can be drawn, respectively. These are commonly determined from stress–strain curves **(Figure I.11).**

The tensile strength decreases with increasing temperature. Increasing density causes an increase in tensile strength, as does an increase in molecular weight. Impact strength can be defined as the amount of energy that the PE can take up before some permanent damage is done. The area under the stress–strain curve, i.e., approximately the product of tensile strength and elongation, can be somewhat arbitrarily taken as the 'impact strength'. The impact strength increases rapidly with molecular weight. As for temperature, elongation and tensile strength act oppositely, so that a

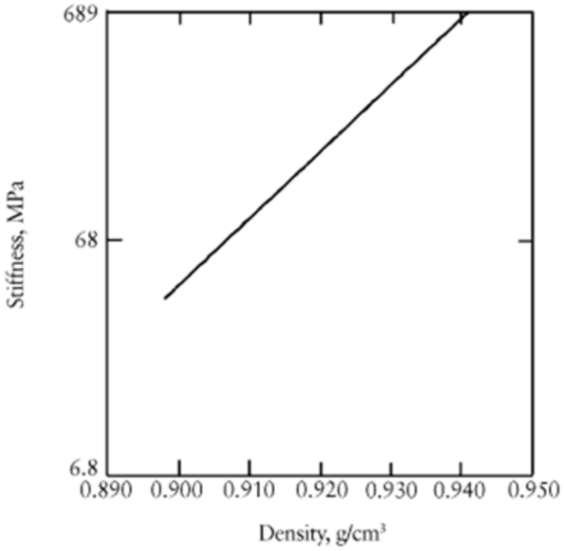


Figure I.9 Effect of density on the stiffness (elastic modulus) of PE.

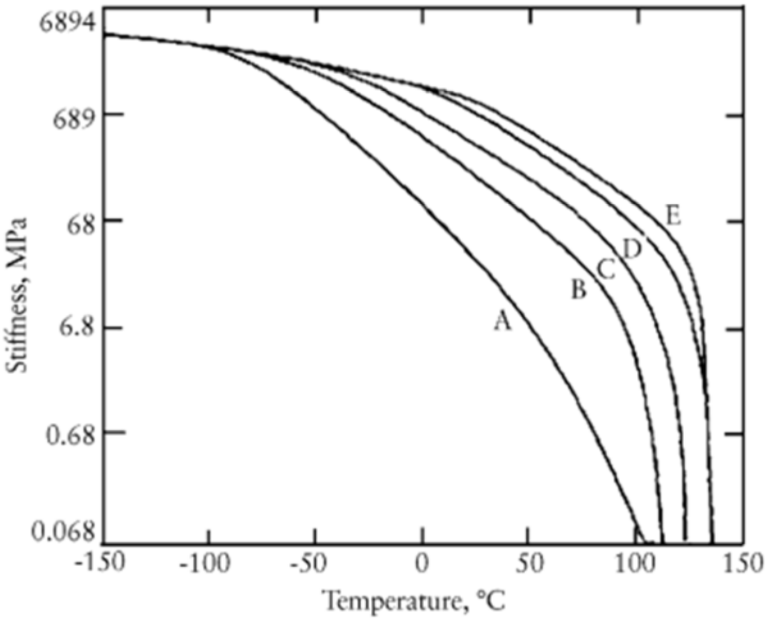


Figure I.10 Effect of temperature on the stiffness of PE of various densities. A: 0.895 g/cm^3, B: 0.918 g/cm^3; C: 0.935 g/cm^3; D: 0.950 g/cm^3; E: 0.968 g/cm^3.

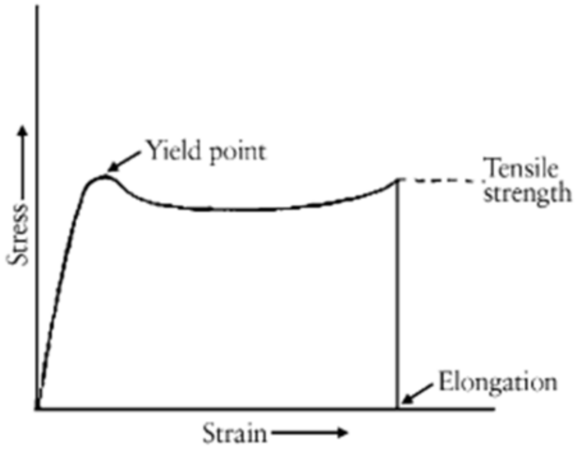


Figure I.11 stress–strain curve for a typical crystalline olefin polymer.

Maximum in impact strength can be expected in a particular temperature range. At normal rates of loading, impact strength decreases with increasing density; at very low rates of strain, however, high-density polymers may have considerable impact strength.**[4]**

I.1.3.4 Physical Properties

I.1.3.4.1 Density

‘‘Density’’ is one of the descriptors most commonly used when discussing polyethylene resins. This is primarily because many of the physical properties of a polyethylene sample can be predicted to a fair approximation based solely upon its density. When the density of different resins measured under controlled conditions can be used as one factor to help predict their relative properties. The relationship between certain mechanical properties and the density of a sample arises from the semicrystalline nature of polyethylene. The higher the proportion of crystalline phases, the higher the density. The relationship between the ordered and disordered regions in a polyethylene sample controls its material properties, and it is this relationship, via the degree of crystallinity, that density probes. Thus, knowledge of the density of the sample reveals something of its semicrystalline morphology. The factors that govern the density of a polyethylene sample are those that influence its degree of crystallinity. Thus density is a function of molecular weight characteristics, branch content, and preparation conditions. When all other factors remain constant, the density of a specimen will increase as the branch content, molecular weight, or rate of crystallization decrease or the degree of orientation increases. Of these factors, branch content is the most influential, followed jointly by molecular weight and degree of orientation and lastly by the rate of crystallization. Thus the samples that have the lowest densities are those that are highly branched, regardless of other factors. Conversely, the densest are unbranched resins with a low molecular weight that have been crystallized slowly or are highly oriented. **Figure I.12** illustrates the effect of increasing branch content on the density of a series of linear low density polyethylene (LLDPE) samples having weight-average molecular weights ranging from 65,000 to 130,000. Also included for comparison is a high density polyethylene (HDPE)

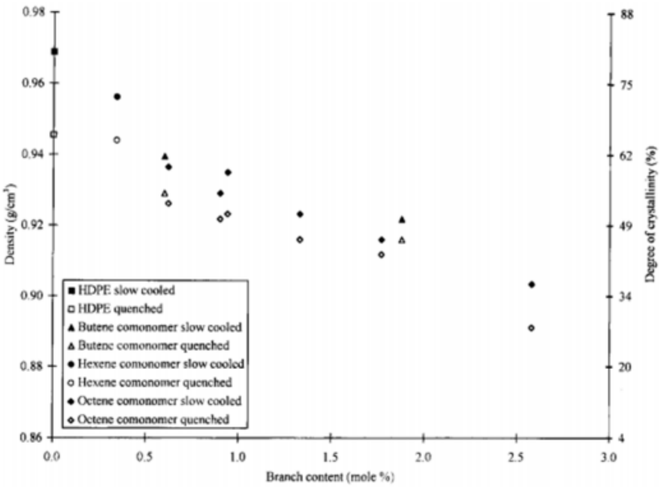


Figure I.12: Plot of density as a function of branch content for compression-molded high density and linear low density polyethylene.

Resin having a weight-average molecular weight of approximately 61,000. For reference, the degree of crystallinity calculated from density is plotted on the right-hand axis. Each material was compression molded and then crystallized under one of two regimes, by quench cooling or by slow cooling in air between thick aluminum plates. Two relationships are readily apparent from this figure: Density drops as the branch content increases (particularly at low branch contents), and, to a lesser extent, an increased cooling rate reduces the density; the effect being more pronounced at lower co-unit contents (i.e., higher densities). The densities of linear low density polyethylene resins are essentially independent of the length of the branch. The degree of crystallinity falls by just over 50% in going from the slow-cooled high density polyethylene sample to its linear low density polyethylene counterpart that has 2.6 branches per 100 atoms in the back bone. As the comonomer content is increased further, the density continues to fall, but at a reduced rate. **Figure I.13** illustrates the effect of increasing molecular weight on the density of high density polyethylene samples (note that molecular weight is plotted on a logarithmic scale). Crystallization procedures were similar to those of **FigureI.12**. Density falls as molecular weight rises, with the crystallization rate playing a Secondary role. A tenfold increase in molecular weight results in an approximately 15% reduction of the degree of crystallinity. Due to difficulties associated with accurately determining the branch distribution and molecular weight of low density polyethylene (LDPE), too few data exist to plot the effects of these characteristics on their densities. It would be expected that the density of low density polyethylene samples would follow relationships qualitatively similar to those of linear low density polyethylene. The relationship between density and degree of orientation is clouded because the accurate determination of orientation is complicated and highly drawn samples often contain voids that make the accurate determination of density difficult. The inclusion of non-olefinic comonomers such as vinyl acetate, methacrylic acid, and norbornene, or chemical modification with such elements as chlorine and oxygen, destroys the simple relationship linking density and degree of crystallinity. Invariably, polyethylene resins that contain elements other than carbon and hydrogen have an elevated density in comparison to homopolymers or olefinic branched materials with similar degrees of crystallinity. Local density within a specimen does not necessarily reflect its bulk density. Differences in cooling rate and shear effects can result in a distribution of densities within a sample. The most common manifestation of this is in thick injection-molded parts. The skin cools quickly against the chilled mold surface, which inhibits the development of crystallinity, while the core cools more slowly, allowing it to develop a higher degree of crystallinity. Within broad limits, the densities of the different types of polyethylene fall within the ranges indicated. These ranges are subject to some flexibility depending on polymerization and crystallization conditions; it would be possible to find extreme examples of each type of polyethylene outside the ranges quoted.**[2]**

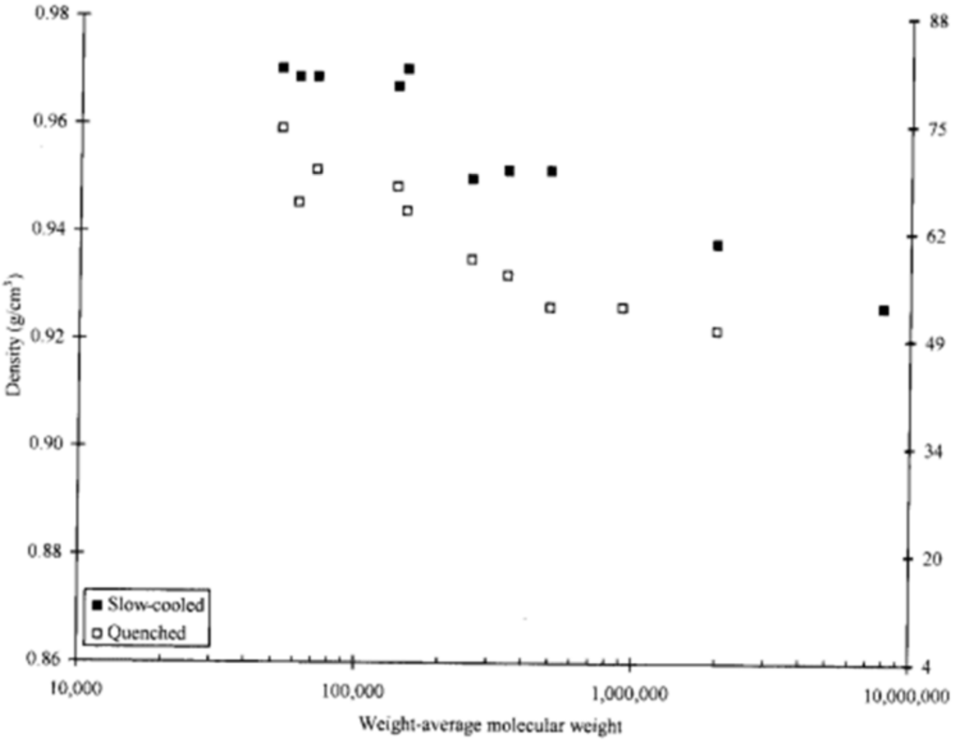
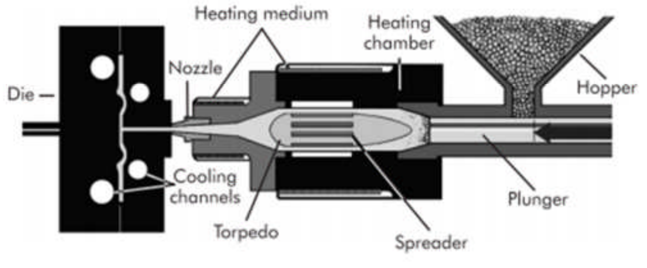


Figure I.13 Plot of density as a function of molecular weight for compression-molded linear polyethylene.

I.4 Production Methods

I.1.4.1 Injection Molding

Since its first use in the United States, Polyethylene has increasingly become a material of choice because of its ease of processing. The highest percentage of use for Polyethylene has been in the injection molding process. Polyethylene can be processed on all of the conventional injection molding machines. The various grades and types of Polyethylene can withstand an extremely wide range of molding conditions. Under ordinary circumstances, because of its excellent resistance to moisture, pre-drying is not required. At times, though, there can be a certain amount of moisture con densation on the pellets and the use of a hopper dryer will eliminate this problem. The hopper dryer can also improve molding conditions because the material is fed into the heating chamber resulting in uniform heat conditions. To obtain the best physical properties and the best looking parts, it is a prerequisite that close adherence to the fundamentals of plastics engineering are followed. Theoretically, the process of injection molding Polyethylene is very similar to that of any of the other types of thermoplastics. As is shown in the diagram "A Principle of Injection Molding," the raw material or pellets are fed into a hopper at the top of the machine. As the machine cycles, a specific amount of material is metered down through a chute into the rear of the heating cylinder. Each successive cycle causes the plunger to move forward, forcing the cold material into the heating chamber. It is then passed through small orifices between the torpedo and the inside wall of the cylinder. With each successive cycle, the material moves closer to the nozzle. The nozzle is removable for a number of reasons. One reason being that different types of materials are sometimes best handled with different types of nozzles. Another reason, as in the case with dry-colored Polyethylene, is to obtain better color distribution in the molded part. Specially designed dispersion plugs can be inserted into the nozzle. he mold is clamped tightly to the face of the nozzle with the orifice in the spree bushing the same size as the opening in the nozzle. By repeatedly pressing the cold material into the rear of the heating chamber, the hot material is forced into the closed mold. The mold is kept at a controlled temperature determined by the speed of the cycle and the required quality of the molded part. At a precise time during the cycle, the mold opens and the part is ejected or removed, either mechanically or manually. The molded part can be complete in itself with no further finishing or, as explained elsewhere in this book, it can be a part of a multiple-section product. In injection molding Polyethylene, the mold should be of Working with Polyethylene 15 the finest quality. Dimensional tolerances, shrinkage, and part finish or gloss are of the utmost importance. The design of the mold, and specifically the method of cooling and ejection of parts, is an important factor not to be taken lightly; nor is the decision of which machine to use for any specific part.



A Principle of Injection Molding

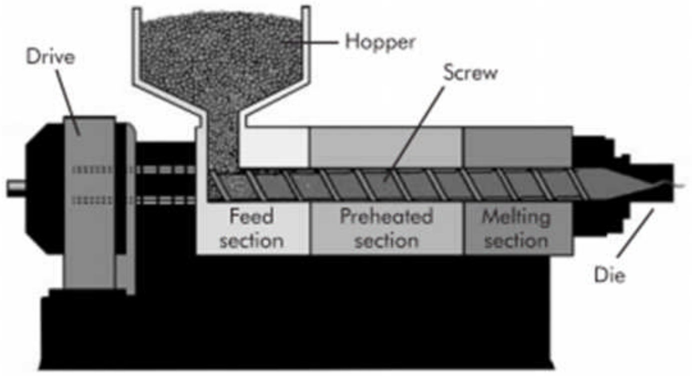
For injection molding extremely large products, such as a 20 gallon (76 L) can, some injection molding machines are equipped with a pre-plasticizing unit. This unit is located directly above the heating chamber. It is similar in design to the regular heating chamber and is used to facilitate the injection of pre-melted material into the heating chamber. This method of injection molding imparts certain advantages, such as better color dispersion in the part, increased speed of molding, and increased machine capacity. As every experienced molder will testify, it is practically impossible to predict the exact molding conditions to use for any given product. The variables in the injection molding process are many. By starting a project with the correctly engineered tools and using the recommendations of the raw material suppliers, the ability to produce quality parts, economically, will be more thoroughly assured **[5].**

I.1.4.2 Extrusion

The extrusion method of processing Polyethylene is very similar to that of extruding any other type of thermoplastic. This method of processing is perhaps more widely used with Polyethylene than with some of the other thermoplastics. All thermoplastic extrusion machines are built with the basic purpose of producing an article of almost any desired length. The main differences in the extrusion of the various thermoplastics are the variance of controls, heat, speed, and pressures. It is always true, regardless of the grade or type of Polyethylene used, that certain fundamental principles of extrusion dictate the selection of the die design and choice of machine.

A conventional extrusion machine is similar in design to a rubber extruder and can be compared to a meat grinder. As shown in the diagram “A Principle of Extrusion” the material is fed from the hopper into a heated barrel. The power-driven, revolving screw works the material forward through the heated barrel, gradually plasticizing it until it becomes quite soft and homogenized. It is then forced through adie designed in the shape of the desired extruded product. The extruded product can be either a profile, tubing or pipe, or flat sheet stock and film. With each grade or type of Polyethylene to be extruded, there are certain requirements needed in the machine and the design of the die to produce a more uniform and dimensionally correct product. Polyethylene is generally very soft as it comes from the die. This necessitates the use of a specially designed cooling apparatus and, in many cases, various types of holding fixtures while the product is being removed from the machine by either a conveyor system or a set of pull rolls.

The extrusion method has certain basic operating fundamentals that are similar to many other processes. However, the number of variables inherent in extrusion make it particularly dependent on the experience of the operator, the ability to have the machine and the take-off equipment in perfect synchronization, and the ability to understand there quirements of the finished product.**[5]**

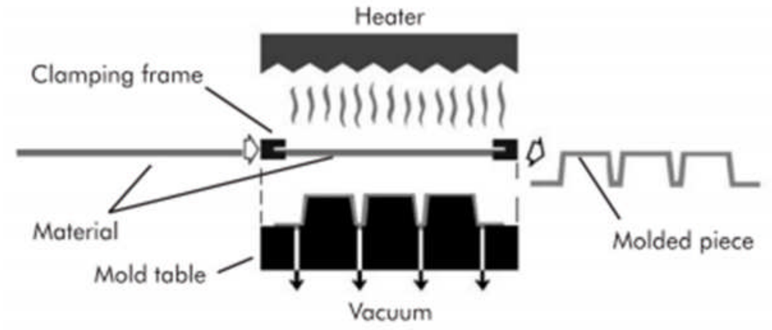


A Principle of Extrusion

I.1.4.3 Thermoforming

The thermoforming of Polyethylene sheet is accomplished by methods used with other thermoplastics. The only variation is that, instead of having a single heat source above the material before forming, the low heat transfer characteristics of Polyethylene sheet require the use of heating on both sides of the sheet. As shown in the diagram “A Principle of Thermoforming (Vacuum Forming),” first the sheet is heated to a fairly soft state. It is then intercepted by a mold, either convex or concave in design, and with the help of a vacuum, is pulled into the desired shape. The part is then cooled and removed from the mold. Excess material is then trimmed from the part. In vacuum forming Polyethylenes, the stiffer high-density types are more often used than the low density.

There are many variations in thermoforming, each differing mainly in the manner in which the sheet is brought into contact with the die and the way the pressure is applied. Each method is specifically designed to produce parts of varied design. No one method is adaptable to all products. The choice of a method that is best suited for any product should be decided by persons experienced in thermoforming and who have a good knowledge of plastics materials.**[5]**



A Principle of Thermoforming (Vacuum Forming)

I.1.5 Advantage of Polyethylene

Polyethylene is a versatile and widely used thermoplastic polymer. Some Advantages of polyethylene include :

1. High durability: Polyethylene is a durable material that can withstand wear and tear, making it ideal for use in products that require long-lasting performance.
2. Chemical resistance: Polyethylene is highly resistant to most chemicals, making it suitable for use in a variety of applications, including food packaging, medical equipment, and chemical containers.
3. Flexibility: Polyethylene is a flexible material that can be easily molded into a wide range of shapes and sizes, making it suitable for use in various industries.
4. Low cost: Polyethylene is a cost-effective material, making it a popular choice for mass-produced products.
5. Lightweight: Polyethylene is a lightweight material, making it easy to transport and handle.
6. Recyclable: Polyethylene is a highly recyclable material, which makes it an environmentally friendly option for many applications.
7. Insulation properties: Polyethylene has excellent insulation properties, making it a good choice for use in insulation materials for electrical wiring and other applications.
8. Water resistance: Polyethylene is highly resistant to water, making it an excellent choice for use in products that require water resistance, such as water tanks and pipes.

Overall, polyethylene is a versatile material that offers many advantages, making it a popular choice for use in a wide range of products and applications.**[6]**

I.1.6 Drawbacks of polyethylene

Polyethylene is a commonly used plastic material that has many benefits, such as its flexibility, durability, and low cost. However, it also has several drawbacks, including:

1. Environmental Impact: Polyethylene is not biodegradable and can take hundreds of years to decompose, leading to accumulation of plastic waste in landfills and oceans.
2. Flammability: Polyethylene is highly flammable and can easily catch fire, making it a safety hazard in certain situations.
3. Chemical Resistance: Polyethylene is susceptible to degradation when exposed to certain chemicals, such as strong acids and bases, which can limit its use in certain applications.
4. UV Degradation: Polyethylene can break down when exposed to UV radiation from the sun, leading to reduced performance and lifespan.
5. Limited Temperature Range: Polyethylene has a relatively low melting point and is not suitable for use in high-temperature applications.
6. Recycling Difficulties: Although polyethylene is recyclable, the recycling process can be difficult and costly, particularly for contaminated or mixed types of plastics.
7. Health Risks: Polyethylene may release harmful chemicals, such as bisphenol A (BPA), during production or use, which can pose health risks to humans and animals.**[7]**

I.1.7 Applications of polyethylene

Polyethylene is a versatile polymer with a wide range of applications across many different industries. Here are Some exemples:

1. Packaging: Polyethylene is commonly used in packaging materials such as plastic bags, shrink wrap, and food containers.
2. Construction: Polyethylene is used in the construction industry for pipes, insulation, and sheeting.
3. Automotive: Polyethylene is used in the automotive industry for fuel tanks, car interiors, and exterior parts.
4. Medical: Polyethylene is used in medical applications such as orthopedic implants, prosthetic devices, and surgical instruments.
5. Agriculture: Polyethylene is used in agriculture for greenhouse films, mulch films, and irrigation pipes.

6. Electrical: Polyethylene is used in electrical applications such as insulation for wires and cables.

7. Sports and recreation: Polyethylene is used in a variety of sports and recreational equipment, including kayaks, paddleboards, and artificial turf.

8. Household items: Polyethylene is used in a range of household items such as toys, detergent bottles, and trash bags.

Overall, polyethylene is a versatile material with a wide range of applications in many different industries.**[8]**

I.2 Polyethylene Terephtalate

I.2.1 Synthesis Method of Polyethylene Terepthalate

PET can be produced by different synthetic routes:

A) The direct esterification reaction of ethylene glycol with terephthalic acid

B) The polytransesterification reaction of dimethyl terephthalate with ethylene glycol.

C) The reaction of terephthalic acid with ethylene oxide.

Processes a) and b) are the most widely used in industry **[9].**

The following Figure (**Figure I.14)** shows the steps for PET synthesis by means of these two methods

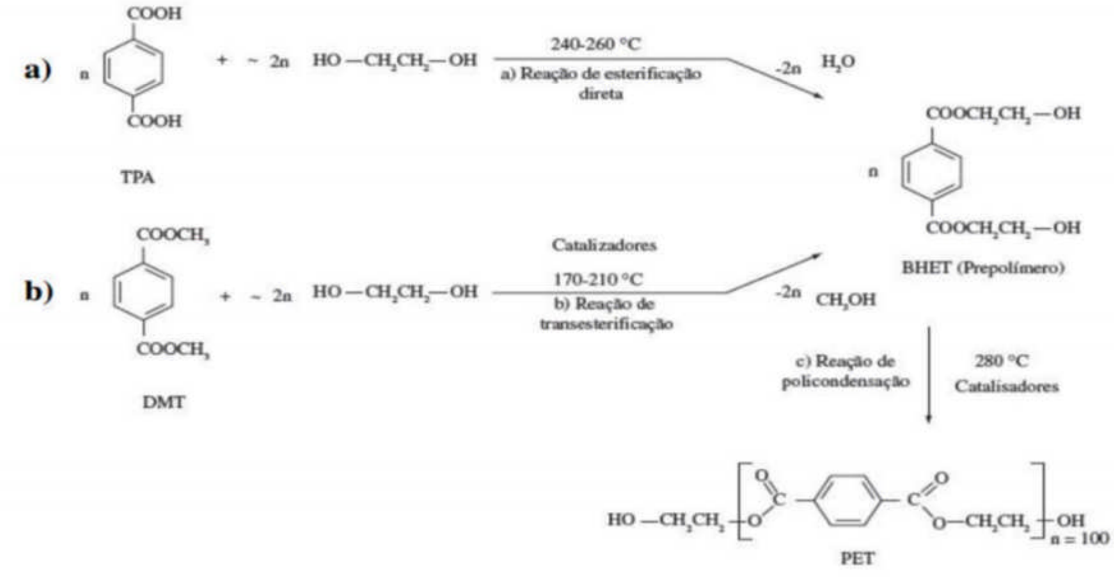


Figure I.14: PET synthesis methods **[10].**

In both cases, the first step consists in the formation of the monomer bis (2-hydroxyethyl) terephthalate (BHET). In reaction a water is generated as reaction by-product, which is an advantage over process b where the excess of ethylene glycol generates methanomust be removed by distillation. Then, the second step is a polycondensation of the intermediate product BHET producing an excess of ethylene glycol which is removed under vacuum.

The reaction is accelerated by the addition of organometallic catalysts. The catalysts to antimony base (usually acetates and oxides) are used in 90% of the world production of PET **[11], ,** in particular antimony trioxide ($\mathbf{Sb_2O_3}$)due to its low price compared to acetate and glycoxide of antimony. Other catalysts of to polycondensation based on germanium, titanium, aluminum and zeolites exist but are much less used because of their price or the fact that they generate PET of lower quality **[12].**

The two synthesis reactions a) and b) generate a PET of equivalent quality but more than 70% of global PET production is based on the polycondensation of ethylene glycol by terephthalic acid (reaction b).

The PET used for the manufacture of fibers or films has a molar mass of the order of 20,000g/mol. Higher viscosity is needed for PET intended for bottle manufacturing. In this case, the molecular weight is around 25,000 g/mol **[13].**

During PET synthesis comonomers such as ethylene glycol, diethylene glycol, isophthalic acid, 1,3-propanodiol, 1,4-butanodiol, dicarboxylic acid naphthalene and cyclohexane dimethanol are added to give certain properties to PET bottles, in particular those used for packaging water carbonated. **Holland and Hay [14],** demonstrated the presence of mixtures commercial PET copolymers with between 2 - 4 mol% diethylene glycol. The role of these substances is to limit the thermal crystallization of the polymer and to provide flexibility during the manufacture of the preform and bottle blowing. These substances improve the properties mechanical properties, barrier properties and gas impermeability of the polymer. Reducing the crystallinity rates of the bottles we obtain a transparent container, which gives a impression of purity (a desirable characteristic in the case of water bottles) and thus makes it possible to have lighter bottles. The most commonly used comonomer for production of PET for water conditioning is diethylene glycol.

I.2.2 Chemical Structure of Polyethylene terephtalate

Poly (oxy-ethanediyl-1,2 oxycarbonyl phenylene carbonyl) is a plastic material of the group of aromatic polyesters. It is commonly called poly (ethylene terephthalate) (PET). The constituent monomer of PET **(Figure I.15)** is formed from an associated phenyl on each side to a carboxyl radical (-COO-) (terephthalate group), one of which is connected to a ethyl radical (ethylene group). Polyethylene terephthalate is a polyester aromatic thermoplastic obtained by reaction of ethylene glycol and acid terephthalic **(Figure I.15).**

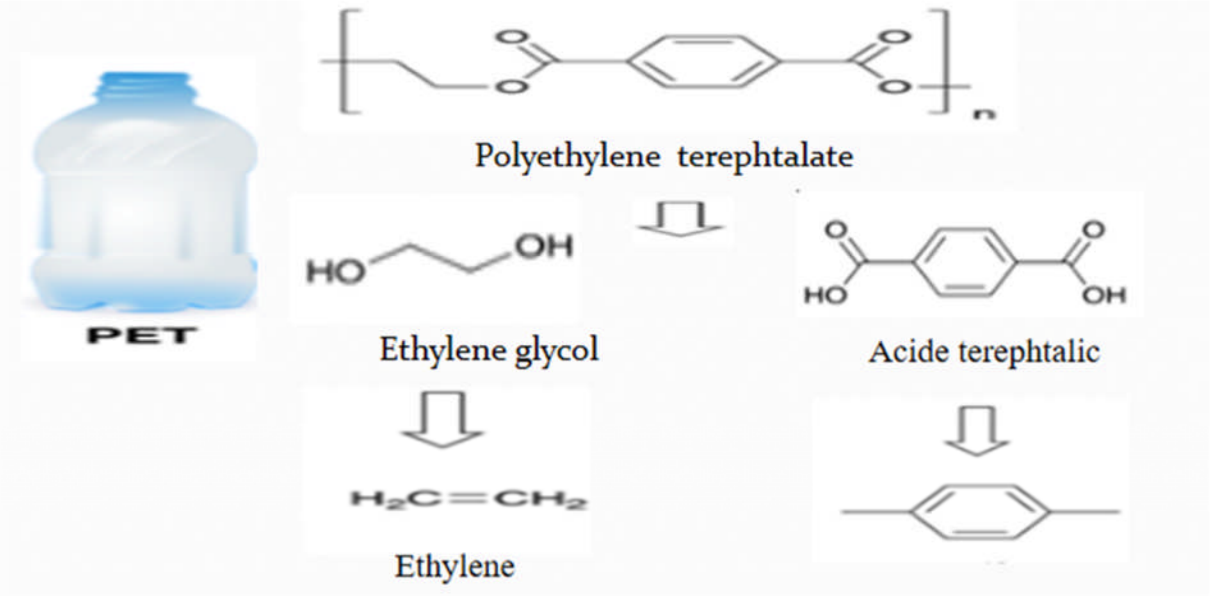


Figure I.15: Chemical structure of PET

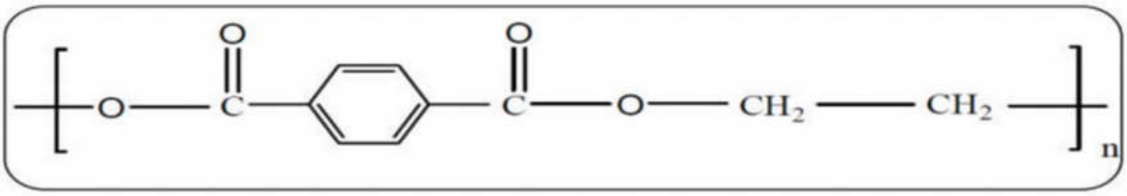


Figure I.16: Repeat unit of polyethylene terephthalate **[15].**

I.2.3 Properties of PET

PET is known for its interesting mechanical properties and barriers. Its structure chemical gives it characteristics that allow it to be used in many technical fields **[16].**

These properties can be classified into several types:

I.2.3.1 Physico-chemical properties of PET

PET has a glass transition temperature of around 80°C and a high melting point, around 260°C, thanks to the presence of a benzene nucleus.

The core also gives a semi-rigid appearance to the PET. It also has good mechanical and thermal properties, high chemical resistance and low gas permeability **[17].** PET is a semi-crystalline polymer, the density of the crystalline phase is 1.515g.cm-3 and that of the amorphous phase is 1.335g.cm^{-3} **[18].** The glass transition temperature depends on the magnitude of the stresses, the free volume and space between crystallite aggregates **[19].** So she is often more higher in the case of a semi-crystalline PET film than in the case of an amorphous film.

However, in the case of a sample crystallized with annealing, if the distance between the crystallites is sufficient not to hinder the cooperative movements of the chains macromolecular, the glass transition temperature can be close to that of a amorphous sample.

I.2.3.2 Barrier Properties

Semi-crystalline PET is well known for its low permeability to gases and certain solvents. For example, an important quality in the context of the manufacture of bottles containing sodas or carbonated drinks, which it is essential to preserve as much as possible long as possible the gaseous nature. **Table I.6** lists the barrier properties of PET depending on its crystallinity **[16].**

Table I.6: Barrier properties of amorphous and semi-crystalline PET at T = 25°C. **[20]**

PET (amorphous/semi-crystalline) amorphous PET	Permeability coefficient (cm^3 x 10^{13})	Diffusion coefficient (cm^2 .s$^-$1 x 10^6)	Solubility (cm3 x 10^6)
Nitrogen N_2	0.011	0.0019	0.55
Oxygen O_2	0.044	0.0045	0.98
Carbon dioxide CO_2	0.227	0.0008	28
Semi-crystalline PET (40%)			

Nitrogen N_2	0.005	0.0013	0.45
Oxygen O_2	0.026	0.0035	0.72
Carbon dioxide CO_2	0.118	0.0006	20

According to the table above, PET is a material with low gas permeability. These values depend on the measurement conditions and in particular on the temperature. The more the material is crystalline and/or oriented, the weaker its permeability will be since the organization of macromolecules leaves little room for gas molecules to penetrate or cross the material.

I.2.3.3 Thermal Properties

Thermal analysis of PET by DSC (Differential Scanning Calorimetry) shows three main transitions described in **Figure I.17.**

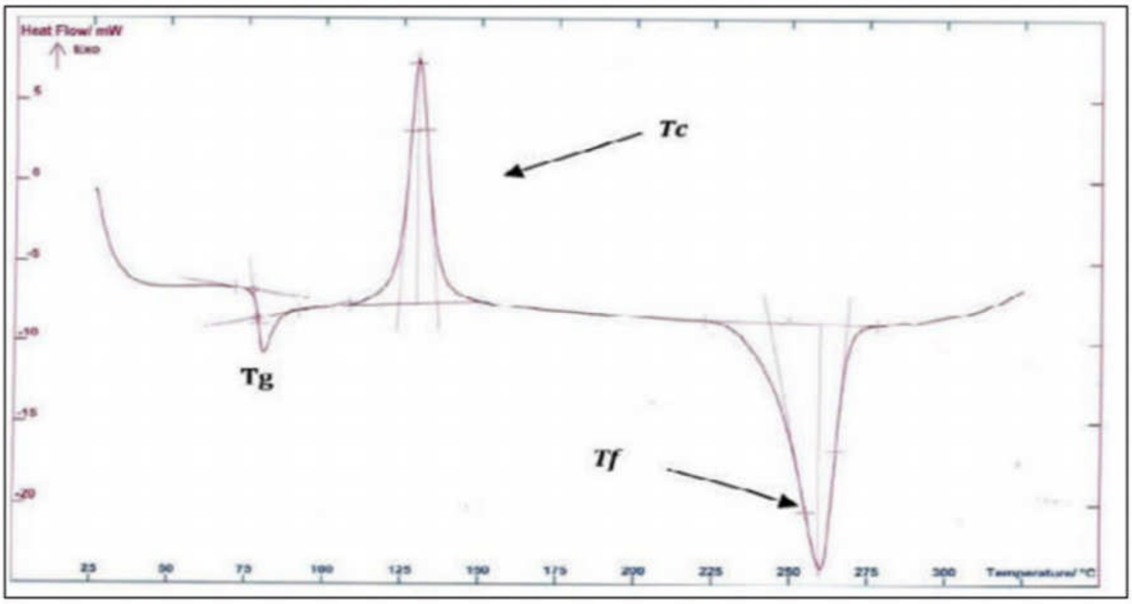


Figure I.17: DSC thermograms of PET.

The first, around T=75°C, is the glass transition and corresponds to a variation of the molecular mobility of amorphous phase chains. The second transition appears around 145°C and corresponds to a recrystallization of PET amorphous. This exothermic transition appears for matrices whose crystallinity rate initial is relatively low, and gradually disappears when the rate of crystallinity increase.

Finally, the third transition is endothermic and takes place around 260-270°C. It corresponds to melting the polymer. The rigidity of the chains, linked to the presence of aromatic rings, explains the high melting point of PET and gives good thermal stability in the absence constraints **[21].**

I.2.3.4 Thermomechanical properties

PET, mainly used at room temperature, comes in a glassy state and therefore appears as a rigid material. The extrusion and injection of this polymer are done usually at a temperature above the melting temperature where the chains of this polymer are sufficiently mobile.

I.2.3.5 Rheological Properties

The implementation of PET is then generally done in the molten state, between 270 and 290°C. To these temperatures, the thermal degradation of PET can significantly affect and irreversible its rheological properties. To limit this degradation, it is useful, during implementation, to dry the polymer in order to reduce its residence time in order to avoid any oxidation **[16].**

At high temperatures, near the melting temperature, PET becomes liquid.

When the polymer is cooled, crystallization occurs so slowly that the polymer will become rubbery. By further decreasing the temperature, the material becomes glassy and brittle having properties similar to a crystalline solid. The temperature at which this occurs is called glass temperature (Tg). It is 342°K for PET **[22].**

I.2.3.6 Morphological Properties

The morphology of PET has been widely studied in order to explain its behavior thermal and mechanical properties. The structure of PET as mentioned can be amorphous or partially crystalline. The degree of crystallinity has a strong influence on the properties of this material. Indeed, this crystallized state significantly improves certain mechanical properties (stiffness, tensile and tear strength) **[23].**

I.2.4 Advantage of Polyethylene terephtalate

Polyethylene terephthalate (PET) is a versatile and widely used thermoplastic polymer with several advantages:

1. Lightweight: PET is a lightweight material, making it ideal for applications where weight reduction is important, such as in packaging materials. It helps in reducing transportation costs and energy consumption.
2. Transparency: PET has excellent clarity and transparency, allowing products packaged in PET containers to be easily visible. This is especially beneficial for food and beverage products where visual appeal is important.
3. Strength and durability: PET exhibits high strength and durability, making it suitable for various applications. It can withstand mechanical stress, making it a popular choice for packaging materials, including bottles, jars, and containers.
4. Chemical resistance: PET has good resistance to chemicals, including acids, alkalis, and solvents. This property makes it suitable for packaging a wide range of products, including food, beverages, pharmaceuticals, and personal care items.
5. Recyclability: PET is highly recyclable. It can be easily sorted, cleaned, and reprocessed into new products. Recycled PET, commonly known as rPET, is used to make various products such as bottles, fibers, and packaging materials, reducing the environmental impact of plastic waste.
6. Barrier properties: PET has excellent gas and moisture barrier properties, which helps in preserving the freshness and quality of products. It prevents the entry of oxygen, carbon dioxide, and other gases, making it suitable for packaging perishable goods.
7. Cost-effective: PET is a cost-effective material compared to many other plastics. It is readily available and can be produced at a relatively low cost, making it a preferred choice for various applications.
8. Versatility: PET can be easily processed and molded into various shapes and forms. It can be blow-molded into bottles, extruded into films and sheets, or spun into fibers. Its versatility makes it suitable for a wide range of industries, including packaging, textiles, automotive, and electronics.

Overall, the advantages of PET, such as its lightweight nature, transparency, strength, chemical resistance, recyclability, and versatility, make it a popular choice for numerous applications in various industries.**[24]**

I.2.5. Drawbacks of Polyethylene terepthalate

Polyethylene terephthalate (PET) is a widely used polymer that has several drawbacks:

1. Poor heat resistance: PET has a relatively low melting point compared to other polymers, limiting its usability in high-temperature applications. It can deform or melt when exposed to temperatures above 70-80 degrees Celsius.

2. Brittle nature: PET is a relatively brittle material, meaning it is prone to cracking or breaking under stress or impact. It lacks the flexibility and toughness of other plastics like polypropylene or polyethylene.

3. Permeability to gases and liquids: PET has relatively high permeability to gases, including oxygen, carbon dioxide, and water vapor. This property can limit its use for packaging applications where long shelf life or moisture barrier is required.

4. Environmental concerns: PET is derived from non-renewable fossil fuels and is not biodegradable. Improper disposal or recycling of PET products can contribute to environmental pollution and waste accumulation.

5. Recycling challenges: Although PET is recyclable, there are challenges associated with the recycling process. Contamination from other materials, such as food residues or other plastics, can reduce the quality of recycled PET. Additionally, the recycling infrastructure and collection systems may not be widely available in all regions, hindering proper recycling practices.

6. Susceptibility to UV degradation: PET is prone to degradation when exposed to ultraviolet (UV) radiation. Over time, exposure to sunlight can cause discoloration, embrittlement, and reduced mechanical properties of PET products.

7. Chemical resistance limitations: PET is generally resistant to mild acids and bases, but it may be attacked by certain solvents, such as strong acids, alkalis, and some organic solvents. This limits its suitability in applications where exposure to harsh chemicals is expected.

8. Chemical resistance limitations: PET is generally resistant to mild acids and bases, but it may be attacked by certain solvents, such as strong acids, alkalis, and some organic solvents. This limits its suitability in applications where exposure to harsh chemicals is expected.

It's important to note that PET also has several advantageous properties, such as clarity, lightweight, and good gas barrier properties, which make it suitable for various applications, especially in the packaging industry. However, these drawbacks should be taken into consideration when evaluating its use in specific applications.**[25]**

I.2.6 Applications of polyethylene terephthalate

Polyethylene terephthalate (PET) is a versatile polymer that finds numerous applications due to its excellent properties. Here are some common uses of PET:

1. Packaging: PET is widely used in the packaging industry for food, beverages, personal care products, and household items. It is used to make bottles, jars, trays, films, and blister packs. PET's transparency, durability, and barrier properties make it ideal for preserving and protecting various products.
2. Textiles: PET can be processed into fibers known as polyester. These polyester fibers are used to make a wide range of textile products, including clothing, upholstery, carpets, and bedding. PET fibers are durable, lightweight, wrinkle-resistant, and have good moisture-wicking properties.
3. Electrical insulation: PET is an excellent electrical insulator, which makes it suitable for applications in the electrical and electronics industry. It is used in the manufacturing of electrical tapes, cable insulation, flexible printed circuit boards, and other electronic components.
4. Automotive: PET is used in various automotive applications due to its lightweight, impact resistance, and dimensional stability. It is used in the manufacturing of car interiors, such as seat fabrics, headliners, carpets, and trunk liners. PET-based films are also used for laminating and window films in automobiles.
5. Construction materials: PET is employed in construction materials like insulation boards, roofing membranes, and geotextiles. These products take advantage of PET's strength, moisture resistance, and thermal insulation properties.
6. Medical applications: PET is used in the medical field for various applications. It is commonly used to manufacture disposable medical equipment like syringes, IV tubes, blood bags, and wound dressings due to its biocompatibility and resistance to sterilization processes.
7. 3D printing: PET filament is widely used in 3D printing due to its high strength, low warping, and ease of printing. It is used to create a wide range of objects, including prototypes, mechanical parts, and consumer products.
8. Environmental applications: PET is used in the production of recycling bins and containers for waste management. It is also employed in wastewater treatment systems as filter media due to its high surface area and chemical resistance.

These are just a few examples of the many applications of polyethylene terephthalate. Its versatility, affordability, and desirable properties have made it a popular choice in various industries.**[26]**

References

[1] Dennis B. Malpass , Introduction to industrial polyethylene (properties , catalysts and processes) , (wiley – Scrivener) **2010** , canada, pp 88- 96

[2] ANDREW J. PEACOCK, Handbook of polyethylene (structures, properties, and applications), Marcel Dekker, Inc., **2000**, New York •Basel, 534 p

[3] Muralisrinivasan Natamai Subramanian,Polymer Blends and Composites Chemistry and Technology,John Wiley & Sons, Inc,**2017**,USA, 324 p

[4] Yury V. Kissin,Polyethylene End-Use Properties and their Physical Meaning,Hanser Publishers, Munich,**2013**,USA, 144 p

[5] By Bill Fry,Speaking of Plastics Manufacturing,Society of Manufacturing Engineers Dearborn, Michigan,**1999**, 35 p

[6] Advontage of polyethylene,consulted to the follwing link line:https://chat.openai.com/c/ac2af08d-b3b9-4249-b6d3-b5c1d3dc8090 (chat gpt) 07-05-**2023**

[7] Drawbacks of polyethylene,consulted to the follwing link line:https://chat.openai.com/c/ac2af08d-b3b9-4249-b6d3-b5c1d3dc8090 (chat gpt)07-05-**2023**

[8] Application of polyethylene,consulted to the follwing link line:https://chat.openai.com/c/4d2438ba-1120-4c87-a6a8-a97bfb2d5631 (chat gpt)07-05-**2023**

[9] Pennarun, PY, Migration from recycled PET bottles. Elaboration and validation of a usable model of functional barriers, University of Reims Champagne-Ardenne, Reims (France). **2001**.

[10] Romão, W., Spinacé, MAS and De Paoli, MA. Poly(ethylene terephthalate), PET: A review on the synthesis processes, degradation mechanisms and its recycling (Portuguese). Polymeros: Ciência e Tecnologia 19(2), 121-132. **2009**.

[11] Westerhoff, P., Prapaipong, P., Shock, E. and Hillaireau, A.,. Antimony leaching from polyethylene terephthalate (PET) plastic used for bottled drinking water. Water Research 42(3), 551-556. **2008**.

[12] ILSI, Packaging materials: 1. Polyethylene terephthalate (PET) for food packaging applications. International Life Science Institute. Brussels, Belgium). **2000**.

[13] Etienne, S. and David, L., **.** Introduction to Polymer Physics, Dunod, Paris (France). **2002**.

[14] Holland, BJ and Hay, JN. The thermal degradation of PET and analogous polyesters measured by thermal analysis-Fourier transform infrared spectroscopy. Polymer 43(6), 1835-1847. **2002**.

[15] BORDIVAL,« Modeling and numerical optimization of the infrared heating step for the manufacture of PET bottles by injection-blow molding". Doctoral thesis. Paris: Doctoral School Fundamental and Applied Sciences. **2009**, 196 p.

[16] VERDU, J, , "Treatment of plastics: Chemical ageing".Techniques of the engineer A3150, **1990**.

[17] C. DUSTRIEZ. "Correlations between the dielectric and mechanical properties of polymers; influence of the temperature ". Doctoral thesis. Lyon: Doctoral School of Materials. **2004**, 164p

[18] J. LIN, S. SHENOGIN and S. NAZARENKO, "Oxygen solubility and specific volume of rigid amorphous fraction in semi-crystalline poly (ethylene terephthalate)". Polymer, **2002**, Vol. 43,PP. 4733-4743.

[19] BB SAUER et al., “TMDSC and atomic force microscopy studies of morphology and recrystallization in polyesters including oriented films”. Journal of Thermal Analysis and Calorimetry, **2000**, Vol. 59,PP. 227-243.

[20] PETIT-BOILEAU, S, “small surface preparation of PET before metallization: study and comparison of excited laser and non-equilibrium plasma processes”, doctoral thesis, university of Paris 6, 2003.

[21] PIERRE-YVES PENNARUN, “Migration from recycled PET bottles. Development and validation of a model applicable to functional barriers”, 292p. Thesis: Chemistry: Reims (France). **2001**.

[22] NAÏT-ALI KAKO, L ,“recycled pet in food packaging: experimental approach and modeling”, Thesis: Chemistry of Materials: Montpellier, **2008**.

[23] L. LADOUCE et al. “Non-linear creep behavior of PET”. Journal of Materials Science, **1994**, Vol. 29, p.5399-5406.

[24] Advantages of Polyethylene terephtalate, consulted to the following link line: https://chat.openai.com/?model=text-davinci-002-render-sha (chat gpt):13-05-**2023**

[25] Drawbacks of polyethylene terephtalate, consulted to the following link line: https://chat.openai.com/?model=text-davinci-002-render-sha (chat gpt):13-05-**2023**

[26] Applications of polyethylene terephtalate, consulted to the following link line: https://chat.openai.com/?model=text-davinci-002-render-sha (chat gpt):13-05-**2023**

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],**

$$\left(\frac{\partial 2\Delta Gm}{\partial \phi i^2}\right) T, \quad P > 0 \qquad \textbf{(II.2)}$$

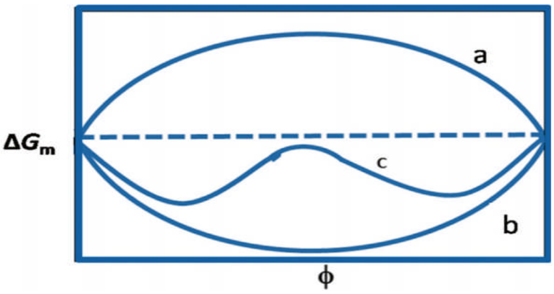


Figure II.1 Free energy of mixing for **(a)** completely immiscible, **(b)** completely miscible, and **(c)** partially miscible **[4, 21].**

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.

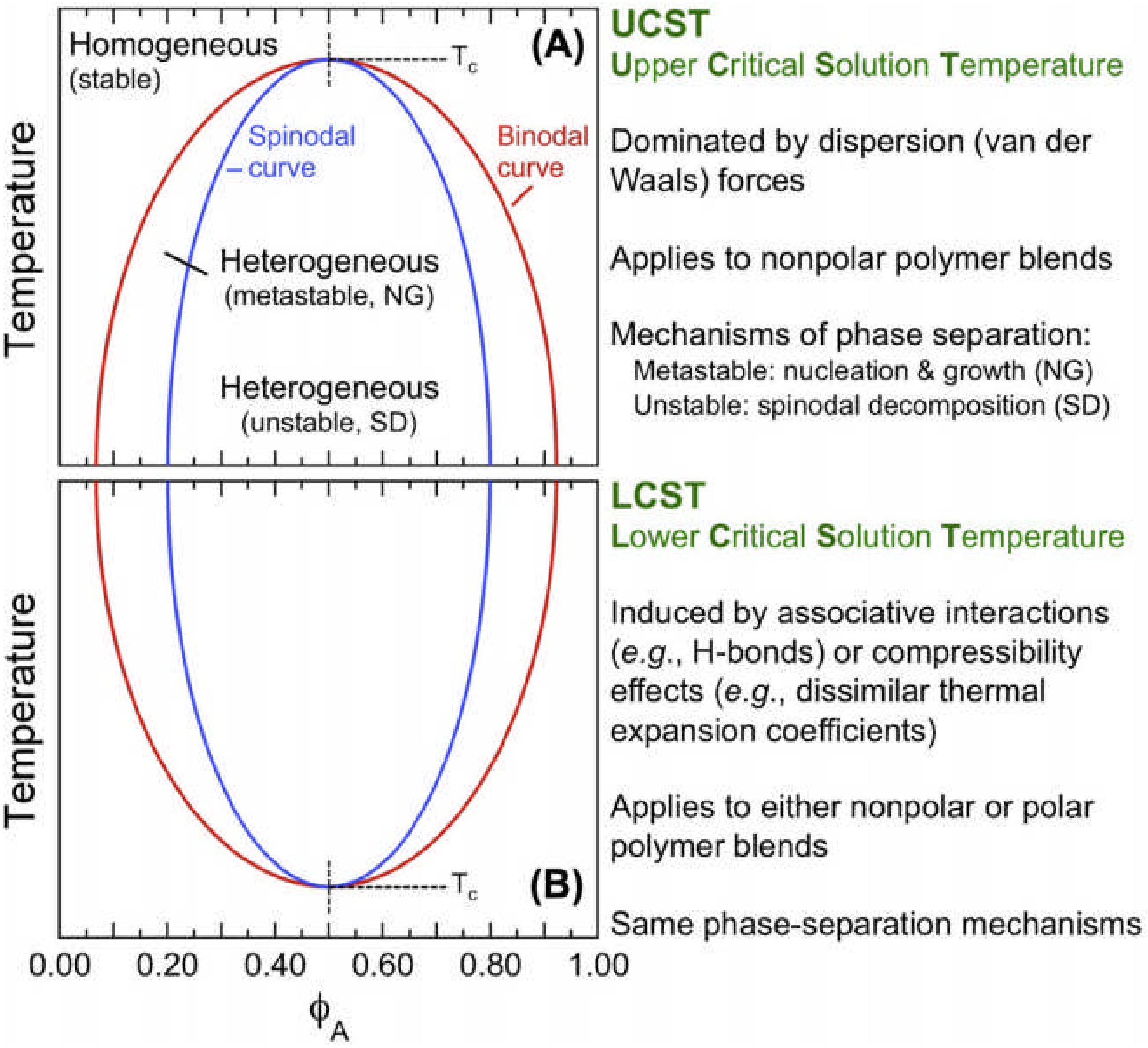
$$\text{Spinodal : } \left(\frac{\partial^2 \Delta G_m}{\partial \phi^2}\right)_{\mathbf{p,T}} = \mathbf{0} \qquad \mathbf{(II.3)}$$

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.

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

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



UCST

Upper Critical Solution Temperature

Dominated by dispersion (van der Waals) forces

Applies to nonpolar polymer blends

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

LCST

Lower Critical Solution Temperature

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.

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

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,

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

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 $\chi$is the Flory-Huggins interaction parameter **[3,17,25,26].**

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

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

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

$$\Delta H_m = RT\chi\phi_1\phi_2 \qquad (\mathbf{II.8})$$

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 ($\Delta Hm<0$). 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

$$\chi_{c\,r} = \frac{1}{2}\left(\frac{1}{\sqrt{r1}} + \frac{1}{\sqrt{r2}}\right)^2 \qquad (\mathbf{II.9})$$

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 ageneral method to judge the miscibility of blends. As already discussedsingleTgof blend represents a miscible blend and twoTgrepresents a phaseseparated blend system. The main experimental techniques which aregenerally used to measureTgof components involve differential scanningcalorimetry (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].**

II.4 Preparation Methods of Polymer Blends

Polymer blends are formed by combining two or more different polymers to create a material with unique properties. The preparation methods of polymer blends can vary depending on the desired outcome and the specific polymers being used. Here are some commonly employed preparation methods for polymer blends:

1. Solution blending: This method involves dissolving the polymers in a compatible solvent to create a homogeneous solution. The solutions of individual polymers are then mixed together and the solvent is evaporated to obtain a blend. This method is suitable for polymers that are soluble in the same or compatible solvents.
2. Melt blending: In this method, the polymers are melted and mixed together at elevated temperatures. The molten polymers are typically processed using techniques such as twin-

screw extrusion, single-screw extrusion, or melt blending in a mixing chamber. The blend is then cooled and solidified to obtain a homogeneous material.

3. In-situ polymerization: This method involves the simultaneous polymerization of different monomers to form a polymer blend. The monomers are mixed together, and a suitable initiator or catalyst is added to initiate the polymerization reaction. The reaction conditions are controlled to ensure the desired blend composition and molecular weight distribution.

4. Solid-state blending: In this method, solid polymer pellets or powders are mechanically mixed together using techniques such as blending in a ball mill, high-speed mixer, or tumble blender. The blending process can be carried out at ambient or elevated temperatures, depending on the polymers' melting points and thermal stability.

5. Reactive blending: Reactive blending involves chemically modifying the polymer chains to facilitate their intermixing. Functional groups or reactive monomers are incorporated into the polymer chains, and a chemical reaction is initiated to form covalent bonds between the polymer chains. This method can improve the compatibility and mechanical properties of the polymer blend.

6. Compatibilization: In some cases, polymer blends can exhibit phase separation and poor interfacial adhesion between the different polymer phases. To enhance the compatibility and blend properties, compatibilizers are often used. These are small molecules or polymers that have an affinity for both polymer components and can improve the interfacial adhesion between them. Compatibilizers can be added during the blending process, and their presence helps to reduce phase separation and enhance the mechanical properties of the blend.

It's important to note that the selection of the appropriate preparation method depends on factors such as the polymer characteristics, desired blend properties, and processing conditions. Various combinations of these methods can also be used to tailor the properties of polymer blends according to specific requirements**.[63]**

II.5 Properties of Polymer Blends

Polymer blends refer to the combination of two or more different polymers to create a new material with enhanced or unique properties. Here are some key properties of polymer blends:

1. Compatibility: Polymer blends can exhibit varying degrees of compatibility between the different polymer components. Compatibility refers to the degree of mixing and

intermolecular interactions between the polymers. Compatibility can affect the overall mechanical, thermal, and processing properties of the blend.

2. Mechanical properties: Polymer blends can offer improved mechanical properties compared to the individual polymers. For example, blending a rigid polymer with a flexible one can enhance the blend's toughness and impact resistance. The mechanical properties of polymer blends depend on factors such as the composition, morphology, and interfacial interactions between the polymers.

3. Thermal properties: Polymer blends can have modified thermal properties compared to the individual polymers. The glass transition temperature (Tg), melting point (Tm), and crystallinity of the blend can be different from those of the individual polymers. Blending polymers with different Tg or Tm can broaden the temperature range over which the material remains useful.

4. Processing characteristics: Polymer blends can exhibit improved processability compared to single polymers. The blending process can be used to adjust the melt viscosity and flow behavior of the polymer, making it easier to process via methods like injection molding or extrusion. The processability of a blend depends on factors such as the melt compatibility, molecular weight, and melt rheology of the polymers.

5. Morphology: The morphology of a polymer blend refers to the arrangement and distribution of the polymer phases within the blend. The morphology can be influenced by factors like the composition, processing conditions, and intermolecular interactions. Morphological control is crucial in achieving desired properties in polymer blends, such as improved toughness, optical clarity, or barrier properties.

6. Chemical resistance: Polymer blends can exhibit a unique combination of chemical resistance properties. The resistance to various chemicals and solvents can be different from that of the individual polymers. Blending polymers with different chemical resistance properties can result in a blend that is more resistant to a broader range of chemicals.

7. Electrical properties: Polymer blends can possess tailored electrical properties. For instance, blending a conductive polymer with an insulating one can result in a blend with intermediate conductivity. The electrical properties of a blend can be influenced by factors like the composition, morphology, and degree of interfacial interactions between the polymers.

8. Optical properties: Polymer blends can exhibit modified optical properties compared to the individual polymers. The transparency, refractive index, and light scattering behavior of a

blend can be different from those of the constituent polymers. Blending polymers with different optical properties can be utilized for applications in optics, display technologies, or packaging.

It's important to note that the properties of polymer blends can vary significantly depending on the specific polymers being blended, their relative ratios, processing conditions, and other additives incorporated into the blend. Thus, the properties of polymer blends can be tailored to meet specific requirements for a wide range of applications**.[64]**

II.6 Factors Affecting the Properties of Polymer Blends

When it comes to polymer blends, there are several factors that can affect their properties. Here are some of the key factors to consider:

1. Polymer Composition: The choice of polymers in the blend greatly influences its properties. Each polymer brings its own characteristics, such as molecular weight, chemical structure, and functionality, which can affect the blend's behavior.
2. Polymer Compatibility: The compatibility between the polymers in a blend plays a significant role. If the polymers are immiscible or have limited miscibility, phase separation can occur, leading to distinct phases and different material properties.
3. Molecular Weight and Distribution: The molecular weight of the polymers and their distribution within the blend impact various properties, including viscosity, mechanical strength, and processing behavior. A broad distribution may lead to phase separation or affect melt processing.
4. Blend Ratio: The ratio of polymers in the blend can significantly influence properties like mechanical strength, thermal stability, and transparency. Altering the blend ratio can change the dominant phase or the degree of phase dispersion.
5. Processing Conditions: The processing conditions used during blending, such as temperature, shear rate, and mixing time, can affect the blend's properties. These conditions can impact the degree of mixing, morphology development, and potential degradation.
6. Additives and Fillers: The incorporation of additives, such as plasticizers, stabilizers, or flame retardants, can modify the properties of polymer blends. Fillers like nanoparticles or fibers can also influence mechanical, electrical, and thermal properties.

7. Morphology and Phase Separation: The morphology formed in a polymer blend, including the size, shape, and distribution of phases, significantly impacts its properties. Achieving a desirable morphology often requires optimizing the factors mentioned above.

8. Interfacial Interactions: The interfacial interactions between different polymers at the molecular level can affect properties like adhesion, toughness, and barrier properties. These interactions depend on factors such as chemical structure, polarity, and intermolecular forces.

9. Thermal Properties: The glass transition temperature (Tg), melting temperature (Tm), and crystallinity of individual polymers in a blend can influence the blend's thermal behavior, such as its processing window, thermal stability, and dimensional stability.

10. Environmental Factors: The environmental conditions, such as temperature, humidity, and exposure to chemicals or UV radiation, can impact the long-term properties and stability of polymer blends.

Understanding these factors and their interplay is crucial for designing polymer blends with tailored properties for specific applications. Experimental characterization and theoretical modeling techniques are often employed to investigate and optimize the properties of polymer blends.**[65]**

II.7 Drawbacks of Polymer Blends

Polymer blends, which are mixtures of two or more different polymers, offer several advantages over single polymers, such as improved mechanical properties, enhanced processability, and cost reduction. However, they also have some drawbacks that need to be considered. Here are some common drawbacks of polymer blends:

1. Phase Separation: Polymer blends often face the challenge of phase separation, where the individual polymers tend to separate into distinct phases rather than forming a homogeneous blend. This can lead to a loss of desirable properties and compromise the performance of the material.

2. Compatibility Issues: Different polymers may have incompatible chemical structures or polarities, making it difficult for them to blend effectively. Lack of compatibility can result in poor adhesion between polymer phases, reducing the overall strength and integrity of the blend.

3. Morphology Control: Achieving a desired morphology in a polymer blend can be challenging. The arrangement of polymer domains within the blend is crucial for determining

the material properties. Without proper control over the morphology, it can be challenging to achieve the desired balance of properties.

4. Reduced Mechanical Properties: In some cases, polymer blends may exhibit reduced mechanical properties compared to the individual components. This can be attributed to factors such as phase separation, poor interfacial adhesion, or the presence of weaker components within the blend.

5. Processing Difficulties: Processing polymer blends can be more complex than processing single polymers. The different viscosities, melting points, and processing temperatures of the components can pose challenges during fabrication processes like extrusion, injection molding, or film casting.

6. Stability and Aging: Polymer blends can undergo changes in their properties over time due to the presence of multiple components with different degradation mechanisms or susceptibility to environmental factors. This can impact the long-term stability and durability of the material.

7. Limited Property Combinations: While polymer blends can offer a broader range of properties compared to single polymers, there are still limitations in terms of property combinations. Some properties may be mutually exclusive, making it difficult to achieve certain desired characteristics simultaneously.

8. Compatibility with Additives: Incorporating additives, such as fillers or additives for specific functionalities, into polymer blends can be challenging. The compatibility between the additives and the polymer matrix may vary, affecting the overall performance and functionality of the blend.

It's worth noting that these drawbacks are not applicable to all polymer blends and can vary depending on the specific polymer combinations, processing techniques, and desired properties. Researchers and engineers continuously work on addressing these challenges through formulation modifications, blending techniques, and advanced processing methods to enhance the performance of polymer blends.**[66]**

II.8 Applications of Polymer Blends Industrial Fields

Polymer blends, which are composed of two or more polymers mixed together, have various applications across industrial fields. Here are some examples:

1. Automotive Industry: Polymer blends are used extensively in the automotive industry for components such as bumpers, interior trim, door panels, and dashboards. Blends of polymers like polypropylene (PP) and acrylonitrile butadiene styrene (ABS) offer improved impact resistance, strength, and durability.
2. Packaging: Polymer blends find wide applications in the packaging industry. Blends of polyethylene (PE) and ethylene vinyl acetate (EVA) are used for film and sheet applications, providing enhanced properties such as heat sealability, toughness, and flexibility.
3. Electronics: Polymer blends are utilized in the electronics industry for applications like encapsulation of electronic components, adhesives, and coatings. Blends of epoxy resins with other polymers enhance mechanical properties, thermal stability, and moisture resistance.
4. Construction: Polymer blends are employed in the construction industry for various purposes. Blends of polyvinyl chloride (PVC) and acrylonitrile butadiene styrene (ABS) are used for pipes and fittings, providing a balance between rigidity and impact resistance. Polymer blends also find applications in insulation materials, sealants, and adhesives.
5. Medical Devices: Polymer blends are utilized in the manufacturing of medical devices. Blends of biocompatible polymers, such as polylactic acid (PLA) and polyglycolic acid (PGA), are used for sutures, drug delivery systems, and tissue engineering scaffolds.
6. Textiles: Polymer blends are employed in the textile industry to enhance the properties of fabrics. Blends of natural and synthetic fibers, such as cotton/polyester blends, provide improved strength, wrinkle resistance, and dyeability.
7. Aerospace: Polymer blends find applications in the aerospace industry for lightweight components, thermal protection systems, and composite materials. Blends of thermosetting resins like epoxy with high-temperature polymers such as polyimides offer improved mechanical properties and resistance to extreme conditions.
8. Sports and Recreation: Polymer blends are used in the manufacturing of sports equipment and recreational products. Blends of thermoplastic elastomers (TPEs) with rigid polymers provide impact resistance, flexibility, and comfort. They are used in applications like shoe soles, protective gear, and inflatable products.

These are just a few examples of how polymer blends are applied in various industrial fields. The versatility of polymer blends allows manufacturers to tailor the properties of materials to meet specific requirements, leading to improved performance and cost-effectiveness in many applications.**[67]**

References

[1] Blends P, Paul DR, Newman S. NY: Acdemic Press; **1978**; 2:391.

[2] Brown SB. Reactive compatibilization of polymer blends. In: Polymer blends handbook. Springer; **2003**. p. 339-415.

[3] Paul D, Barlow J. Polymer blends. J Macromol Sci Rev Macromol Chem **1980**;18(1):109-68.

[4] Paul DR. Polymer blends. Elsevier; **2012**.

[5] Thomas S, Grohens Y, Jyotishkumar P. Characterization of polymer blends: miscibility, morphology and interfaces. John Wiley & Sons; **2014**.

[6] Utracki LA, Favis B. Polymer alloys and blends. New York: Marcel Dekker; **1989**.

[7] Utracki LA, Wilkie CA. Polymer blends handbook. Springer; **2002**.

[8] Bahrami R, Löbling TI, Schmalz H, Müller AH, Altstädt V. Micromechanics of “raspberry” morphology in PPE/SAN polymer blends compatibilized with linear ABC triblock terpolymers. Polymer **2015**;80:52-63.

[9] Chiu F-C. Poly (vinylidene fluoride)/polycarbonate blend-based nanocomposites with enhanced rigiditydselective localization of carbon nanofillers and organoclay. Polym Test **2017**;62:115-23.

[10] Otero-Navas I, Arjmand M, Sundararaj U. Carbon nanotube induced double percolation in polymer blends: morphology, rheology and broadband dielectric properties. Polymer **2017**; 114:122-34.

[11] Wang H, Fu Z, Zhao X, Li Y, Li J. Reactive nanoparticles compatibilized immiscible polymer blends: synthesis of reactive SiO_2 with long poly (methyl methacrylate) chains and the in situ formation of janus SiO_2 nanoparticles anchored exclusively at the interface. ACS Appl Mater Interfaces **2017**;9(16):14358-70.

[12] Utracki L. Economics of polymer blends. Polym Eng Sci **1982**;22(17):1166-75.

[13] Roman C, García-Morales M, Gupta J, McNally T. On the phase affinity of multi-walled carbon nanotubes in PMMA: LDPE immiscible polymer blends. Polymer **2017**;118:1-11.

[14] Jiao Q, Shen J, Ye L, Li Y, Chen H. Poly (oxymethylene)/poly (butylene succinate) blends: Miscibility, crystallization behaviors and mechanical properties. Polymer **2019**;167:40-7.

[15] Métivier T, Cassagnau P. Compatibilization of silicone/fluorosilicone blends by dynamic crosslinking and fumed silica addition. Polymer **2018**;147:20-9.

[16] Yu L, Dean K, Li L. Polymer blends and composites from renewable resources. Prog Polym Sci **2006**;31(6):576-602.

[17] Paul D, Barlow J. A binary interaction model for miscibility of copolymers in blends. Polymer **1984**;25(4):487-94.

[18] Robeson LM. Polymer blends. Compr Rev **2007**. ISBN-10: 3-446-22569-2 ISBN-13: 978-3-446-22569-5.

[19] Utracki LA. Compatibilization of polymer blends. Can J Chem Eng**2002**;80(6):1008-16.

[20] Rostami A, Masoomi M, Fayazi MJ, Vahdati M. Role of multiwalled carbon nanotubes (MWCNTs) on rheological, thermal and electrical properties of PC/ABS blend. RSC Adv**2015**;5(41):32880-90.

[21] Polásková M. Polymer blends with microfibrillar-phase morphology. **2006**.

[22] Li S, Feng L, Lu H, Feng S. From LCST to UCST: the phase separation behaviour of thermo-responsive polysiloxanes with the solubility parameters of solvents. New J Chem **2017**;41(5):1997-2003.

[23] Yao W, Wang H, Cui G, Li Z, Wang J. Tuning phase behaviour of PEG functionalized ionic liquids from UCST to LCST in alcoholewater mixtures. Phys Chem Phys**2016**;18(42):29192-8

[24] Kuila A, Maity N, Chatterjee DP, Nandi AK. Phase behavior of Poly (vinylidene fluoride)-graft-poly (diethylene glycol methyl ether methacrylate) in alcoholewater system: coexistence of LCST and UCST. J Phys Chem B **2016**;120(9):2557-68.

[25] Ten Brinke G, Karasz FE. Lower critical solution temperature behavior in polymer blends: compressibility and directional-specific interactions. Macromolecules **1984**;17(4):815-20.

[26] Tambasco M, Lipson J, Higgins JS. Blend miscibility and the Flory-Huggins interaction parameter: a critical examination. Macromolecules **2006**;39(14):4860-8.

[27] Wippler C. Dynamic mechanical properties of VAMAS polycarbonate/polyethylene blends. Polym Eng Sci **1990**;30(17):1106-13.

[28] Laokijcharoen P, Coran A. The evolution of morphology in NR/HDPE blends. Part I. Microscopy for unvulcanized blends. Rubber Chem Technol **1998**;71(5):966-74.

[29] Go JH, Ha CS. Rheology and properties of EPDM/BR blends with or without a homogenizing agent or a coupling agent. J Appl Polym Sci **1996**;62(3):509-21.

[30] Brahimi B, Ait-Kadi A, Ajji A, Fayt R. Effect of diblock copolymers on dynamic mechanical properties of polyethylene/polystyrene blends. J Polym Sci B Polym Phys**1991**;29(8):945-61.

[31] Ghosh P, Chattopadhyay B, Sen AK. Thermal and oxidative degradation of PEEPDM blends vulcanized differently using sulfur accelerator systems. Eur Polym J **1996**;32(8):1015-21.

[32] Oliveira MG, Soares BG. The effect of the vulcanizing system on cure and mechanical properties of NBR/EPDM blends. Polym Polym Compos **2001**;9(7):459-68.

[33] Arif PM, Sarathchandran C, Narayanan A, Saiter A, Terzano R, Allegretta I, et al.Multi-walled carbon nanotube promotes crystallisation while preserving co-continuous phase morphology of polycarbonate/polypropylene blend. Polym Test **2017**;64:1-11.

[34] Stelescu MD. Physico-mechanical characteristics of some EPDM/plasticized PVC blends. Macromol Symp **2008**:70-7. Wiley Online Library.

[35] Zaharescu T, Mihalcea I. Behaviour of ethylene-propylene elastomers in salt solutions: I. SEM investigation of gamma irradiation effects. Polym DegradStabil**1995**;50(1):39-43.

[36] Ajitha A, Aswathi M, Geethamma VG, Kalarikkal N, Thomas S, Volova TG. An effective EMI shielding material based on poly (trimethylene terephthalate) blend nanocomposites with multiwalled carbon nanotubes. New Journal of Chemistry **2018**;42(16):13915-26.

[37] Li J-X, Chan C-M. Effect of the size of the dispersed NBR phase in PVC/NBR blends on the stability of PVC to electron irradiation. Polymer **2001**;42(16):6833-9.

[38] Le HH, Parsekar M, Ilisch S, Henning S, Das A, Stöckelhuber KW, et al. Effect of non-rubber components of NR on the carbon nanotube (CNT) localization in SBR/ NR blends. Macromol Mater Eng**2014**;299(5):569-82.

[39] Kunjappan AM, Ramachandran AA, Padmanabhan M, Mathew LP, Thomas S.Selective localization of MWCNT in poly (trimethylene terephthalate)/poly ethylene blends: theoretical analysis, morphology, and mechanical properties. Macromol Symp **2018**:1800104. Wiley Online Library.

[40] Chandra R, Mishra S, Parida T. Studies on dynamic behaviour and flow properties of HDPE/EPDM blends by torque rheometer. Polym Int **1995**;37(2):141-7.

[41] Essawy HA, Tawfik ME, El-Sabbagh SH. Rubber nanocomposites based on compatibilized NBR/SBR blends using a series of amphiphilicmontmorillonites. J Elastomers Plast **2014**;46(2):113-31

[42] Fel E, Khrouz L, Massardier V, Cassagnau P, Bonneviot L. Comparative study of gamma-irradiated PP and PE polyolefins part 2: properties of PP/PE blends obtained by reactive processing with radicals obtained by high shear or gamma-irradiation. Polymer **2016**;82:217-27.

[43] Nair ST, Vijayan PP, Xavier P, Bose S, George SC, Thomas S. Selective localization of multi walled carbon nanotubes in polypropylene/natural rubber blends to reduce the percolation threshold. Compos Sci Technol **2015**;116:9-17.

[44] Maria HJ, Lyczko N, Nzihou A, Joseph K, Mathew C, Thomas S. Stress relaxation behavior of organically modified montmorillonitefilled natural rubber/nitrile rubber nanocomposites. Appl Clay Sci **2014**;87:120-8.

[45] Friedrich K, Evstatiev M, Fakirov S, Evstatiev O, Ishii M, Harrass M. Microfibrillar reinforced composites from PET/PP blends: processing, morphology and mechanical properties. Compos Sci Technol **2005**;65(1):107-16.

[46] Wang J, Pan S, Zhang Y, Guo S. Crosslink network evolution of BIIR/EPDM blends during peroxide vulcanization. Polym Test **2017**;59:253-61.

[47] Ding X, Wang J, Zhang S, Wang J, Li S. Composites based on CB/CF/Ag filled EPDM/NBR rubber blends with high conductivity. J Appl Polym Sci **2015**;132(4).

[48] Ray SS, Pouliot S, Bousmina M, Utracki LA. Role of organically modified layered silicate as an active interfacial modifier in immiscible polystyrene/polypropylene blends. Polymer **2004**;45(25):8403-13.

[49] Uthaipan N, Jarnthong M, Peng Z, Junhasavasdikul B, Nakason C, Thitithammawong A. Effects of crosslinked elastomer particles on heterogeneous nucleation of isotactic PP in dynamically vulcanized EPDM/PP and EOC/PP blends. J Polym Res **2017**;24(8):118.

[50] Gögelein C, Beelen HJH, van Duin M. Morphological explanation of high tear resistance of EPDM/NR rubber blends. Soft Matter **2017**;13(23):4241-51.

[51] Li H, Wang J, Li G, Lu Y, Wang N, Zhang Q, et al. Preparation of core-shell structured particle and its application in toughening PA6/PBT blends. Polym Adv Technol **2017**;28(6):699-707.

[52] Abd-El-Messieh S, Mansour S, El-Nashar D, Ikladious N. Evaluation of polyester resin as a new compatibilizer for SBR/PVC blends. Can J Chem Eng**2004**;82(2):358-70.

[53] Setua D, Nando G. High-performance oil/fuel-resistant blends of ethylene propylene diene monomer (EPDM) and epoxidized natural rubber (ENR). In: High performance polymers and their nanocomposites; **2018**. p. 315-46.

[54] Mural PKS, Madras G, Bose S. Positive temperature coefficient and structural relaxations in selectively localized MWNTs in PE/PEO blends. RSC Adv**2014**;4(10):4943-54.

[55] Ahmed K. Stress-strain and diffusion behavior of industrial waste-filled acrylonitrile-butadiene rubber/high density polyethylene blends. Chem Lett**2014**;43(5):690-2.

[56] El-Nashar D. The compatibilization of EPDM/SBR blends by EPDM-graft-styrene copolymer. Polym Plast Technol Eng**2005**;43(5):1425-41.

[57] Lu X, Weiss R. Relationship between the glass transition temperature and the interaction parameter of miscible binary polymer blends. Macromolecules **1992**;25(12):3242-6.

[58] Brostow W, Chiu R, Kalogeras IM, Vassilikou-Dova A. Prediction of glass transition temperatures: binary blends and copolymers. Mater Lett**2008**;62(17e18):3152-5.

[59] An L, He D, Jing J, Wang Z, Yu D, Jiang B, et al. Effects of molecular weight and interaction parameter on the glass transition temperature of polystyrene mixtures and its blends with polystyrene/poly (2, 6-dimethyl-p-phenylene oxide). Eur Polym J **1997**;33(9):1523-8.

[60] Kalogeras IM, Brostow W. Glass transition temperatures in binary polymer blends. J Polym Sci B Polym Phys**2009**;47(1):80-95.

[61] Tjong S, Meng Y. Effect of reactive compatibilizers on the mechanical properties of polycarbonate/poly (acrylonitrile-butadiene-styrene) blends. Eur Polym J **2000**;36(1):123-9.

[62] Mathew L, Saha P, Kalarikkal N, Thomas S, Strankowski M. Tuning of microstructure in engineered poly (trimethylene terephthalate) based blends with nano inclusion as multifunctional additive. Polym Test **2018**;68:395-404.

[63] Preparation methods of polymer blends, consulted to the following link line: https://chat.openai.com/?model=text-davinci-002-render-sha (chat gpt):12-05-**2023**

[64] Properties of polymer blends, consulted to the following link line : https://chat.openai.com/c/23347204-61a6-4bb2-8182-75de6554662c(chat gpt):12-05-**2023**

[65] Factors of fecting the properties of polymer blends, consulted to the following link line: https://chat.openai.com/c/b44e513a-d8e4-42d6-9e30-14da0a89ed6f (chat gpt) :12-05-**2023**

[66] Draw backs of poly blends, consulted to the following link line : https://chat.openai.com/?model=text-davinci-002-render-sha (chat gpt) :12-05-**2023**

[67] Application of polymer blends industrial fields, consulted to the following link line: https://chat.openai.com/?model=text-davinci-002-render-sha (chat gpt): 12-05-**2023**

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 phasemorphology and poor interfacial adhesion between the blend phases. Thismay be so, as most polymers are immiscible. When the viscoelastic behaviorof polymer blends is observed, the melt viscosity of immiscible polymerblends are found to depend on the interfacial interactions and phasemorphology. Hence compatibilization by addition of an interfacial agent isneeded to attain synergistic effect for making it most useful. There areseveral methods for the compatibilization of polymer blends, but theprinciple of all techniques is the homogenization of mixture of the polymerby adding a compatibilizing agent.

Compatibilizers are macromolecular in nature and bring interfacial activities in heterogeneous polymer blends. The compatibilizer, which can beadded directly to the immiscible polymer blend and generated in situ duringthe blending process, usually has one part miscible with one polymer andthe other part miscible with the second polymer. The compatibilizersmainly retard the formation of the Rayleigh disturbances, on the generatedthreads of polymer 1, which results in decreased interfacial tension. Thelower interfacial tension stretches the threads longer, making their diameteralso smaller. The smaller size of the generated droplets of polymer 1 helps tobring the average particle size to submicron level. The compatibilizer alsoprevents the coalescence at the surface of the generated phase. Compatibilizers can thus generate and stabilizefiner blend morphology. Severalstrategies 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. Industrialsuitability of compatibilization techniques depends on several factors, suchas cost, final performance, recyclability, and possible biodegradability.

Some ofthe general strategies involve the following:

➢Adding previously made grafted block copolymers.

➢Adding reactive polymers (advantage is the short processing time of aminute or even less).

➢ Addition of low-molecular-weight chemicals like peroxide activateinert polyolefins, resulting in the formation of branched copolymers,a functional chemical that forms block copolymers or a mixture of aperoxide and a functional chemical, all of which leads to the formationof branch/graft copolymers: Lack of chemical selectivity is the problemin this approach although this compatibilization method is quite simple.

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

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

➢Addition of selective crosslinking agents is yet another method. Thismethod of specific interactions compatibilization is done by introducingsuitable 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 discussesthe compatibilization of polymer blends by graft copolymers, random copolymers, micro and nanofillers, coupling agents, janus particles and shearpulverization in a detailed manner. **[8]**

III.3 Why do we need compatibilizers?

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

The high interfacial tension between the polymer components will offerpoor interfacial adhesion between the components and hence shows poorproperties inferior to that of individual polymer components**.** Thus itcan be said that un-stabilized morphology, phase separation, poor interfacialadhesion between the polymeric components of immiscible polymer blendwill lead to the poor physic-mechanical properties. So, it is necessary tofindout 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 thephases in a polymer blend system can be characterized by the interfacialtension, which when approaching zero the blend becomes miscible. Thatis, if there are strong interactions between the polymer components, thenthepolymerblendwillbemiscibleinnature. Largeinterfacialtensionleads the phase separation and the phase separated particles possibly undergoing coalescence; this will result in large particle size for the disperseddomains. The large interfacial tension between polymer componentsin polymer blends can be reduced by the addition of interfacial agentsknown as compatibilizers; these are generally molecules that can bealigned along the interfaces between the two polymer phases, reducing theinterfacial tension and thereby increasing the compatibility of the polymerblends.

Compatibilizers play a key role to improve the interfacial adhesionbetween the components and to reduce the interfacial tension between thecomponents. They exhibit interfacial activities in heterogeneous polymerblends. The interfacial activities of compatibilizers help to stabilize themorphology by enhancing interfacial adhesion. Compatibilizers resist thecoalescence of dispersed phases, thereby reducing the interfacial tension andthe size of the dispersed domains which results in an increase of adhesion atthe interface and improved properties of thefinal product. Commonly usedcompatibilizers are block, graft, or random copolymers consisting of dissimilar blocks **[9,10].**

The high interfacial tension between the polymer components willoffer poor interfacial adhesion between the components, thereby polymerblends become immiscible in nature and show poor properties inferior tothat of individual polymer components. Thus compatibilizers can behelpful for the conversion of immiscible polymer blends into usefulpolymeric products with improved properties. By adding compatibilizersinto immiscible polymer blends one can increase the application ofimmiscible blends in an industrial level. The overall action of compatibilizers involves the improvement in the compatibility between thecomponents by enhancing the interaction between the components,reducing the interfacial tension between the components, improving theinterfacial adhesion between the components, etc. and the compatibilizingaction 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.

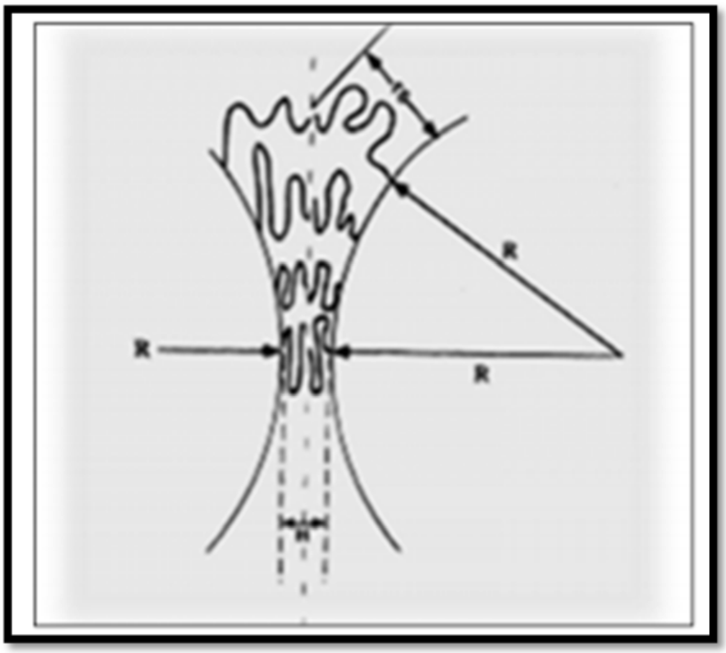


Figure III.1 Steric hinderence by compatibilizers. Compatibilizers acting as both anchors and repulsive springs ensuring the stability and prevention to coalescence**[16].**

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

➢Permitfiner 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 athird component or additive can be added to make the blend compatible.The compatibilizer will form at surfaces or provide an interphase. Acompatibilizer is analogous to a surfactant. A surfactant can emulsify orcompatibilize oil and water dispersions by stabilizing interfaces in themicellar mechanism. Compatibilizers function in the same way; they can,however, form an interphase containing some of each component. Acompatibilizer can be a small molecule or a polymer. If the compatibilizer isimmiscible, but compatible with both polymers of a blend, then it will tendto reside at the interface. An inclusion of filler particles, particularlynanoparticles 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 blendtend 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 thenanoparticles. Graphene has been oriented in blends to enhance conductivity by providing continuous pathways along the graphene even when thegraphene is at low concentration; the percolation threshold is lowered. PLAand poly-caprolactone blends have been prepared with graphene trapped atthe interface to obtain massive enhancement of thermal conductivity atvolume fraction of graphene as low as 0.53% **[18].** PP blends withpoly(ethylene terephthalate) (PET) have been prepared with graphenemostly in the PET phase of the co-continuous or double percolated blendthat exhibited increased electrical conductivity and electromotive forceshielding in the GHz frequency range **[19].**

III.5.2 Compatibilizer mutually miscible

When the compatibilizer is mutually miscible with both blended polymersthen it can form an interphase. The interphase is a region offinite thicknessbetween the two blended polymers. The interphase is a composition orstructure gradient between the two blended polymers and it may provide afunctional mechanical gradient to the properties. An example is a blend ofPVC with a poly(alkyl acrylate) where a plasticizer such as di-octyl phthalatehas been added; this ester will be miscible in both phases and function as aplasticizer for the PVC. The poly(alkyl acrylate) may also be plasticized bythe ester, but regardless it can be a toughening agent for PVC. Tougheningis performed by a separate phase of a deformable polymer, not a misciblephase that gives plasticization that decreases the modulus and strengthoverall. PVC has been shown to be miscible with some ester and etherrepeat unit polymers, such as poly(methyl methacrylate) and poly(oxyethylene) due to donoreacceptor interactions between chlorines and esteror ether oxygens**[20].** Plasticizers such as dioctyl phthalate or poly(ethyleneadipate), are miscible with the host PVC and also with blended polymersused for toughening PVC, such as poly(alkyl acrylate)s or poly(alkylmethacrylate).

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 canmigrate from the polymer within which it is miscible to the interface. Thedriving force for this migration will be to reduce the interfacial energy,which will occur when the compatibilizer develops at least a monolayer atthe interface. In each situation where the interfacial energy is minimized,there is opportunity for dispersed particle size reduction, which involvescreation 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 morethan 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].** Theuse 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 acritical concentration it may cause interfacial saturation **[28].** Therefore, therewere 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 opensnew windows to polymer technology and applications. Two polymers having good intrinsic properties, but are immiscible and incompatible ornonreactive 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 toselect most favorite pair of polymers and ease to handle compatibilizing agents. Conventionally single compatibilizing agents have been utilized, buta 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 thestudy. The interface modifiers which are added to the blend system may getinserted into the interface region and get broken down to extremely smallsize. 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. Acompatibilizing agent that suits different pairs of polymers is a challenge indevelopment. It is most of the times the localization of the compatibilizingagent in a binary or ternary blend system is unpredictable. Tuning thelocalization to a particular phase is another challenge. Development ofcompatibilizers that can be recycled and reused is a necessary situation.Exploring new materials, technology, methods, and characterization inblending invites the researchers to hit new horizons.

III.9 Applications 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 isthe most important issue worldwide and scientists endeavor to enhance thelevel of people's health, so various strategies have been developed so far to meethealth requirements. Nowadays polymers are known as the building blocks ofboth 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 vastfield in which a proper therapy ortreatment 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, astherapeutic system like drug carrier, and as regenerative scaffold in tissue engineering has been the subject of several reports **[32,33].**

Biocompatibility is thefirst requirement of a polymer to be utilized inbiomedical applications. Polymers used in biomedical engineering can becategorized into two main groups including synthetic and natural polymers.Each group has some pros and cons, for instance, natural polymers likechitosan 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. Forthe 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, there by governing the cell activity. A scaffold having uniform to pology results in monotonic cellular growth. There is agreement that polymer blends are hardly miscible, but they can be partially miscibleby 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, PPgrafted 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 cellproliferation enhanced due to restricted phase separation**[38].** It should benoticed that high concentration of the compatibilizer sometimes results intoxicity, signifying the need for optimizing compatibilizer content.

Various types of biocompatible polymer blends have been fabricated sofar and utilized in biomedical applications. It is always required for bio-based polymer blends to be processed appropriately. Typically, blends arefabricated 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 properlyon 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 theinferior 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 couldin the form of blend provide synergistic properties, very limited miscibilitywindow of such blends when melted was the reason for using appropriate compatibilizer. Based onfinal applications, precise choice of biopolymersfor blending together with a proper compatibilizer required for interfacial adhesion toward high performance encouraged having this chapter written.

References

[1] Utracki LA, Favis B. Polymer alloys and blends. New York: Marcel Dekker; **1989**.

[2] Blends P, Paul DR, Newman S, vol. 2. NY: Acdemic Press;**1978**. p.391.

[3] Xanthos M. Interfacial agents for multiphase polymer systems: recent advances. Polym Eng Sci **1988**;28(21):1392-400.

[4] Lambla M, Yu R, Lorek S. Coreactive polymer alloys. In: Multiphase polymers: blends and ionomers; **1988**. p. 67-83.

[5] Saleem M, Baker W. In situ reactive compatibilization in polymer blends: effects of functional group concentrations. J Appl Polym Sci **1990**;39(3):655-78.

[6] Xanthos M, Dagli S. Compatibilization of polymer blends by reactive processing. Polym Eng Sci **1991**;31(13):929-35.

[7] Liu N, Baker W. Reactive polymers for blend compatibilization. Adv Polym Technol **1992**;11(4):249-62.

[8] Cor Koning, Martin Van Duin, Christophe Pagnoulle’, Robert Jerome, Strategies for compatibilization of polymer blends, Progress in Polymer Science Volume 23, Issue 4, **1998**, Pages 707-757

[9] Bharati A, Wübbenhorst M, Moldenaers P, Cardinaels R. Dielectric properties of phase-separated blends containing a micro-capacitor network of carbon nano-tubes: compatibilization by a random or block copolymer. Macromolecules **2017**;50(10):3855-67.

[10] Van der Donck T, Wübbenhorst M, Moldenaers PP. Tuning the phase separated morphology and resulting electrical conductivity of carbon nano-tube-filled PAMSAN/PMMA blends by compatibilization with a random or block copolymer. Polymer **2017**;108:483-92.

[11] Saleem M, Baker W. In situ reactive compatibilization in polymer blends: effects of functional group concentrations. J Appl Polym Sci **1990**;39(3):655-78.

[12] Sinha Ray S, Bousmina M. Compatibilization efficiency of organoclay in an immiscible polycarbonate/poly (methyl methacrylate) blend. Macromol Rapid Commun **2005**;26(6):450-5.

[13] Yoon KH, Lee HW, Park OO. Properties of poly (ethylene terephthalate) and maleic anhydride-grafted polypropylene blends by reactive processing. J Appl Polym Sci **1998**;70(2):389-95.

[14] Ajitha A.R.,Sabu Thomas, Compatibilization of Polymer Blends: Micro and Nano Scale Phase Morphologies, Interphase Characterization and Properties, Book **2020**, 640 Pages

[15] Utracki LA. Commercial Polymer Blends. Chapman & Hall, London; New York. 1998

[16] Macosko, C. W., Guegan, P., Khandpur, A. K., Nakayama, A., Marechal, P., Inoue,T. Macromolecules **1996**, 29, 5590-5598

[17] Salzano de Luna M, Filippone G. Effects of nanoparticles on the morphology of immiscible polymer blends e challenges and opportunities. Eur Polym J **2016**;79:198-218.

[18] Huang J, Yutian Z, Lina X, Jianwen C, Wei J, Xiaoan N. Massive enhancement in the thermal conductivity of polymer composites by trapping graphene at the interface of a polymer blend. Compos Sci Technol **2016**;129:160-5

[19] Sadeghi A, Yeganeh MR, Khademzadeh J. Highly conductive PP/PET polymer blends with high electromagnetic interference shielding performances in the presence of thermally reduced graphene nanosheets prepared through melt compounding. Polym Compos **2019**.

[20] Subramaniam RT, Yahaya AH, Arof AK. Miscibility studies of PVC blends (PVC/ PMMA and PVC/PEO) based polymer electrolytes. Solid State Ionics **2002**;148(3):483-6.

[21] Koning Cor, Van Duin Martin, Pagnoulle Christophe, Jérôme Robert, Strategies For Compatibilization Of Polymer Blends, Progress in polymer science **1998**, vol. 23, iss. 4, pp. 707-757

[22] Anastasiadis SH, Gancarz I, Koberstein JT. Interfacial tension of immiscible polymer blends: temperature and molecular weight dependence. Macromolecules **1988**;21(10):2980-7.

[23] Majumdar B, Keskkula H, Paul D, Harvey N. Control of the morphology of polyamide/styrene-acrylonitrile copolymer blends via reactive compatibilizers. Polymer **1994**:4263-79.

[24] Koning C, Van Duin M, Pagnoulle C, Jerome R. Strategies for compatibilization of polymer blends. Prog Polym Sci **1998**;23(4):707-57.

[25] Van Puyvelde P, Velankar S, Moldenaers P. Rheology and morphology of compatibilized polymer blends. Curr Opin Colloid Interface Sci **2001**;6(5e6):457-63.

[26] La Mantia FP, Ceraulo M, Mistretta MC, Botta L, Morreale M. Compatibilization of polypropylene/polyamide 6 blend fibers using photo-oxidized polypropylene. Materials **2018**;12(1):81.

[27] Rigoussen A, Raquez J-M, Dubois P, Verge P. A dual approach to compatibilize PLA/ ABS immiscible blends with epoxidized cardanol derivatives. Eur Polym J **2019**;114:118-26.

[28] Rastin H, Saeb MR, Jafari SH, Khonakdar HA, Kritzschmar B, Wagenknecht U. Reactive compatibilization of ternary polymer blends with coreeshell type morphology. Macromol Mater Eng **2015**;300(1):86-98.

[29] Kim S, Kim JK, Park C. Effect of molecular architecture of in situ reactive compatibilizer on the morphology and interfacial activity of an immiscible polyolefin/polystyrene blend. Polymer **1997**;38(8):1809-15.

[30] Jazani OM, Arefazar A, Peymanfar MR, Saeb MR, Talaei A, Bahadori B. The influence of NBR-g-GMA compatibilizer on the morphology and mechanical properties of poly (ethylene terephthalate)/polycarbonate/NBR ternary blends. Polym Plast Technol Eng **2013**;52(13):1295-302.

[31] Bakhshandeh B, Zarrintaj P, Oftadeh MO, Keramati F, Fouladiha H, Sohrabijahromi S, et al. Tissue engineering; strategies, tissues, and biomaterials. Biotechnol Genet Eng Rev **2017**;33:144-72.

[32] Zarrintaj P, Moghaddam AS, Manouchehri S, Atoufi Z, Amiri A, Amirkhani MA, et al. Can regenerative medicine and nanotechnology combine to heal wounds? The search for the ideal wound dressing. Nanomedicine **2017**;12:2403-22.

[33] Nilforoushzadeh MA, Amirkhani MA, Zarrintaj P, Salehi Moghaddam A, Mehrabi T, Alavi S, et al. Skin care and rejuvenation by cosmeceutical facial mask. J Cosmet Dermatol **2018**;17(5):693-702.

[34] Nilforoushzadeh MA, Zare M, Zarrintaj P, Alizadeh E, Taghiabadi E, HeidariKharaji M, et al. Engineering the niche for hair regeneration-a critical review. Nanomed Nanotechnol Biol Med **2018**;15(1):70-85.

[35] Tariverdian T, Zarintaj P, Milan PB, Saeb MR, Kargozar S, Sefat F, et al. Nanoengineered biomaterials for kidney regeneration. In: Nano-engineered biomaterials for regenerative medicine. Elsevier; **2019**. p. 325-44

[36] Diban N, Stamatialis D. Polymeric hollowfiber membranes for bioartificial organs and tissue engineering applications. J Chem Technol Biotechnol **2014**;89:633-43.

[37] Naffakh M, Díez-Pascual AM, Marco C. Polymer blend nanocomposites based on poly (l-lactic acid), polypropylene and WS2 inorganic nanotubes. RSC Adv **2016**;6:40033-44.

[38] Calandrelli L, Calarco A, Laurienzo P, Malinconico M, Petillo O, Peluso G. Compatibilized polymer blends based on PDLLA and PCL for application in bioartificial liver. Biomacromolecules **2008**;9:1527-34.

[39] Przybysz M, Zedler Ł, Saeb MR, Formela K. Structure-property relationships in peroxide-assisted blends of poly (ε-caprolactone) and poly (3-hydroxybutyrate). React Funct Polym **2018**;127:113-22.

[40] Hassanpour Asl F, Saeb MR, Jafari SH, Khonakdar HA, Rastin H, Pötschke P, et al. Looking back to interfacial tension prediction in the compatibilized polymer blends: discrepancies between theories and experiments. J Appl Polym Sci **2018**;135:46144.

Chapter IV

Literature Review

IV.1 Literature Review

Polymer blending is an important field in polymer research due to unique synergistic properties obtained by polymer mixing. The reason for polymer blends manufacturing is the need for elimination or diminishing the drawbacks that characterize the individual polymers. Furthermore, there is also the desire to drop the price of the expensive polymers with specific properties by mixing them with the cheaper ones, without significant deterioration of their properties. Unfortunately, most of the polymers are immiscible at the molecular scale, the entropy of mixing is very low and, without specific interactions, biphasic systems were obtained from melt mixing. These heterogeneous polymer systems might be enhanced by various methods, including both reactive and non-reactive processes. For example, the use of compatibilizer is a very effective method for establishing the interactions between polymers in blends. The compatibilizer then locates at the border of two polymer phases and induces enhanced interactions between polymer components due to reduced interfacial tension. Reactive compatibilization processes can promote the in situ formation of copolymers during melt blending when some polymer types, containing certain functional groups (carboxyl), react with the other polymer components.

In some cases, even though there is lack of chemical interactions between the components in an immiscible blend, the fine micron scale morphology obtained through melt blending is capable of affecting individual component transitions, such as crystallization and glass transition, through physical interactions. The bulk morphology created by melt mixing is shown to depend on parameters like composition, viscosity ratio of the components, rheological and interfacial properties, processing conditions, and mixing time. The interface and domain size effects are also reflected in other common properties of the polymer like melting and crystallization behavior, degree of crystallinity, and the spherulite size. However, less is known about the parameters controlling the surface properties. Surface properties are important for compatibility or adhesion and are receiving increasing attention in literature. It is shown that surface properties are influenced by different parameters: thermal history and changes in bulk thermodynamics (crystallization of one of the phases).

Another aspect, which is also very important in polymer blend preparation, is the type of mixing process. The properties of the polymer blends depend not only on the type of the components but also significantly on the mixing method that includes the order of the components added. For this purpose, multi-step process for polymer blends preparing is often used. That kind of preparation manifests especially in the change of the mechanical, thermal, and processing properties of polymer blends. It is known that different modes of component addition affect the mechanical and morphological properties of the blends.

Recently blending also reveals as a very promising method for polymer recycling. However, the immiscibility of some polymer types, like PET and HDPE, causes poor interfacial adhesion and mechanical properties of recyclate. Polyethylene present in a PET matrix is an impurity originating from bottle caps and causes problems during recycling i.e. deteriorates PET properties. For that reason, the properties of such PET/HDPE blends should be improved using some types of compatibilizers. Compatibilizer causes the decrease in the size of polymer domains, which leads to better blend properties.

Depending on compatibilizer structure, different interactions between the blend components will be established with the final result of the improved adhesion and compatibility.

The compatibility in immiscible PET/HDPE polymer blends can be enhanced by reactive and non-reactive compatibilization, when the reduction in interfacial tension and the improvement of interfacial adhesion as well as better blend morphology are obtained. The effective compatibilization in PET/HDPE systems was determined by the effect of the compatibilizer type: EGMA, PE-g-MA, GMA, and different isocyanate compatibilizers, compatibilizer content and mixing procedure.

In this section and for the sake of illustration, a brief presentation of some of the works that have been published and which covered different aspects of the subject, will be made.

These studies are presented in a chronological order.

For example; **T. D. Traugott et al [1]** have studied the mechanical compatibilization of High Density Polyethylene/Poly(ethy1ene Terephthalate) (HDPE/PET) blends using styrene/ethylene-co-butene-l/styrene triblock copolymer and ethylene-propylene diene monomer (EPDM) as a compatibilizing agents. Mechanical properties have investigated by means of tensile and Impact test. They have found that the addition of small amounts of a triblock copolymer greatly improved the ductility of these incompatible blends, whereas the addition of an ethylene-propylene elastomer did not affect much the mechanical properties.

In another study; The orientation characteristics and the effects of orientation on the structure and mechanical properties of ternary blends based on PET, HDPE, as well as compatibilizing agent have been studied by **P.Sambaru and S. A. Jabarin [2]**. These oriented blends have been characterized using infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). The tensile and tensile impact properties were also investigated. Scanning electron microscope was used for the morphological examination. From their results, Infrared measurements show that PET within the blend has undergone strain induced crystallization upon orientation. It has also been observed that the mechanical properties, such as the modulus and ultimate stress, show improvement upon orientation. Simultaneously stretched blends show better physical properties than sequentially oriented blends. The results show that blends with compatibilizer show strain hardening upon orientation, whereas the blend without compatibilizer does not strain harden upon orientation. The blends with less PET content have been difficult to orient. The morphology of these blends show fibril structure, highly oriented in the direction of stretch.

S. S. Dagli and Kunal M. Kamdar [3] have investigated the reactive compatibilization between the two thermoplastic polymer blends based on PET/HDPE. Blends of HDPE/PET can be compatibilized by utilizing ester groups or terminal carboxyl as well as hydroxyl groups present in PET. An ethyleneglycidyl methacrylate copolymer (EGMA) was found to be very effective in compatibilizing this blend by forming a compatibilizer in-situ. The in-situ formation of the compatibilizer and its distribution could be affected by different sequences and modes of component addition. To determine the best protocol of component addition for such a reactive compatibilization process, different sequences and modes of component addition were tried out in an intensive batch mixer and in a twin-screw extruder. They have found that a small amount of EGMA appeared to be sufficient for the compatibilization. For a HDPE (nonpolar)/PET (polar) system, initial closer contact of EGMA (polar) with HDPE resulted in better compatibilization. During the comelting of the HDPE and EGMA, the EGMA molecules appear to orient themselves in a way that favors the copolymer formation right at the interface. Initial close contact of EGMA with PET resulted in a coarser morphology and inferior mechanical properties. Such a sequence could result in the EGMA-PET copolymer molecule’s remaining in the PET phase and not being able to emerge at the interface. When a blend is undergoing compatibilization in-sib not only is the formation of compatibilizer molecules very important but also their positioning at the interface. Grouping functionalized polymer with the nonpolar blend component appears to achieve both the formation of compatibilizer molecules and their positioning at the interface.

In another article, **S.Kim and coworkers [4]** have investigated the effect of functional group on PET/HDPE blends using Poly(ethylene –co-acrylic acid) (PEAA) as a compatibilizing agent. The mechanical, thermal and morphological properties of PET/HDPE systems with/and without PEAA as a reactive compatibilizer were investigated by means of flexural, impact strenght, differential scanning calorimetry (DSC),and Scanning electron microscopy (SEM), respectively. They have found that the addition of PEAA improves the mechanical properties such as flexural yield strain and impact strength when HDPE forms matrix phase. In the other hand, when PET is the matrix, no significant improvement of mechanical properties is noted, suggesting that the crystallization rate can be an important factor in the blend composed of two crystalline components. The addition of PEAA also effects morphological examination such as reducing the size of dispersed phase and making the interface obscure indicating the role of PEAA as a reactive compatibilizer. The crystallinity of PET and HDPE is slightly reduced by the addition of PEAA. These effects could be attributed to the improvement and enhanced the interfacial adhesion and reduce the interfacial tension between the two polymer phases imparted by the compatibilizing agent.

In another study, **Y. Pietrasanta et al [5]** have reported the reactive compatibilization of HDPE/PET blends by glycidyl methacrylate functionalized polyolefins. Blends of high-density polyethylene (HDPE) and poly (ethylene terephthalate) (PET) in weight compositions of 20/80, 40/60, 60/40 and 80/20 were modified with glycidyl methacrylate functionalized polyolefins with the aim of improving the compatibility and in particular elongation and impact strength. The compatibilizers used were ethylene/glycidyl methacrylate copolymers (E/GMA) and ethylene/ethyl acrylate/ glycidyl methacrylate terpolymers (E/EA/GMA) with variable contents of reactive functions (1 to 8 wt.-% of glycidyl methacrylate). The effects of the compatibilizers were investigated by studying the mechanical properties of the blends. From their results, they have found that the addition of 5 wt % of functionalized polyolefins was found sufficient to improve ductility and impact strength of all compositions. A more pronounced compatibilizing effect was obtained with the functionalized terpolymer containing the smallest amount of glycidyl methacrylate. With this emulsifying agent, elongation at break is increased by a factor of four for the compositions near the inversion of phases.

In Situ Compatibilization of HDPE/PET Blends have reported by **J. M. Lusinchi et al [6],** The reactive compatibilization of immiscible polymers such as high-density polyethylene (HDPE) and poly(ethylene terephthalate) (PET) by interfacial grafting of maleic anhydride (MA) without initiator in the molten state was investigated in this study. Grafting reaction of MA onto HDPE was carried out in a Rheocord HAAKE mixer varying reaction parameters such as the temperature, the shear rate, and the time of reaction. Then, the purified copolymers were characterized by infrared spectrometry and the MA content of HDPE-g-MA copolymers was determined by volumetric titration. It has been shown that thermomechanical initiation is sufficient to reach grafting yield of 0.3 to 2.5wt% of MA. They studied then the compatibilization of HDPE/PET blends by interfacial grafting of MA. The in situ interfacial reaction leads to the formation of HDPE-g-MA copolymer which acts as a compatibilizer in the blends. The foremost interest of their work is that it provides a simple way of compatibilization of immiscible blends of polyolefin and polyester in one transformation step without using free-radical initiators. The mechanical properties of the blends are strongly improved by the addition of small quantities of MA. The SEM observations of the compatibilized blends show a deep modification of the structure (i.e., enhanced regularity in the nodule dispersion and better interfacial adhesion).

In another publication, **Dong-Hyun kim et al [7]**, have investigated the compatibility of High-Density Polyethylene/Poly(ethylene terephthalate) blend by the use of Blocked Isocyanate Group. The blocked isocyanate group (BHI) was synthesized to improve the storage stability of HI (2-hydroxyethyl methacrylate combined with isophorone diisocyanate). High-density polyethylene grafted with the blocked isocyanate group (HDPE-g-BHI) was used as a reactive compatibilizer for an immiscible high-density polyethylene/poly (ethylene terephthalate) (HDPE/PET) blend. A possible reactive compatibilization mechanism is that regenerated isocyanate groups of HDPE functionalized by BHI react with the hydroxyl and carboxyl groups of PET during melt blending. The morphological examination, dynamic mechanical, thermal, and tensile test were also investigated by means of SEM, DMA, DSC, and tensile test, respectively. The HDPE-g-BHI/PET blend showed the smaller size of a dispersed phase compared to the HDPE/PET blend, indicating improved compatibility between HDPE and PET. This increased compatibility was due to the formation of an in situ graft copolymer, which was confirmed by dynamic mechanical analysis. Differential scanning calorimetry (DSC) analysis represented that there were few changes in the crystallinity for the continuous PET phase of the HDPE-g-BHI/PET blends, compared with those of the HDPE/PET blends at the same composition. Tensile strengths and elongations at the break of the HDPE-g-BHI/ PET blends were greater than those of the HDPE/PET blends.

T.L. Dimitrova et al [8] have studied the compatibilization of PET/HDPE blends through a new class of copolyester. Polyethylene terephthalate (PET) and polyethylene are incompatible polymers and their blends show, in general, poor properties. Compatibilization is then a necessary step to obtain blends with good mechanical and barrier properties. In their work, different compatibilizing agents were used, i.e. a maleic anhydride elastomer and some new products containing graft-copolymers having polyester segments grafted onto polyethylene backbone chains. Both the functionalized elastomer and the new products drastically improve the morphology and the ductility of the blend. In the case of the modified elastomer the compatibilizing action has been attributed to the formation of H-bonds whereas the copolymers contained in the new products act as compatibilizing agents as they contain polyester segments and polyethylene segments with thermodynamic affinity with PET and polyethylene, respectively.

N. Torres et al [9] have reported the Compatibilization of HDPE–PET Blends by Adding Grafted or Statistical Copolymers. The reactive compatibilization of blends of HDPE–PET [high-densitypolyethylene–poly(ethyleneterephthalate)]wasinvestigatedinthisstudy.

The compatibilizers used were two grafted copolymers prepared by reactive extrusion containing 1.20–2.30 wt% GMA such as HDPE-g-GMA and one statistical copolymer containing 1 wt% GMA such as Lotader AX8920. HDPE was successfully functionalized using a melt free-radical grafting technique. Grafting was initiated in two ways: adding an Initiator in the polymer–monomer mixture or activation by ozone of polymer. Ozonization of HDPE by the introduction of a peroxide lead to a better grafting yield and to better grafting efficiency of the samples. The effects of the three compatibilizers were evaluated by studying the morphology, thermal and mechanical properties of HDPE–PET(70/30wt%)blends. Significant improvements were observed, especially in morphology, elongation at break, and Charpy impact strength of the compatibilized blends. A more pronounced compatibilizing effect was obtained with the statistical copolymer, for which the elongation at break and the impact strength were increased by 100%, while the uncompatibilized blends showed a 60% decrease in the Young’s modulus and the strength at break. We also were able to show that the grafting yield increase of 1.20–2.30 wt % of GMA did not affect the properties of the blends because the grafted copolymers possess very similar chemical structures. However, compatibilization of blends with grafted copolymers is an interesting method, particularly for recycled blends, because the synthesis of these compatibilizers is easy and cheap in comparison to statistical copolymer.

A Preliminary Investigation on the Use of Poly [(ethylene terephthalate)-co-(e-caprolactone)] Copolymer as Compatibiliser of HDPE/PET Blends was studied by **P. Laurienzo et al [10]**

A preliminary study on the possibility to use the copolymer poly[(ethylene terephthalate)-co-(e-caprolactone)]as a compatibilising agent in blends of high density polyethylene (HDPE) and poly(ethylene terephthalate) (PET) is reported. The copolymer was synthesized by polycondensation no flow-molecular weight PCL precursors, previously end-capped with reactive isocyanate groups, and oligomers of PET obtained from PET waste through a controlled depolymerization procedure. HDPE/ PET blends at a composition of 70/30 w/w with and without the addition of 10wt %of compatibiliser were prepared in a single-screw mixer extruder. The effect of compatibiliser was evaluated by studying the thermal, dynamic-mechanical and mechanical properties and the morphology of the blends. The compatibiliser was found to be a good emulsifying agent from a morphological point of view. Nevertheless, the mechanical properties of the blend were not improved by the addition of the compatibiliser.

In another publication, **L. Kratofil and coworkers [11]** have reported the effect of compatibilizers on blends based on Waste PET/HDPE. The fraction of HDPE in PET/HDPE blends was 3, 5, 6 and 10 wt%. Isocyanate HI compatibilizer was first synthesized and then added to the blends at a fraction of 5 wt %. Another compatibilizer named Ethylene-propylene-diene monomer masterbatch (EPDM-M) was prepared by mixing and added at various ratios from 15, 30 and 50 wt%. Uncompatibilized as well as compatibilized samples were characterized by scanning electron microscopy SEM for morphological examination. Blends prepared with isocyanate HI compatibilizer were also studied by FTIR spectroscopy. They have found that the higher fraction of HDPE in blends enables more interactions with compatibilizer that results in fine morphology. They have also found that Appearance of new vibrations in the FTIR spectra confirms that during the blending reactions between isocyanate HI compatibilizer and blend components appear. Previous results show that used compatibilizers significantly improved and enhanced the compatibility of polymers in studied blends.

In another research; dynamic mechanical thermal properties of compatibilized PET with radiation oxidized HDPE was studied by **P. J. H.Franco et al [12].** Binary blends of HDPE/PET exhibit poor mechanical properties because of their incompatibility. HDPE was oxidized by gamma-ray pre-irradiation in air, subsequently heated to destroy peroxides formed by this irradiation and to form polar groups in the HDPE, and then extruded with PET as a compatibilizing method of the blend. The dynamic mechanical thermal properties were investigated. From their results, an improvement was observed when the PET content was increased while the HDPE used was irradiated. The largest increase in the mechanical properties was observed for PET contents between 10 and 20% (w/w). The improvement in the dynamic mechanical properties is believed to occur because of a percolation effect of the PET in the HDPE matrix and the radiation-improved compatibility by means of polar groups formed in the polyethylene.

S. Mbarek et al [13] have studied the dispersed phase morphology and fractionated crystallization of high-density polyethylene in PET/HDPE blends. The influence of the addition of an ethylene-glycidyl methacrylate (E-GMA) copolymer on the morphology and on the crystallization of the blends was also investigated. Their results indicated that the small particle sizes can be equally obtained by the addition of a compatibilizer of the E-GMA type, which acts as an emulsifier. However, for the HDPE with the highest molecular weight, the E-GMA copolymer has low efficiency with regards to the dispersion due to its poor miscibility with the HDPE. The fractionated crystallization is not observed and the distribution of sizes shows small particles of E-GMA coexisting with large HDPE droplets. They have also found that for a high molecular weight polyethylene, the compatibilizer shows less efficiency as far as dispersion is concerned.

S.C Li and coworkers [14] have reported the compatibilization of HDPE/PET using Ethylene–Butyl Acrylate–Glycidyl Methacrylate (EBAGMA) Terpolymer as a reactive compatibilizer. HDPE/PET/EBAGMA blends were prepared by means of melt extrusion. The effects of the EBAGMA and PET contents, recovery temperature, and stretch ratio on the thermostimulative shape-memory behavior of the blends were also studied. The results show that the addition of EBAGMA to the HDPE/PET blends obviously improved the compatibility as a result; the interfacial adhesion between the PET and HDPE phases was evidently enhanced.

In another paper, Yang Pan et al **[15]** have studied and Improved the compatibility of PET/HDPE blend by using GMA grafted thermoplastic elastomer. Graft-modified ethylene-1-octene copolymer (POE-g-GMA) and styrene-butadiene-styrene triblock copolymer (SBS-g-GMA) were used as a compatibilizers in the PET/HDPE system. The morphological behavior; mechanical as well as rheological properties were also investigated by means of SEM analysis, impact strength test, and capillary rheometer, respectively. They have found that with increase in compatibilizer amount, uniform phase morphology was observed in all the blends. Thus, exhibiting enhanced mechanical properties, especially, the notched Izod impact strength. In comparison with SBS-g-GMA, compatibilizer POE-g-GMA demonstrated greater impact on the compatibility. The addition of 15% POE-g-GMA produced blends with best mechanical properties. Besides, both POE-g-GMA and SBS-g-GMA enhanced the melt viscosity of PET/HDPE blends.

In the other paper, blends of recycled polyethylene terephthalate (r-PET) and high-density polyethylene (HDPE) with and without a compatibilizer were studied by A. Hellati and S. Boufassa **[16].** These blends were prepared using a Brabender Haake Rheocord at 270°C and 32rpm. Ethylene vinyl acetate was chosen as the compatibilizer and its proportion was set to 5, 7, and 10 wt%. The thermal properties and crystallization behavior were determined by Differential Scanning Calorimetry (DSC). Micromechanical properties were also investigated using a Vickers micro-indentation tester. The DSC analysis indicates that the melting temperature of r-PET and HDPE in all the blends, compatibilized and uncompatibilized, remains constant and almost the same as those of the pure component. On the other hand, it is shown that the degree of crystallinity of HDPE in the blends calculated by DSC depends on the composition of the polymeric mixture. However, the Hardness (H) decreases with increasing r-PET content until 50/50 composition of r-PET/HDPE is reached, whereas for larger r-PET content values, H increases. The same trend was obtained with the addition of the compatibilizer.

References

[1] Traugott, T.D.; Barlow, J.W.; Paul, D.R. Mechanical Compatibilization of High Density Polyethylene–Poly(Ethylene Terephthalate) Blends. *J. Appl. Polym. Sci.* **1983**, *28*, 2947–2959, doi:10.1002/app.1983.070280922.

[2] Sambaru, P.; Jabarin, S.A. Properties and Morphology of Oriented Ternary Blends of Poly(Ethylene Terephthalate), High Density Polyethylene, and Compatibilizing Agent. Polym. Eng. Sci. **1993**, 33, 827–837, doi:10.1002/pen.760331307.

[3] Dagli, S.S.; Kamdar, K.M. Effects of Component Addition Protocol on the Reactive Compatibilization of HDPE/PET Blends.*Polym. Eng. Sci.***1994**, *34*, 1709–1719, doi:10.1002/pen.760342302.

[4] S.Kim Chan Eun Parck.jeong Ho An.Doosung Lee and Jinhwan Kim **.**the effect of functional group content on Polyethylene–Poly(Ethylene Terephthalate) \High Density Polyethylene blends compatibilized with Poly(ethylene –co-acrylic acid).polumer jornal vol 29 n 3,**1997**.pp274-278 , https://doi.org/10.1295/polymj.29.274

[5] Pietrasanta, Y.; Robin, J.-J.; Torres, N.; Boutevin, B. Reactive Compatibilization of HDPE/PET Blends by Glycidyl Methacrylate Functionalized Polyolefins. *Macromol. Chem. Phys.***1999**, *200*, 142–149, doi:10.1002/(SICI)1521-3935(19990101)200:1<142::AID-MACP142>3.0.CO;2-W.

[6] Lusinchi, J.M.; Boutevin, B.; Torres, N.; Robin, J.J.In Situ Compatibilization of HDPE/PET Blends.*J. Appl. Polym. Sci.* 2001, *79*, 874–880, doi:10.1002/1097-4628(20010131)79:5<874::AID-APP120>3.0.CO;2-B.

[7] Kim, D.-H.; Park, K.-Y.; Kim, J.-Y.; Suh, K.-D. Improved Compatibility of High-Density Polyethylene/Poly(Ethylene Terephthalate) Blend by the Use of Blocked Isocyanate Group. *J. Appl. Polym. Sci.***2000**, *78*, 1017–1024, doi:10.1002/1097-4628(20001031)78:5<1017::AID-APP110>3.0.CO;2-6.

[8] Dimitrova, T.L.; La Mantia, F.P.; Pilati, F.; Toselli, M.; Valenza, A.; Visco, A.On the Compatibilization of PET/HDPE Blends through a New Class of Copolyesters. *Polymer* **2000**, *41*, 4817–4824, doi:10.1016/S0032-3861(99)00709-0.

[9] Torres, N.; Robin, J.J.; Boutevin, B. Study of Compatibilization of HDPE-PET Blends by Adding Grafted or Statistical Copolymers.*J. Appl. Polym. Sci.***2001**, *81*, 2377–2386, doi:10.1002/app.1678.

[10] Laurienzo, P.; Immirzi, B.; Malinconico, M. A Preliminary Investigation on the Use of Poly[(Ethylene Terephthalate)-Co-(ε-Caprolactone)] Copolymer as Compatibiliser of HDPE/PET Blends. *Macromol. Mater. Eng.***2001**, *286*, 248–253, doi:10.1002/1439-2054(20010401)286:4<248::AID-MAME248>3.0.CO;2-9.

[11] Kratofil, L.; Hrnjak-Murgić, Z.; Jelencć, J.; Andricć, B.; Kovacć, T.; Merzel, V. Study of the Compatibilizer Effect on Blends Prepared from Waste Poly(Ethylene-Terephthalate) and High Density Polyethylene. *International Polymer Processing* **2006**, *21*, 328–335, doi:10.3139/217.0123.

[12] Herrera-Franco, P.J.; Hernández-Sánchez, F.; Adem, E.; Burillo, G. Dynamic Mechanical Properties of Compatibilized PET with Radiation Oxidized HDPE. *Polym. Bull.* **2006**, *56*, 47–52, doi:10.1007/s00289-005-0461-7.

[13] Mbarek, S.; Jaziri, M.; Chalamet, Y.; Elleuch, B.; Carrot, C. Dispersed Phase Morphology and Fractionated Crystallization of High-Density Polyethylene in PET/HDPE Blends. *Int J Mater Form* **2009**, *2*, 15–24, doi:10.1007/s12289-008-0386-4.

[14] Li, S.-C.; Lu, L.-N.; Zeng, W. Thermostimulative Shape-Memory Effect of Reactive Compatibilized High-Density Polyethylene/Poly(Ethylene Terephthalate) Blends by an Ethylene-Butyl Acrylate-Glycidyl Methacrylate Terpolymer. *J. Appl. Polym. Sci.* **2009**, *112*, 3341–3346, doi:10.1002/app.29530

[15] Pan, Y.; Wu, G.; Ma, H.; Zhou, S.; Zhang, H. Improved Compatibility of PET/HDPE Blend by Using GMA Grafted Thermoplastic Elastomer. *Polymer-Plastics Technology and Materials* **2020**, *59*, 1887–1898, doi:10.1080/25740881.2020.1765382.

[16] Hellati, A.; Boufassa, S. Evaluation of the Role of Ethylene Vinyl Acetate on the Thermo-Mechanical Properties of PET/HDPE Blends. *Eng. Technol. Appl. Sci. Res.* 2022, *12*, 9546–9550, doi:10.48084/etasr.5313.

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 maysay they are truly a novelty to the world. A blend will usually consist of amatrix and dispersed phase, though various composition-dependentco-continuous morphologies can be formed. The polymers for blends canbe chosen from compatible polymers, separate compatibilizer additives included, or various reaction strategies used to enhance compatibility.

The polymer mixture of polyethylene terephthalate (PET) and high density polyethylene(HDPE) constitutes a significant portion of post-consumer waste. The two polymers are immiscible and need to be compatibilized in order to be used in commercial applications. The immiscibility of PET and HDPE is because of their quite different molecular structures, polarities, and crystallization behaviors. The unfavorable interactions between themolecular chains would lead to large interfacial tension in the melt and make it difficult to disperse the components during mixing. Such unfavorable interactions also lead to unstablemorphology and poor interfacial adhesion, resulting in inferior mechanical properties.Compatibilityand adhesion between the two polymer phases can be improved by the addition of suitableblock or graft copolymers which act as emulsifyingagents localized at the interface between immisciblephases. Another possibility is to generate copolymers in-situ during the preparation of blends, using functionalized polymers. These two possibilities were used by many researchers to compatibilize HDPE/PET blends because these two incompatible and widely used polymers lead toa material with poor mechanical properties.

In conclusion; 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 issignificant and may exceed specific interactions. Such polymer blends arenever 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 fromeach polymer.

Abstract

The compatibilization of polymer blends, such as high-density polyethylene (HDPE) and polyethylene terephthalate (PET), is a process that aims to improve the compatibility and the properties of the blend. HDPE/PET exhibit poor miscibility due to differences in their chemical structure and polarity. This leads to phase separation and weak interfacial interactions between the polymers, resulting in reduced mechanical, thermal, and other properties of the blend. Compatibilization methods such as Physical and chemical compatibilization are employed to overcome these challenges and enhance the performance of polymer blends. Physical compatibilization involves incorporating a compatibilizing agent into the blend, which can effectively improve the interfacial adhesion and promote molecular-level mixing between the polymers.

Keywords: High-Density Polyethylene, Polyethylene Terephthalate, Immiscible Blend Phase Separation, Physical Compatibilization, Chemical Compatibilization.

Résumé

La compatibilisation des mélanges de polymères, tels que le polyéthylène à haute densité (HDPE) et le polyéthylène téréphtalate (PET).est un procédé qui vise à améliorer la compatibilité et les propriétés du mélange. Le PEHD/PET présente une faible miscibilité en raison des différences de structure chimique et de polarité. Cela conduit à une séparation de phase et à de faibles interactions interfaciales entre les polymères, ce qui entraîne une réduction des propriétés mécaniques, thermiques et autres du mélange.

Des méthodes de compatibilité telles que la compatibilisation physique et chimique sont utilisées pour surmonter ces défis et améliorer les performances des mélanges de polymères. La compatibilité physique implique l'incorporation d'un agent de compatibilisation dans le mélange, qui peut améliorer efficacement l'adhérence interfaciale et favoriser le mélange au niveau moléculaire entre les polymères.

Mots clés: Polyéthylène à haute densité, Polyéthylène téréphtalate, Mélanges Immiscible, Séparation de phase, Compatibilization Physique, Compatibilization Chimique.

ملخص

إن توافق خلائط البوليمر، مثل البولي إيثيلين عالي الكثافة والبولي إيثيلين تيريفثاليت هي عملية تهدف الى تحسين توافق و خصائص المزيج. يتميز البولي إيثيلين عالي الكثافة والبولي إيثيلين تيريفثاليت باختلاط منخفض بسبب الاختلافات في التركيب الكيميائي والقطبية. وهدا ما يؤدي الى فصل الطور و التفاعلات البينية الضعيفة بين البوليمرات ، مما يؤدي ذلك أيضا الى انخفاض كبير في الخصائص الميكانيكية و الحرارية و غيرها من الخواص للخليط.

تستخدم طرق التوافق مثل التوافق الفيزيائي و الكيميائي للتغلب على هذه التحديات و تحسين أداء خلائط البوليمر. يتضمن التوافق المادي دمج عامل التوافق في المزيج والذي يمكن ان يحسن بشكل فعال من الالتصاق البيني و يعزز المزج على المستوى الجزيئي بين البوليمرات .

الكلمات المفتاحية

بولي إيثيلين عالي الكثافة ، بولي إيثيلين تيريفثاليت ، فصل طور المزيج غير القابل للامتزاج ، التوافق الفيزيائي ، التوافق الكيميائي.