



REPUBLIQUE ALGERIENNE DEMOCRATIQUE ET POPULAIRE



MINISTERE DE L'ENSEIGNEMENT SUPERIEUR ET DE LA RECHERCHE SCIENTIFIQUE

UNIVERSITE DE 20 AOUT 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 Poly (ethylene terephthalate)/Polypropylene
(PET/PP) Thermoplastic Polymer Blends: Effect of Compatibilizers
on the Rheological, Mechanical, Morphological and Thermal
Properties***

Soutenu le **03/07/2023**

Réalisé par :

1- Kéchiri Sid Ali

2- Lekhchine Khawla

3- Hafsi Marwa

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
Dedications	I
Acknowledgements	II
Table of Contents	III
List of Figures	VI
List of Tables	VIII
List of Notations and Abbreviations	X
General Introduction	1

Chapter I

Theoretical background

I.1 Introduction	6
I.2 Polypropylene	6
I.2.1 Synthesis Methods of Polypropylene (Polymerization reaction)	6
I.2.2 Chemical structure of polypropylene	7
I.2.3 Properties of polypropylene	9
I.2.4 Major Advantages of polypropylene	11
I.2.5 Drawbacks of polypropylene	11
I.2.6 Manufacturing processes of polypropylene	11
I.2.7 Applications of Polypropylene	16
I.3 Polyethylene terephthalate	17
I.3.1 Synthesis method of PET	17
I.3.2 Chemical structure of PET	19
I.3.3 Properties of PET	19
I.3.4 Major Advantages of PET	22
I.3.5 Drawbacks of PET	23

Table of contents

I.3.6 Manufacturing processes of PET.....	23
I.3.7 Applications of PET	25
References.....	26

Chapter II

Thermodynamics of Polymer Blends

II.1 General Introduction.....	28
II.2 Thermodynamics of Binary Polymer Blend Systems.....	29
II.3 Classification of Polymer Blends	33
II.3.1 Classification based on constituents.....	33
II.3.2 Classification based on the miscibility.....	33
II.3.2.1 Miscible Polymer Blends.....	34
II.3.2.2 Compatible Blends.....	34
II.3.2.3 Immiscible Blends.....	35
II.4 Preparation Methods of Polymer Blends.....	35
II.5 Properties of Polymer Blends.....	36
II.6 Factors Affecting the Properties of Polymer Blends.....	38
II.7 Drawbacks of Polymer Blends.....	39
II.8 Applications of Polymer Blends Industrial Fields.....	40
References.....	42

Chapter III

Compatibilization of Polymer Blends

III.1 General introduction.....	49
III.2 Strategies for compatibilization of polymer blends.....	49
III.3 Why do we need compatibilizers?	50
III.4 Theoretical aspects of compatibilisation.....	52

Table of contents

III.5 Blending with a compatibilizer, a third component.....	53
III.5.1 Compatibilizer immiscible in both blended polymers.....	53
III.5.2 Compatibilizer mutually miscible.....	54
III.5.3 Compatibilizer miscible with one of the blended polymers.....	54
III.6 Role of compatibilizers in blending processes.....	55
III.7 Properties of polymer blends influenced by compatibilization.....	55
III.8 New challenges in compatibilized blends.....	56
III.9 Applications of compatibilized polymer blends in biomedical fields.....	57
References.....	60

Chapter IV

Literature Review

IV.1 Literature Review.....	67
References.....	84
Conclusion	89

Abstract

List of Figures

List of Figures

List of Figures	Page
Chapter I Theoretical Background	
Figure I.1 Polymerization reaction for PP.....	7
Figure I.2 Molecules of propylene and polypropylene.....	7
Figure I.3: Chemical structure of polypropylene.....	8
Figure I.4 Stereo-configuration of propylene isotactic.....	8
Figure I.5 Stereo-configuration of propylene syndiotactic	8
Figure I.6 Stereo-configuration of propylene atactic.....	8
Figure I.7 Early slurry process technology.....	12
Figure I.8 Bulk (slurry) process technology.....	13
Figure I.9 Gas-phase process technology.	13
Figure I.10 Reactor systems in polypropylene technologies.....	15
Figure I.11 Amoco gas-phase process technology.....	15
Figure I.12 Esterification reaction between terephthalic acid and ethylene glycol.....	18
Figure I.13 Transesterification reaction between dimethyl terephthalate and ethylene glycol.....	18
Figure I.14 Molecular Structure of Polyethylene Terephthalate.....	19
Figure I.15 DSC thermograms of PET.....	22
Figure I.16 PET resin manufacturing steps.	23
Figure I.17 Eastman IntegRex manufacturing technology.	24
Chapter II Thermodynamics of Polymer Blends	
Figure II.1: Free energy of mixing for (a) completely immiscible, (b) completely miscible, and (c) partially miscible.....	29
Figure II.2: Phase diagram showing the performance of polymer blends	31

List of Figures

Chapter III Compatibilization of Polymer Blends

Figure III.1: Steric hinderence by compatibilizers. Compatibilizers acting as both anchors and repulsive springs ensuring the stability and prevention to coalescence.....	52
---	-----------

List of Tables

List of Tables **Page**

Chapter I

Theoretical Background

Table I.1 Properties of polypropylene.....	10
Table I.2 Typical applications of PP.	16
Table I.3 Critical requirements for applications where PP is one of the best choices of material.....	17
Table I.4 Application of PET according to its viscosity.....	20
Table I.5 Physical and thermal properties of PET.....	20

Chapter II

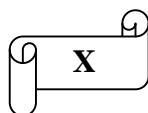
Thermodynamics of Polymer Blends

Table II.1 Examples of polymer blends which are classified based on the constituents.....	33
--	-----------

**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	Ethylene –propylene- diene monomer
EPDM-M	Ethylene –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	Poly lactide
PMMA	Poly(methyl methacrylate)
PET	polyethylene terephthalate
PEAA	Poly(ethylene –co-acrylic)
POE-g-GMA	Polyoxyethylene-grafted- glycidyl methacrylate
PP-g-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
T_g	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
ΔH_m	Melting enthalpy of sample
ΔH_0	Theoretical enthalpy for 100 % crystalline
T_c	Crystallization temperature
T_g	Glass transition temperature
ρ	Density
TS	Tensile strength
m	Mass
ϵ_b	Elongation at break
T	Temperature
σ	Tensile strength
ϵ	Strain
mm	Millimeter
°C	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

General Introduction

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

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

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

General Introduction

the control of blend morphology which may be achieved through this type of reactive compatibilization scheme. It has been demonstrated that the dispersion of the minor polymer blend component decreases in average size with increasing concentration of functional groups, and that a homogeneous material may be achieved at sufficiently high functional group concentrations.

Over the years, several blends of polymers have received scientific attention. Effective polymeric blends could be the key to achieve not only materials with high industrial value and improved performance, but also to develop materials incorporating post-consumer plastics.

Polypropylene (PP) is one of the most commonly consumed polyolefins in the world, due to its versatility, relatively low-price, good flexibility, easy processability and excellent barrier properties. However, PP is susceptible to oxidation, accelerated both by heat and UV radiation, which influences its mechanical properties. It is well-established that a straightforward way to upgrade the properties of PP, particularly the mechanical performance, and broaden its field of applications, is to successfully blend it with other polymers particularly with PET. Generally, blends of PP with PET and other polymers are typically hampered by incompatibility, as the result of negligible entropy of mixing for long chain molecular interactions. Studies on blends of PP and PET, generally showed a clear two-phase morphology, proving the immiscibility behavior of these two polymers. This fact leads to a lack of interfacial adhesion between the two phases and is detrimental for the mechanical performance, as the strong material requires that the applied load is evenly distributed through both phases. The morphology of the dispersed phase is highly dependent upon the processing conditions, volume fraction of components and the quality of the interactions between the two polymers [1–13]. The use of compatibilizers as the third component of the blend has had a beneficial impact of mitigating the differences in the chemical nature and polarity between these two polymers. Generally, compatibilizers are copolymers with structures that interact/react with the components of the blend improving the interfacial adhesion between the immiscible polymer phases.

Overall; This Master Thesis is composed of four chapters. The first presents a theoretical background of Polypropylene (PP), and Polyethylene terephthalate (PET); The second chapter presents the thermodynamic principles of polymer blends, and the third chapter presents the different strategies for compatibilization of polymer blends. The fourth chapter illustrates a brief presentation of some of the works that have been published and which covered different aspects of the subject.

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

References

- [1] Van Bruggen EPA, Koster RP, Picken SJ, Ragaert K (2016) Influence of processing parameters and composition on the effective Compatibilization of polypropylene–poly(ethylene terephthalate) blends. *Int Polym Process* 31(2):179–187
- [2] Champagne MF, Huneault MA, Roux C, Peyrel W (1999) Reactive compatibilization of polypropylene/polyethylene terephthalate blends. *Polym Eng Sci* 39(6):976–984
- [3] Gnatowski A, Koszkul J (2005) Investigations of the influence of compatibilizer and filler type on the properties of chosen polymer blends. *J Mater Process Technol* 162–163:52–58
- [4] Inuwa IM, Hassan A, Samsudin SA, Haafiz MKM, Jawaid M (2017) Interface modification of compatibilized polyethylene terephthalate/polypropylene blends: effect of compatibilization on thermomechanical properties and thermal stability. *J Vinyl Addit Technol* 23(1):45–54
- [5] Abdul Razak NC, Inuwa IM, Hassan A, Samsudin SA (2013) Effects of compatibilizers on mechanical properties of PET/PP blend. *Compos Interfaces* 20(7):507–515
- [6] Oswald HJ, Turi E (1965) The deterioration of polypropylene by oxidative degradation. *Polym Eng Sci* 5(3):152–158
- [7] Maier C, Calafut T (1998) Polypropylene: the definitive User's guide and Databook. William Andrew Inc, New York

General Introduction

- [8] Schoolenberg GE, Vink P (1991) Ultra-violet degradation of polypropylene: 1. Degradation profile and thickness of the embrittled surface layer. *Polymer* 32(3): 432–437
- [9] Xanthos M, Young MW, Biesenberger JA (1990) Polypropylene/ polyethylene terephthalate blends compatibilized through functionalization. *Polym Eng Sci* 30(6):355–365
- [10] White JL, Yang J (2008) In: Domasius N., thein K. (eds) *polyolefin blends*. Wiley, New York
- [11] Cheung MK, Chan D (1999) Mechanical and rheological properties of poly(ethylene terephthalate)/ polypropylene blends. *Polym Int* 43(3):281–287
- [12] Barlow JW, Paul DR (1984) Mechanical compatibilization of immiscible blends. *Polym Eng Sci* 24(8):525–534
- [13] Santos P, Pezzin SH (2003) Mechanical properties of polypropylene reinforced with recycled-PET fibres. *J Mater Process Technol* 143–144:517–520

Chapter I

Theoretical Background

I.1 Introduction

Thermoplastics are a class of polymers that can be melted and re-molded multiple times without undergoing significant chemical degradation.[1] They are widely used in various industrial fields, such as automotive, packaging, electronics, construction, and medical devices. The synthesis of thermoplastics involves several methods that are used in industrial settings. Here are some of the common methods:

- **Polymerization:** This is the most common method used to synthesize thermoplastics. In this process, monomers are chemically bonded together to form a long chain polymer. The polymerization process can be carried out using various techniques such as suspension polymerization, emulsion polymerization, and solution polymerization.
- **Extrusion:** This method involves melting the thermoplastic polymer and extruding it through a die to form a specific shape. Extrusion is commonly used to manufacture products such as pipes, tubes, and sheets.
- **Injection Molding:** This method is used to produce complex parts with high precision and accuracy. The process involves melting the thermoplastic material and injecting it into a mold cavity under high pressure. The molten material is then cooled and solidified, and the part is ejected from the mold.
- **Blow Molding:** This process involves inflating a hollow tube of molten plastic and shaping it into a specific shape using a mold. Blow molding is commonly used to produce bottles, containers, and other hollow objects.
- **Thermoforming:** This method involves heating a sheet of thermoplastic material until it is pliable and then forming it into a specific shape using a mold. Thermoforming is commonly used to produce packaging materials, trays, and containers.

Overall, these synthesis methods are widely used in industrial settings to manufacture various thermoplastic products that meet the requirements of specific applications.[2]

I.2 Polypropylene

I.2.1 Synthesis Methods of Polypropylene (Polymerization reaction)

Polypropylene is prepared by polymerizing of propylene, a gaseous by product of petroleum refining, in the presence of a catalyst under carefully controlled heat and pressure. Propylene is an unsaturated hydrocarbon, containing only carbon and hydrogen atoms.

In the polymerization reaction, many propylene molecules (monomers) are joined together to form one large molecule of polypropylene. Propylene is reacted with an organometallic, transition metal catalyst to provide a site for the reaction to occur, and propylene molecules

are added sequentially through a reaction between the metallic functional group on the growing polymer chain and the unsaturated bond of the propylene monomer as shown in **Figure I.1**. [3]

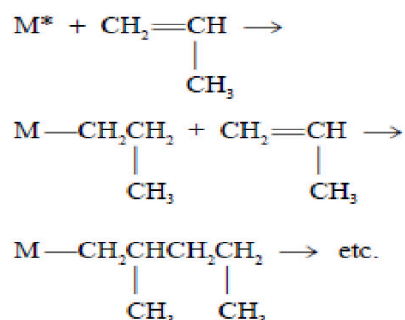


Figure I.1: Polymerization reaction for PP. [3]

One of the double-bonded carbon atoms of the incoming propylene molecule inserts itself into the bond between the metal catalyst (M in the above reaction) and the last carbon atom of the polypropylene chain. A long, linear polymer chain of carbon atoms is formed, with methyl (CH₃) groups attached to every other carbon atom of the chain (**Figure I.2**). Thousands of propylene molecules can be added sequentially until the chain reaction is terminated. [3]

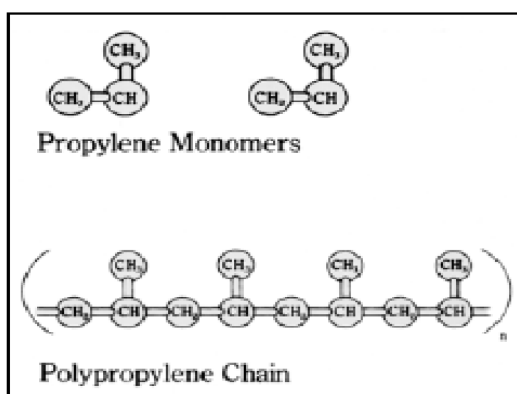


Figure I.2 Molecules of propylene and polypropylene. In the polymerization reaction, propylene monomers (top) are added sequentially to the growing polymer chain (bottom), to form a long, linear polymer chain composed of thousands of propylene monomers. The portion of the chain shown in parentheses is repeated n number of times to form the polymer. [3]

I.2.2 Chemical structure of polypropylene

Polypropylene (PP) is a type of polyolefin that is slightly harder than polyethylene. It is a commodity plastic with low density and high heat resistance. Its chemical formula is (C₃H₆)_n. [2] The structure of polypropylene is represented in **Figure I.3** [4]

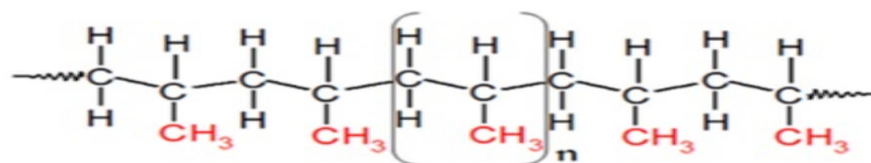


Figure I.3: Chemical structure of polypropylene [4]

Polypropylene can be isotactic, syndiotactic, or atactic, depending on the orientation of the pendant methyl groups attached to alternate carbon atoms [3]

- a) **Isotactic polypropylene:** isotactic polypropylene (iPP) in which all the methyl groups are on the same side of the zigzag plane, results from polymerization of only one isomeric configuration from propylene monomer. **Figure I.4** [3]

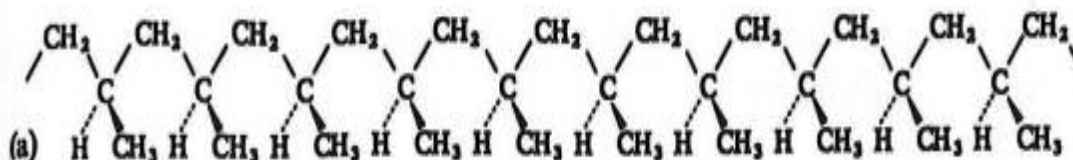


Figure I.4 Stereo-configuration of propylene isotactic [3]

- b) **Syndiotactic polypropylene:** syndiotactic polypropylene (sPP) is defined by methyl groups arranged alternatively on either side of the zigzag chain, and is obtained by alternative addition of the two stereo-isomeric configurations from propylene monomer. **Figure I.5** [3]

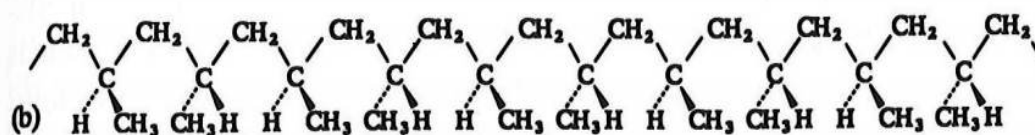


Figure I.5 Stereo-configuration of propylene syndiotactic [3]

- c) **Atactic polypropylene:** atactic polypropylene (aPP) is formed with sterically random sequence of methyl groups. This polymer, which is incapable of crystallization, can be obtained by a classical radical reaction. **Figure 1.6** [3]

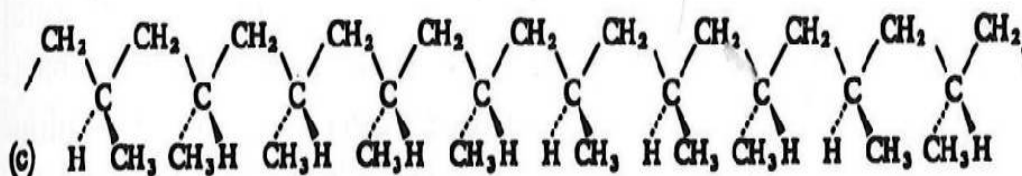


Figure I.6 Stereo-configuration of propylene atactic [3]

I.2.3 Properties of polypropylene

Polypropylene comes with various useful properties (Table I .1) [5]

1) Physical properties

- **Volumic mass**

PP is the lightest of the common thermoplastics, with a density of 0.905 g/cm^3 .

- **Melt index**

For practical applications, the melt index (IF) is considered, measured at 230°C under a load of 2.16 or 5 Kg. A high value of the melt index corresponds to a low melt viscosity and a low molar mass.

The melting temperatures of homopolymers are around 165°C . These temperatures make it possible to understand that hollow bodies are suitable for hot filling and that objects are sterilizable. The amorphous zones of the polymer have behavior that depends on the temperature and in particular the glass transition temperature T_g . A few degrees below T_g , the material becomes fragile and brittle.

- **Permeability**

PP is permeable to gases, except water vapor. The permeability decreases when the crystallinity rate increases. [5]

2) Mechanical properties

- **Tensile characteristic**

The high crystallinity of PP gives it good properties when subjected to tensile stresses; the tensile behavior of PP is strongly influenced by the stretching speed.

- **Rigidity**

The high rigidity of PP allows its use for parts intended to withstand high temperatures.

- **Impact resistance**

The impact resistance of PP increases with its molecular mass and varies in the same direction as the temperature. [5]

3) Electrical properties

The high dielectric strength and low dielectric constant and dissipation factor of polypropylene make it useful as an insulating material.

The electrical properties of PP do not depend on crystallinity or molecular weight. [5]

4) **Thermal properties**

- **Melting temperature**

The theoretical melting temperature of a 1000/0 isotactic polymer is 176°C. The practically inevitable presence of atactic and syndiotactic fraction brings the melting temperature of PP between (165°C and 170°C).

- **Softening temperature**

The softening point depends on the crystallinity of the polymer considered; it is between (145°C and 155°C). [5]

5) **Chemical properties**

Polypropylene is resistant to attack by polar chemicals such as soaps, wetting agents, and alcohols but can swell, soften, or undergo surface crazing in the presence of liquid hydrocarbons or chlorinated solvents.

- PP is very resistant to stress-cracking
- Water absorption by PP is very low
- Good chemical inertness.
- Very sensitive to ultraviolet rays in the presence of oxygen. [5]

Table I.1 Properties of polypropylene.[5]

Shaping	Excellent
Density	0,902 – 0,906
Tensile strength (MPa)	31 – 38
Compressive strength (MPa)	38 – 55
Impact strength, Izod (J/mm)	0,025 – 0,1
Hardness (Rockwell)	R85 – R110
Thermal expansion (10-4/°C)	14,7 – 25,9
Heat resistance (°C)	110 – 150
Dielectric strength (V/mm)	20.000 – 26.000
Dielectric constant (at 60 Hz)	2,2 – 2,6
Dissipation factor (at 60 Hz)	0,0005
Arc resistance (s)	138 – 185
Water absorption after 24h (%)	0,01
burning rate	Slow
Effect of UV	Must be stabilized
Effects of acids	oxidizing acids
Effects of alkaline	Wearing
Effects of solvents	Resistantbelow 80°C
Machiningqualities	Good
Optical qualities	Clear to Opaque

I.2.4 Major Advantages of polypropylene

1. Polypropylene is widely accessible and reasonably priced.
2. Due to its semi-crystalline structure, it possesses a high flexural strength.
3. The surface is also rather slippery.
4. It has a high level of moisture resistance.
5. Polypropylene can withstand a variety of bases and acids with ease.
6. It has a high level of fatigue resistance.
7. The impact strength of polypropylene is high.
8. Another good electrical insulator is polypropylene.[6]

I.2.5 Drawbacks of polypropylene

1. The high thermal expansion coefficient of polypropylene restricts its use in high temperature applications.
2. It is prone to UV deterioration.
3. Polypropylene has weak resistance to aromatic and chlorinated solvents.
4. Due to its poor bonding qualities, it is well known to be challenging to paint.
5. Polypropylene burns easily.
6. It is oxidation-sensitive.[6]

I.2.6 Manufacturing processes of polypropylene

The process technology for producing PP has evolved in tandem with catalyst advancements and the development of new product uses and markets. The interaction between process and catalyst technologies, in particular, was clearly synergistic that of a partnership. Advances in one technology have always had a substantial push-pull influence on the performance of the other. Process technology advancements have resulted in process simplification, lower investment and manufacturing costs, improved plant constructability and operability, and greater process capabilities to produce a broader product mix.

The simplified block diagrams in **Figures I.7- I.9** serve to illustrate the advances in PP process technology from a complex process in **Figure I.7** to one that is simpler in **Figure I.9**. The slurry process technology as illustrated in **Figure I.7** is typical of manufacturing units built in the 1960s and 1970s. This technology was designed for catalysts of the first and second generations. It required a solvent such as butane, heptane, hexane, or even heavier iso-paraffins. The solvent served as the medium for dispersion of the polymer produced in the reactors and for dissolving the high level of atactic byproducts for removal downstream. The use of a solvent also facilitated the catalyst deactivation and extraction (or deashing) step, which required contacting the reactor product with alcohol and caustic solutions. Plants based

on this technology required a large amount of equipment, a great deal of space, and complicated plot plans. They were high in both capital and operating costs, labor intensive, and energy inefficient. Moreover, there were environmental and safety issues associated with the handling of a large volume of solvent and the disposal of the amorphous atactic byproducts, and a large wastewater stream containing residual catalyst components. With the advent of third- and fourth-generation catalysts, many of these older slurry plants stayed viable by cost reduction aided by the higher catalyst activities and lower atactic production. They also benefitted from plant capacity creeps and debottlenecking. The slurry process technology evolved into the more advanced slurry process (**Figure I.8**) in the late 1970s to take advantage of the higher performing third-generation catalysts initially and later the even better fourth-generation catalysts. The improved slurry processes were commonly referred to as the bulk (slurry) process. One major change from the older slurry technology was the substitution of liquid propylene in place of the solvent system. This became possible because catalyst de-ashing and atactic removal were no longer needed to produce acceptable PP resins. With very few exceptions, virtually all slurry plants built over the last two decades were based on bulk process technology. Montell's Spheripol process represents technology of this type, using pipe loop reactors operated liquid full, with a PP slurry in liquid propylene. Additionally, a fluidized bed reactor is used by Spheripol downstream of the bulk pipe loop reactors when impact copolymers are in the product slate. [7]

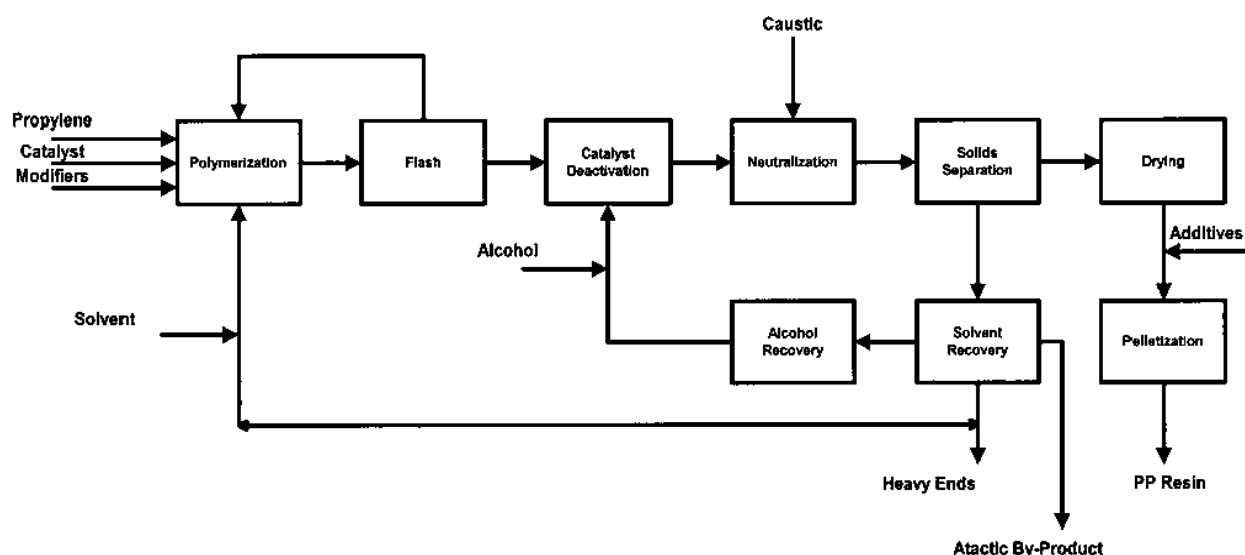


Figure I.7 Early slurry process technology. [7]

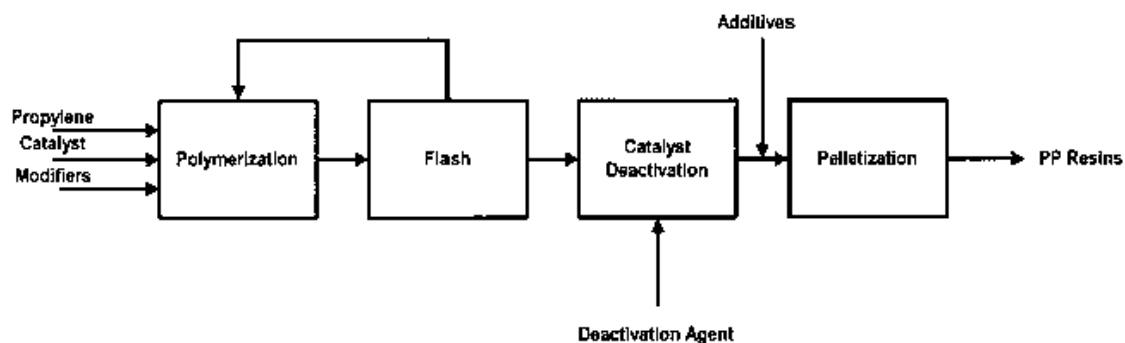


Figure I.8 Bulk (slurry) process technology. [7]

The emergence of gas-phase process technology for PP occurred about the same time as the bulk processes. Gas-phase technology was revolutionary in that it completely avoided the need for a solvent or liquid medium to disperse the reactants and reactor product. This process eliminates the separation and recovery of large quantities of solvents or liquid propylene required in slurry or bulk reactors. The PP products from the gas-phase reactors are essentially dry, requiring only deactivation of the very low level of catalyst residues before the incorporation of additives and pelletization. Thus, this process technology reduced the manufacturing of PP to the bare essential steps. Representatives of commercial gas-phase process technology include Amoco, Union Carbide (Unipol), and BASF (Novolen). Amoco's technology features a horizontal stirred bed reactor system that uses mild mechanical agitation for reactor mixing and temperature control. [7]

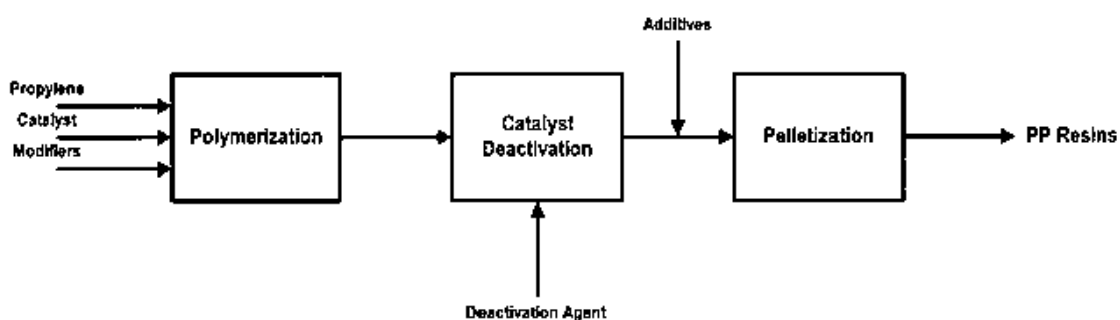


Figure I.9 Gas-phase process technology. [7]

The heat of polymerization is removed by the use of quench cooling or evaporative cooling using a spray of liquid propylene. The Unipol process is based on a gas fluidization principle that relies on a large volume of fluidizing gas for reactor mixing, polymerization heat removal, and temperature control. According to trade literature, Unipol has claimed that the

gas cooling can now be supplemented by some amount of liquid evaporation in the fluidized bed, referred to as the “condensing” mode cooling. The BASF gas-phase reactor is a vertical stirred bed reactor in which the polymerization heat is removed by vaporization of liquid propylene in the bed. In the above three gas-phase processes, a second reactor of a similar design as the first reactor is added for the production of impact copolymers. A sketch of the reactor systems associated with the four types of commercial PP process technology described above—Amoco, Spheripol, BASF, Unipol—is shown in **Figure I.10** The Amoco gas-phase process technology is more completely depicted in **Figure I.11**

In summary, over four decades, PP process technology has never stopped creating value for resin customers through both incremental and generational changes. The changes came about through a partnership with advancements in catalysts to result in better manufacturing economics and simpler plants, making them easier to operate and at higher efficiencies. At the same time, the improved process technology has also added enhancements to many product properties and expanded the product applications. [7]

- **World-Scale Technology**

The PP industry is exciting and will continue to grow globally at a rate attractive to making new investments. Obviously, it is also highly competitive, and the resin customers have high expectations. To favorably compete and to satisfy customers, PP producers must have access to world-scale technology when new investment is being considered. The criteria for world-scale technology are the following:

1. Simple and efficient process
2. Attractive economics for resin manufacture: low plant investment and operating cost
3. Efficient and high performance with fourth-generation catalysts
4. Capability for a wide range of products, with the ability to allow easy product transitions in manufacturing
5. Environmentally clean and safe operations
6. Capability of plant design for high single-line capacity
7. Commitment of technology provider to continuous improvements and innovations

To improve capital utilization and remain competitive, we believe that new plants should have production capacity no less than 150,000 metric tons=yr.

A new trend is to build larger units with production capacity over 200,000 metric tons=yr. [7]

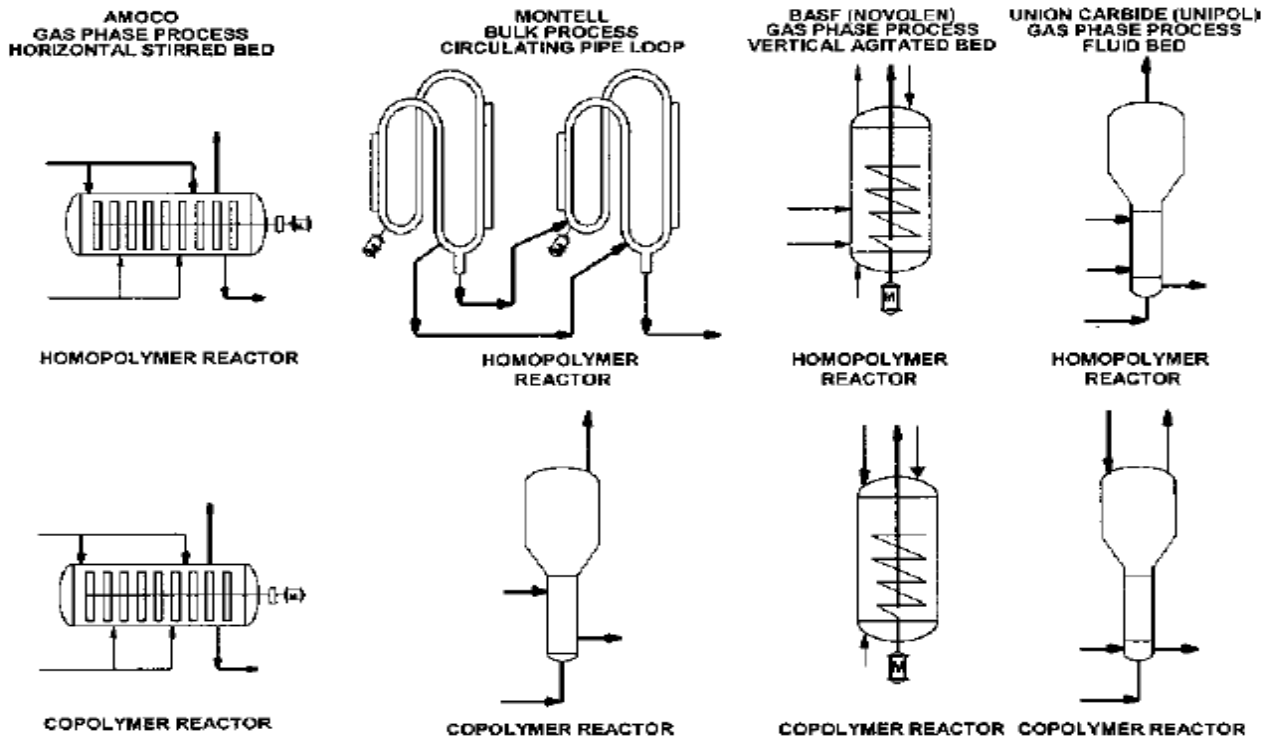


Figure I.10 Reactor systems in polypropylene technologies. [7]

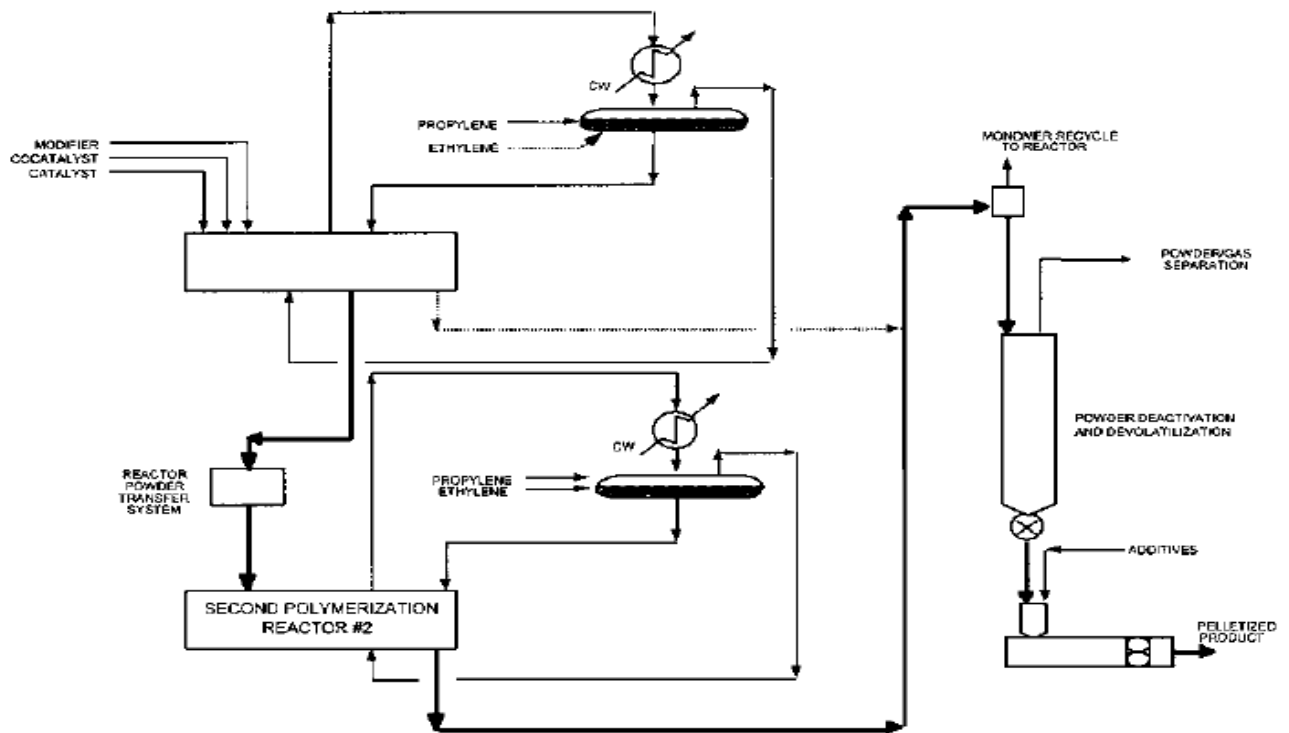


Figure I.11 Amoco gas-phase process technology. [7]

I.2.7 Applications of Polypropylene

The main applications of PP in different market sectors are given in **Table I.2**. Some of the critical requirements for these applications are explained in **Table I.3 [8]**

Table I.2 Typical applications of PP. [8]

Sector	Typical applications
Household goods	Buckets, bowls, bottle crates, toys, bottle caps, bottles, food processor housing, video cassettes, luggage
Automotive industry	Radiator expansion tanks, brake fluid reservoirs fittings, steering wheel covers, wheel arch liner, bumpers, bumper covers, side strips, spoilers, mudguards, battery cases, tool boxes
Fibres	Artificial sport surfaces, monofilaments for rope and cordage, stretched tapes, woven carpet backing, packaging sacks and tarpaulins, staple fibres, coarse fibres, filament yarns, fine fibres
Domestic appliances	Dishwasher parts such as top frame, basement, tubs, extruded gaskets, water duct, water softener compartment, etc. Washing machine parts such as detergent dispenser, door frames, inlet and outlet pipes, bellows, feet and wheel, housings and ducts, etc. Refrigerator parts such as boxes, containers, drawers, ducts, inlet and outlet pipes etc. Microwave oven cabinet, irons and coffee maker body parts
Packaging	Margarine and ice-cream tubs, films, compartmentalised meal trays, thin-walled packaging for, e.g., disposable food trays, dessert cups and confectionery boxes, strapping tapes, blister packaging
Pipes and fittings	Solid rods, punching plates, hot wire reservoirs, tower packings for distillation columns, domestic wastewater pipes, pressure pipes, heat exchangers, corrugated pipes, small diameter tubing, e.g., biro cartridges, drinking straws
Furniture	Stackable chairs

Table I.3 Critical requirements for applications where PP is one of the best choice of material. [8]

Application	Critical requirements
Chairs	Good rigidity, good toughness, colourability, mouldability in complex shapes
Car bumper	High impact strength at low temperatures, excellent weathering, high rigidity
Hair dryers, irons and kitchen appliances	Rigidity, brilliant surface gloss, good heat ageing resistance, antistatic properties, high HDT, mar resistance
Disposable food packaging	Rigidity, transparency (if required), heat sterilisable, no taste, good flow and fast cycling, low cost
Syringes, tubes, cartridges	Transparency, sterilisable and unbreakability (toughness), good flow length
Video cassette boxes	Fatigue strength, high flexibility, warpage
Pipes and fittings	Low frictional loss, good chemical resistance, high continuous use temperature, low noise
Luggage	Impact strength, warpage

I.3 Polyethylene terephthalate

I.3.1 Synthesis method of PET

The two main PET synthesis processes used in industry are:

- esterification of terephthalic acid and ethylene glycol.
- transesterification of dimethyl terephthalate and ethylene glycol.[9]

1) Synthesis by esterification

The direct esterification process is initially the reaction of acid terephthalic acid (TA) and ethylene glycol (EG) with elimination of water (**Figure I.12**) up to obtaining a number-

average degree of polymerization (DP_n) of the order of 5 to 10 monomers/chain. This esterification takes place hot between 260 and 280°C and under pressure of 2 at 6 bar. The reaction of terephthalic acid and ethylene glycol does not require the presence of a catalyst since the carboxylic acid groups of TA are reactive and catalytic. [9]

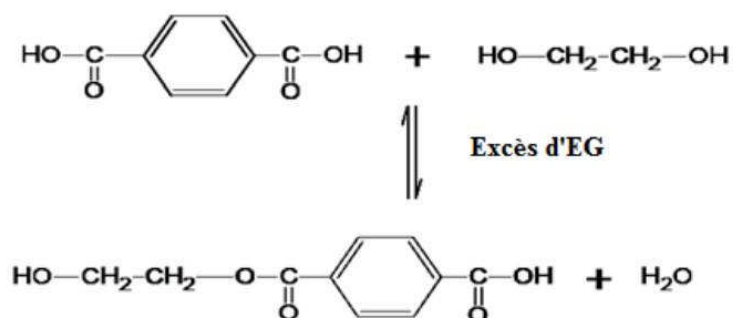


Figure I.12 Esterification reaction between terephthalic acid and ethylene glycol. [9]

2) Synthesis by transesterification

When EG and dimethyl terephthalate (DMT) reagents are present, the mixture is brought to a temperature varying between 160 and 180° C., under vacuum. The addition of a catalyst (salt metallic) is necessary (**Figure I.13**). When the [EG]/[DMT] ratio is between 1.7 and 2, the catalyst is deactivated to avoid an increase in the rate of degradation heat of the polymer. At the end of the reaction, the excess EG and methanol are distilled. [9]

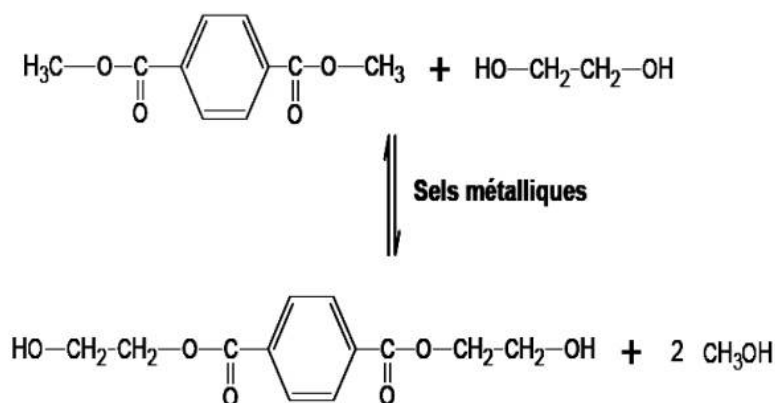


Figure I.13 Transesterification reaction between dimethyl terephthalate and ethylene glycol. [9]

A solid phase polycondensation (PCS) step is then performed to increase the molar mass, in other words the viscosity of the polymer. It takes place after the granulation of PET from the reactor. The PCS begins with the crystallization of the granules which is carried out in several temperature thresholds, under strong agitation, the aim being that they do not stick to each

other. The first of these levels, the longest, lasts approximately two hours and is around 190°C. The others gradually raise the temperature of the polymer to that of the PCS which corresponds to a stay of 10 to 15 hours in a temperature of 210 to 230°C under controlled atmosphere. The time and temperature are adjusted according to the desired chain length.

The parameters of the polymerization are determined according to the characteristics physico-chemical properties of the polymer and depending on its applications, the quality criteria are different. Thus, for a PET dedicated to bottles, in addition to the molar mass, are analysed, for example, the content of terminal carboxylic groups (COOH), which makes account of the degradation of the material and its sensitivity to hydrolysis, and the rate of diethylene glycol (DEG), product of a secondary reaction, known to slow crystallization kinetics. The colorimetry, i.e. the luminance and the color of the polymer, also part of the checks carried out routinely. [9]

I.3.2 Chemical structure of PET

Polyethylene terephthalate (PET) is a general-purpose linear semicrystalline thermoplastic polymer. It belongs to the polyester family of polymers. These resins are known for their excellent combination of properties. These properties include mechanical, thermal, and chemical resistance as well as dimensional stability. Its chemical formula is $C_{10}H_8O_4)_n$. [10] The structure of polyethylene terephthalate is represented in **Figure I.14** .

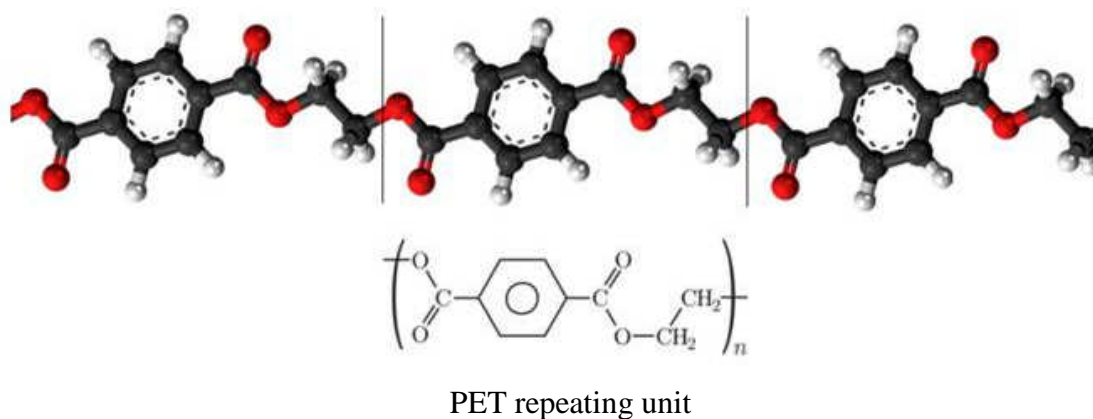


Figure I.14 Molecular Structure of Polyethylene Terephthalate. [10]

I.3.3 Properties of PET

1) Physical properties

- **Viscosity**

One of the most important properties of PET is its intrinsic viscosity. She depends the length of the polymer chains. The longer the chains, the harder the material and therefore its viscosity increases. Depending on its viscosity, PET will not be used in

the same domain. **Table I.4** represents the applications of PET according to viscosity [11].

Table I.4 Application of PET according to its viscosity [11]

Applications	Viscosity indices (ml/g)
Fibers	55-68
Films	57-66
Bottles	72-85
Industrial yarns	80-90

- **Crystallization**

The crystallization temperature of PET is another factor that is important for the fiber manufacturing. Indeed, we seek to raise this temperature to the maximum. There crystallization temperature of PET is variable (160-180°C) and may depend on certain factors. he showed, for example, that the crystallization temperature increased if the PET is plugged, in comparison with a linear PET, and can then wait for 190°C.

On the other hand, the barrier properties of PET increase with the rate of crystallinity, that generally lies author of 20-50% thanks. However, it is possible to obtain rates from crystallinity of up to 90% thanks to pressure treatments. [11]

Table I.5 presents some characteristics of PET varying according to the structure crystalline considered:

Table I.5 Physical and thermal properties of PET. [11]

Properties	amorphous PET	Semi-crystalline PET
Density (g/cm ³)	1,335	1,455 – 1,515
Glass transition (°C)	67	81 – 125 (oriented)
Refractive index	1,576 (25°C)	1,64 (23°C)
Equilibrium melting temperature thermodynamics (°C)	-	280°C

- **Hydroscopy**

PET naturally absorbs water up to 0.16%, this phenomenon is important when the glass transition temperature of the polymer is exceeded ($T_g = 75^\circ\text{C}$): there is hydrolysis reactions of the ester function within the polymer which leads to a drop in the molecular weight and viscosity, and therefore the partial degradation of PET. [11]

2) **Chemical properties of PET**

PET has excellent chemical resistance to concentrated and diluted acids, ketones, fats and oils, but hydrolyzes in the presence of alkaline products. [11]

3) **Thermal properties of PET**

PET can be found in the amorphous or semi-crystalline form. Its density varies from 1.30 to 1.40. The thermal analysis of PET makes it possible to show the presence of three transitions main, as shown in **Figure I.15**. The first is the glass transition. She is reversible and corresponds to a variation in the molecular mobility of the chains of the phase amorphous. Below the glass transition temperature (T_g), generally located towards 80°C ., the polymer is frozen by strong physical interactions. Above, mobility molecular increases (endothermic phenomenon) and it becomes rubbery; its elastic properties increase and it becomes less rigid. This second transition appears about 145°C . and corresponds to a recrystallization of the amorphous PET whose maximum peak of crystallization corresponds to the crystallization temperature (T_c). This transition exothermic appears for matrices whose initial crystallinity rate is relatively weak and gradually disappears when it increases. Finally, the third transition is endothermic and is located around $260\text{-}270^\circ\text{C}$. It corresponds to the melting of the crystallites at the melting temperature (T_f) of PET.[9]

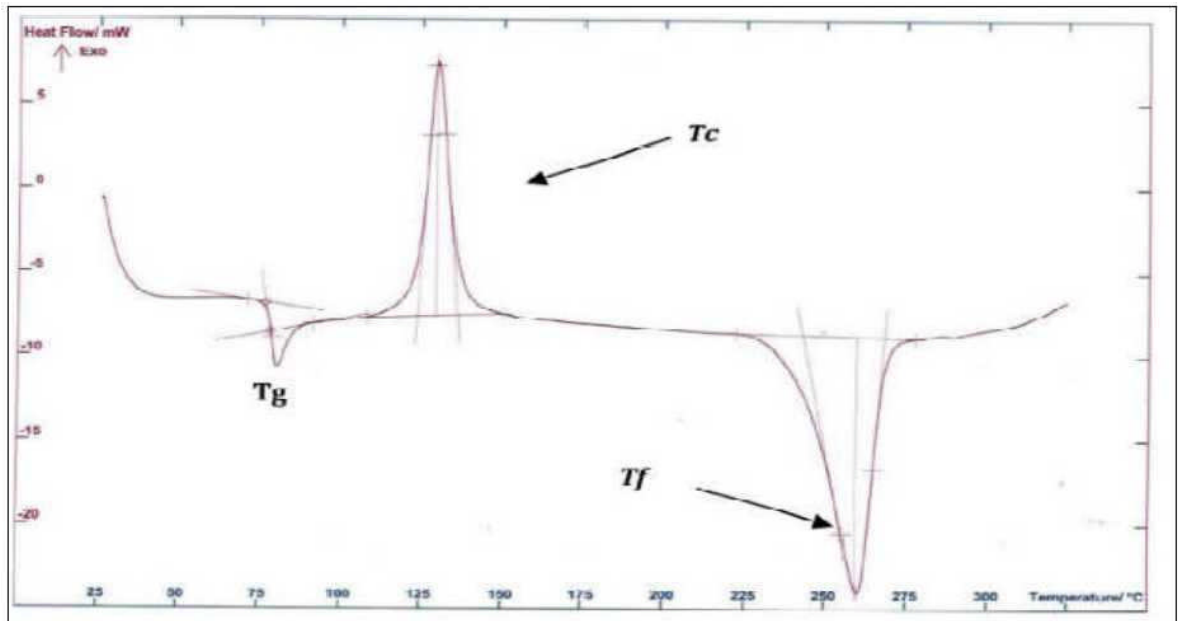


Figure I.15 DSC thermograms of PET.

4) Thermomechanical properties of PET

PET is mainly used at room temperature. He presents himself in a state glassy and appears as a rigid material. At the glass transition temperature, its mechanical properties drop significantly. Above T_g , mobility more important of the chains allows, for example, the stretching and orientation of the polymer by blowing when it is amorphous. The crystallization and the orientation of the PET above and below T_g increase its mechanical properties. When the FART is amorphous, its mechanical modulus increases towards 145°C , consequence of the recrystallization during the heating.[9]

I.3.4 Major Advantages of PET

1. **Lightweight:** PET is a lightweight material, which makes it ideal for packaging applications as it reduces shipping costs and minimizes the amount of waste.
2. **Durable:** PET is a strong and durable material that is resistant to impact, tearing, and punctures. It can withstand high temperatures and is not affected by most chemicals.
3. **Clarity:** PET is a transparent material that allows for a clear view of the contents. It is commonly used for packaging beverages, food, and other consumer goods.
4. **Recyclable:** PET is a highly recyclable material, which makes it an environmentally friendly option. It can be recycled into a variety of products, including new containers, carpet fibers, and clothing.
5. **Cost-effective:** PET is a cost-effective material that is widely available and easy to process. Its low cost makes it an attractive option for manufacturers.

6. Versatile: PET can be molded into a wide variety of shapes and sizes, which makes it suitable for a broad range of applications. It is commonly used for packaging, automotive parts, and consumer goods.[12]

I.3.5 Drawbacks of PET

1. Environmental concerns: PET is not biodegradable and can persist in the environment for hundreds of years. PET waste is a significant contributor to plastic pollution and can harm wildlife and ecosystems.
2. Recycling challenges: Although PET is recyclable, the recycling process is complex and can be costly. Contamination with other plastics or materials can reduce the quality of the recycled material, and some forms of PET, such as colored or opaque PET, are more difficult to recycle.
3. Health risks: There is some concern that chemicals such as antimony, which is used as a catalyst in the production of PET, can leach from PET containers and potentially cause health problems.
4. Heat sensitivity: PET can deform or melt when exposed to high temperatures, which can limit its use in some applications.
5. Limited chemical resistance: PET is not resistant to all chemicals, and exposure to certain substances can cause it to degrade or break down over time.[13]

I.3.6 Manufacturing processes of PET

Polyethylene Terephthalate (PET) is one of the major polymers produced worldwide representing about 18 % of world polymer production and comes in third after Polyethylene and Polypropylene. The main downstream industries based on PET are production of polyester fibers, accounting for around 65% of global consumption, and PET bottle resins consuming around 30%.

PET is produced from high purity ethylene glycol (EG) and Terephthalic acid (TPA). All PET resin manufacture processes are using the same reaction path as shown in the **Figure I.16** below :



Figure I.16 PET resin manufacturing steps. [14]

The conventional PET process consists of two discrete plant sections. The first part consists of melt phase reaction used to produce copolymers with an intrinsic viscosity (IV) suitable for textile applications. But when very high molecular weights are desired, as is the case for

bottle grade PET resins, the polymerization may be carried out in stages. The traditional Buhler process integrates four typical stages for producing bottle grade PET: crystallization, annealing, solid state polymerization (SSP) and cooling. New technologies are currently replacing this design with a tendency to reduce the number of units involved and thus the global process cost.

A radical approach that is rapidly becoming more and more employed is Eastman IntegRex technology (illustrated in **Figure I.17**). The main unit is a tubular reactor that leads to a significant reduction of energy, raw materials consumptions, operation costs and capital costs.[14]

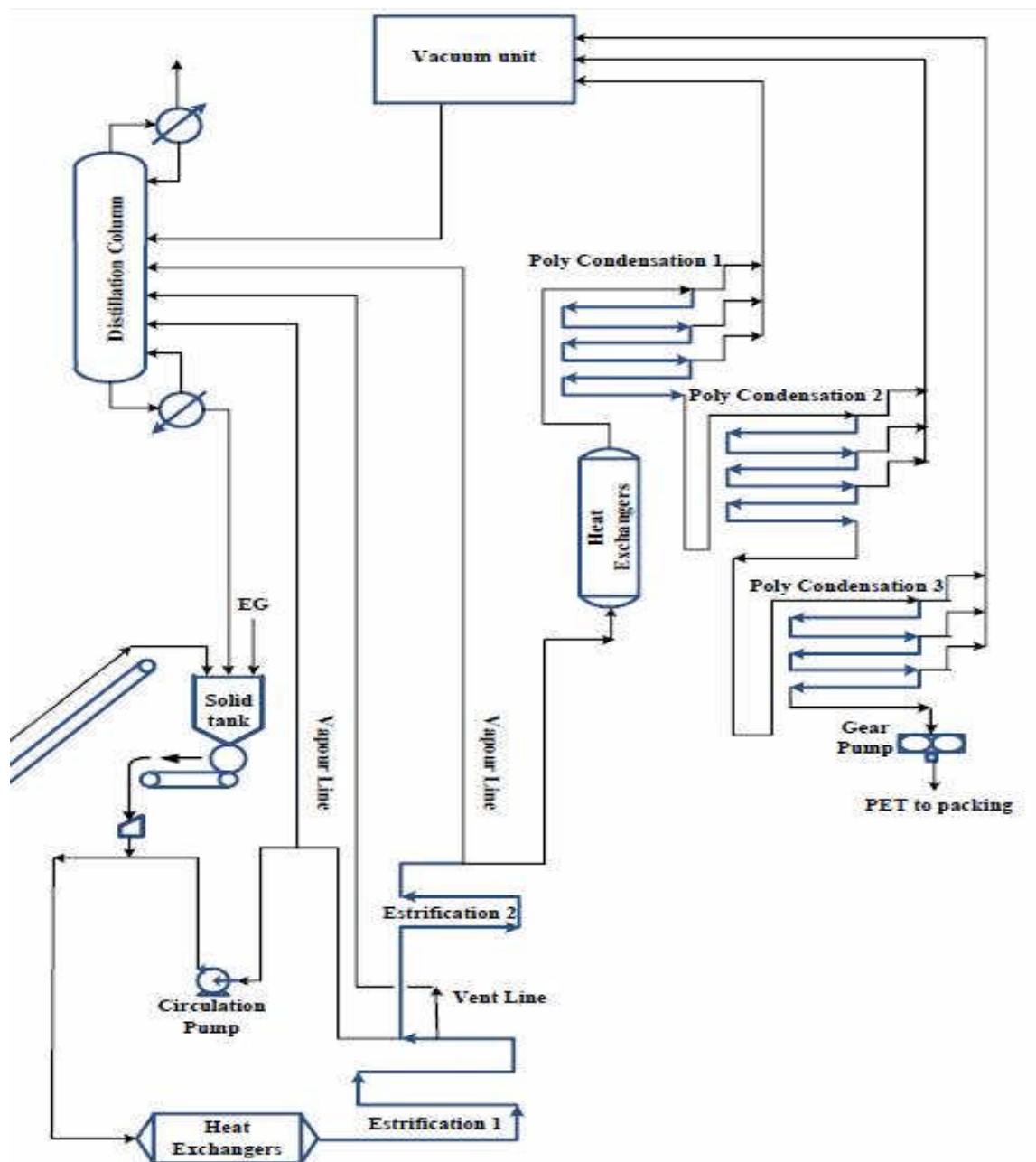


Figure I.17 Eastman IntegRex manufacturing technology. [14]

I.3.7 Applications of PET

The main applications of PET are as follows:

- **Textiles:** textile yarns, fibers...
- **Films:** packaging, photo film holders...
- **Hollow body:** bottles for soft drinks...
- **Automobiles:** fan, alternator, handles of parts for ignition circuit...
- **Medical application:** tubular knitting for vascular prosthesis, larynx prosthesis and from the esophagus...
- **Advanced technologies:** magnetic media, computer tools such as floppy disks video and audio tapes, tapes for computers...

The main non-fiber application of PET is the manufacture of bottles for beverages and the packaging of food products. Its first application in the form of it dates back to 1984 and since that year, it has become the material of choice in the field the bottling and the packaging [11].

Other common uses

- Recyclable bottles (unlike polyvinyl chloride PVC), PET is waterproof to CO₂, hence its use for bottles of lemonade and other drinks effervescent).
- Filling with soft toys and cushions.
- So-called polar textile fibers for the manufacture of clothing (in particular based on PET recycled).
- Oven-resistant packaging.
- Coating added on the aluminum foil to avoid contact with food.
- Solar eclipse observation glasses.
- Cost-based transparent films for optical applications (LCD screens, instruments).
- Disposable packaging of all kinds (boxes for salads, trays of presentation...)
- Printed and then thermoformed plates for the manufacture of illuminated signs.

References

- [1] Heino M, Kirjava J, Hietaoja P, Seppa J (1997) Compatibilization of polyethylene terephthalate / polypropylene blends with styrene-ethylene / butylene–styrene (SEBS) block copolymers. *J Appl Polym Sci* 65(2):241–249
- [2] Moad G (1999) The synthesis of polyolefin graft copolymers by reactive extrusion. *Prog Polym Sci* 24(1):81–142
- [3] Amanizadeh F, Naderi A, Jarestani Y, Kaptan N (2014) Rheologically determined phase behavior and miscibility of reactively compatibilized poly(ethylene terephthalate)/polypropylene blends. *Polym Bull* 71(6):1315–1329
- [4] Papadopoulou CP, Kalfoglou NK (2000) Comparison of compatibilizer effectiveness for PET/PP blends: their mechanical, thermal and morphology characterization. *Polymer* 41(7):2543–2555
- [5] Pang YX, Jia DM, Hu HJ, Hourston DJ, Song M (2000) Effects of a compatibilizing agent on the morphology, interface and mechanical behaviour of polypropylene / poly (ethylene terephthalate) blends. *Polymer* 41(1):357–365
- [6] Chiu HT, Hsiao YK (2006) Compatibilization of poly (ethylene terephthalate)/ polypropylene blends with maleic anhydride grafted polyethylene-octene elastomer. *J Polym Res* 13(2):153–160
- [7] Wang Y, Run M (2009) Non-isothermal crystallization kinetic and compatibility of PTT/PP blends by using maleic anhydride grafted polypropylene as compatibilizer. *J Polym Res* 16:725–737
- [8] Jazani OM, Rastin H, Formela K, Hejna A, Shahbazi M, Farkiani B, Saeb MR (2017) An investigation on the role of GMA grafting degree on the efficiency of PET/PP-g-GMA reactive blending: morphology and mechanical properties. *Polym Bull* 74:4483–4497
- [9] Jerenec S, Šimić M, Savnik A, Podgornik A, Kolar M, Turnšek M, Krajnc P (2014) Glycidyl methacrylate and ethylhexyl acrylate based polyHIPE monoliths: morphological, mechanical and chromatographic properties. *React Funct Polym* 78:32–37

- [10] Inoya H, Leong YW, Klinklai W, Thumsorn S, Makata Y, Hamada H (2011) Compatibilization of recycled poly(ethylene terephthalate) and polypropylene blends: effect of polypropylene molecular weight on homogeneity and compatibility. *J Appl Polym Sci* 124(5):3947–3955
- [11] Inoya H, Leong YW, Klinklai W, Takai Y, Hamada H (2012) Compatibilization of recycled poly(ethylene terephthalate) and polypropylene blends: effect of compatibilization on blend toughness, dispersion of minor phase and thermal stability. *J Appl Polym Sci* 124:5260–5269
- [12] Souza AMC, Caldeira CB (2015) An investigation on recycled PET/PP and recycled PET/PP-EP compatibilized blends: Rheological, morphological, and mechanical properties. *J App Polym Sci* 132:41892
- [13] Duarte IS, Tavares AA, Lima PS, Andrade DLACS, Carvalho LH, Canedo EL, Silva SML (2016) Chain extension of virgin and recycled poly(ethylene terephthalate): effect of processing conditions and reprocessing. *Polym Degrad Stab* 124:26–34
- [14] Miyake A (1959) The infrared spectrum of polyethylene terephthalate. I the effect of crystallization. *J Polym Sci* 38(134):479–495

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

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

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

For miscibility, in addition to a negative value of ΔG_m , the following inequality must also hold [18],

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

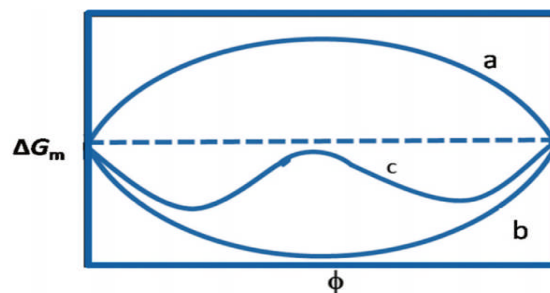


Figure II.1 Free energy of mixing for (a) completely immiscible, (b) completely miscible, and (c) partially miscible [4, 21].

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

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

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

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

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

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

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

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

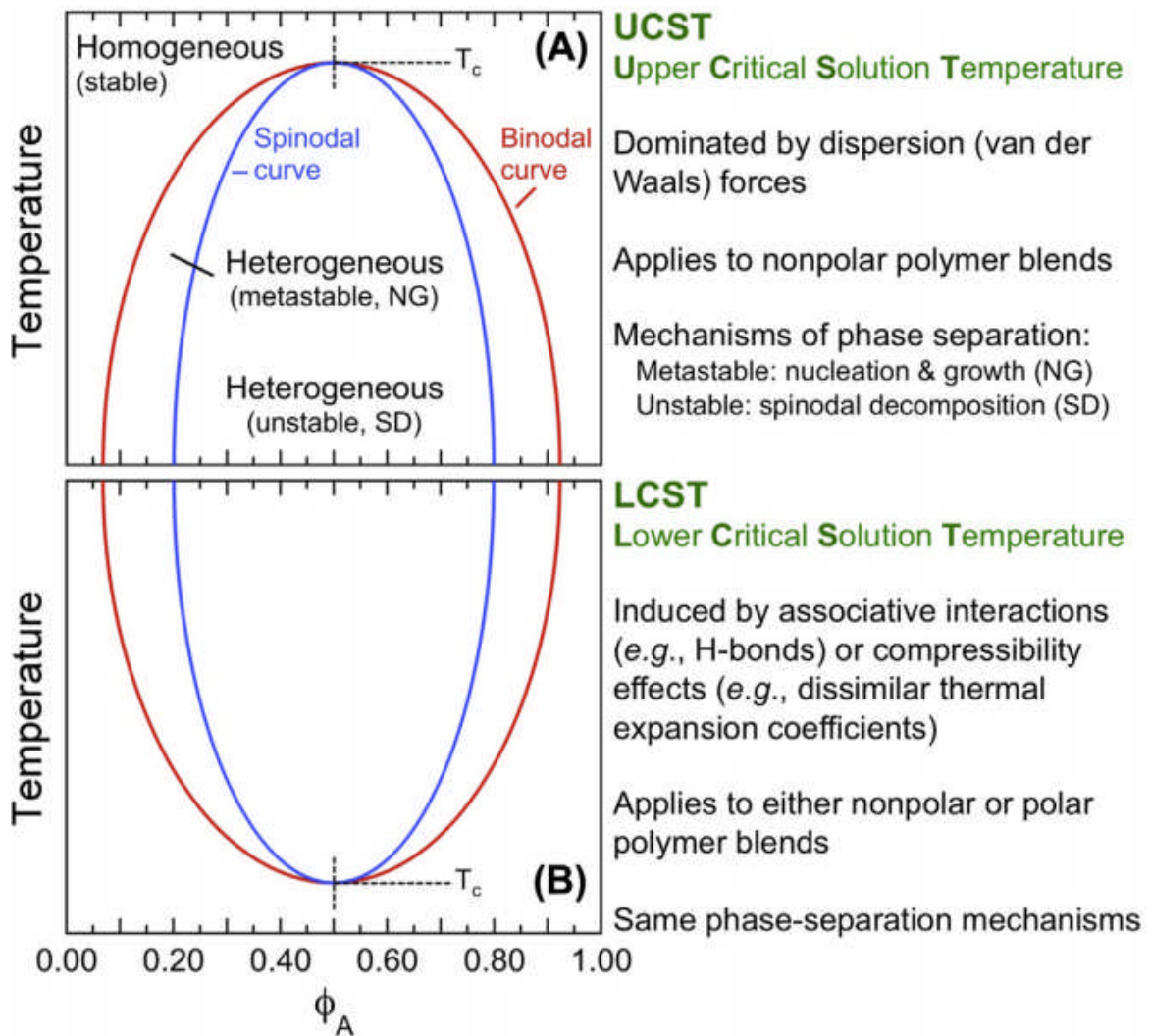


Figure II.2 Phase diagram showing the performance of polymer blends [18].

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

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

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,

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

Here R is the universal gas constant and T is the absolute temperature. ϕ_1 and ϕ_2 are the volume fraction of the component 1 and 2, " r " represents the number of polymer segments (proportional to the degree of polymerization) and χ is the Flory-Huggins interaction parameter [3,17,25,26].

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

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

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

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

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

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

II.3 Classification of Polymer Blends

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

II.3.1 Classification based on constituents

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

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

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

II.3.2 Classification based on the miscibility

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

II.3.2.1 Miscible Polymer Blends

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

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

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

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

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

II.3.2.2 Compatible Blends

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

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

II.3.2.3 Immiscible Blends

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

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

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

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 (T_g), melting point (T_m), and crystallinity of the blend can be different from those of the individual polymers. Blending polymers with different T_g or T_m 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 (T_g), melting temperature (T_m), 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: Academic Press; **1978**; 2:391.
- [2] Brown SB. Reactive compatibilization of polymer blends. In: Polymer blends handbook. Springer; **2003**. p. 339-415.
- [3] Paul D, Barlow J. Polymer blends. J Macromol Sci Rev Macromol Chem **1980**;18(1):109-68.
- [4] Paul DR. Polymer blends. Elsevier; **2012**.
- [5] Thomas S, Grohens Y, Jyotishkumar P. Characterization of polymer blends: miscibility, morphology and interfaces. John Wiley & Sons; **2014**.
- [6] Utracki LA, Favis B. Polymer alloys and blends. New York: Marcel Dekker; **1989**.
- [7] Utracki LA, Wilkie CA. Polymer blends handbook. Springer; **2002**.
- [8] Bahrami R, Löblich TI, Schmalz H, Müller AH, Altstädt V. Micromechanics of “raspberry” morphology in PPE/SAN polymer blends compatibilized with linear ABC triblock terpolymers. Polymer **2015**;80:52-63.
- [9] Chiu F-C. Poly (vinylidene fluoride)/polycarbonate blend-based nanocomposites with enhanced rigidityselective localization of carbon nanofillers and organoclay. Polym Test **2017**;62:115-23.
- [10] Otero-Navas I, Arjmand M, Sundararaj U. Carbon nanotube induced double percolation in polymer blends: morphology, rheology and broadband dielectric properties. Polymer **2017**; 114:122-34.
- [11] Wang H, Fu Z, Zhao X, Li Y, Li J. Reactive nanoparticles compatibilized immiscible polymer blends: synthesis of reactive SiO₂ with long poly (methyl methacrylate) chains and the in situ formation of janus SiO₂ nanoparticles anchored exclusively at the interface. ACS Appl Mater Interfaces **2017**;9(16):14358-70.
- [12] Utracki L. Economics of polymer blends. Polym Eng Sci **1982**;22(17):1166-75.
- [13] Roman C, García-Morales M, Gupta J, McNally T. On the phase affinity of multi-walled carbon nanotubes in PMMA: LDPE immiscible polymer blends. Polymer **2017**;118:1-11.

- [14] Jiao Q, Shen J, Ye L, Li Y, Chen H. Poly (oxymethylene)/poly (butylene succinate) blends: Miscibility, crystallization behaviors and mechanical properties. *Polymer* **2019**;167:40-7.
- [15] Métivier T, Cassagnau P. Compatibilization of silicone/fluorosilicone blends by dynamic crosslinking and fumed silica addition. *Polymer* **2018**;147:20-9.
- [16] Yu L, Dean K, Li L. Polymer blends and composites from renewable resources. *Prog Polym Sci* **2006**;31(6):576-602.
- [17] Paul D, Barlow J. A binary interaction model for miscibility of copolymers in blends. *Polymer* **1984**;25(4):487-94.
- [18] Robeson LM. *Polymer blends*. Compr Rev **2007**. ISBN-10: 3-446-22569-2 ISBN-13: 978-3-446-22569-5.
- [19] Utracki LA. Compatibilization of polymer blends. *Can J Chem Eng* **2002**;80(6):1008-16.
- [20] Rostami A, Masoomi M, Fayazi MJ, Vahdati M. Role of multiwalled carbon nanotubes (MWCNTs) on rheological, thermal and electrical properties of PC/ABS blend. *RSC Adv* **2015**;5(41):32880-90.
- [21] Polásková M. *Polymer blends with microfibrillar-phase morphology*. **2006**.
- [22] Li S, Feng L, Lu H, Feng S. From LCST to UCST: the phase separation behaviour of thermo-responsive polysiloxanes with the solubility parameters of solvents. *New J Chem* **2017**;41(5):1997-2003.
- [23] Yao W, Wang H, Cui G, Li Z, Wang J. Tuning phase behaviour of PEG functionalized ionic liquids from UCST to LCST in alcohol/water mixtures. *Phys Chem Phys* **2016**;18(42):29192-8
- [24] Kuila A, Maity N, Chatterjee DP, Nandi AK. Phase behavior of Poly (vinylidene fluoride)-graft-poly (diethylene glycol methyl ether methacrylate) in alcohol/water system: coexistence of LCST and UCST. *J Phys Chem B* **2016**;120(9):2557-68.
- [25] Ten Brinke G, Karasz FE. Lower critical solution temperature behavior in polymer blends: compressibility and directional-specific interactions. *Macromolecules* **1984**;17(4):815-20.

- [26] Tambasco M, Lipson J, Higgins JS. Blend miscibility and the Flory-Huggins interaction parameter: a critical examination. *Macromolecules* **2006**;39(14):4860-8.
- [27] Wippler C. Dynamic mechanical properties of VAMAS polycarbonate/polyethylene blends. *Polym Eng Sci* **1990**;30(17):1106-13.
- [28] Laokijcharoen P, Coran A. The evolution of morphology in NR/HDPE blends. Part I. Microscopy for unvulcanized blends. *Rubber Chem Technol* **1998**;71(5):966-74.
- [29] Go JH, Ha CS. Rheology and properties of EPDM/BR blends with or without a homogenizing agent or a coupling agent. *J Appl Polym Sci* **1996**;62(3):509-21.
- [30] Brahim B, Ait-Kadi A, Ajji A, Fayt R. Effect of diblock copolymers on dynamic mechanical properties of polyethylene/polystyrene blends. *J Polym Sci B Polym Phys* **1991**;29(8):945-61.
- [31] Ghosh P, Chattopadhyay B, Sen AK. Thermal and oxidative degradation of PEEPDM blends vulcanized differently using sulfur accelerator systems. *Eur Polym J* **1996**;32(8):1015-21.
- [32] Oliveira MG, Soares BG. The effect of the vulcanizing system on cure and mechanical properties of NBR/EPDM blends. *Polym Polym Compos* **2001**;9(7):459-68.
- [33] Arif PM, Sarathchandran C, Narayanan A, Saiter A, Terzano R, Allegretta I, et al. Multi-walled carbon nanotube promotes crystallisation while preserving co-continuous phase morphology of polycarbonate/polypropylene blend. *Polym Test* **2017**;64:1-11.
- [34] Stelescu MD. Physico-mechanical characteristics of some EPDM/plasticized PVC blends. *Macromol Symp* **2008**:70-7. Wiley Online Library.
- [35] Zaharescu T, Mihalcea I. Behaviour of ethylene-propylene elastomers in salt solutions: I. SEM investigation of gamma irradiation effects. *Polym DegradStabil* **1995**;50(1):39-43.
- [36] Ajitha A, Aswathi M, Geethamma VG, Kalarikkal N, Thomas S, Volova TG. An effective EMI shielding material based on poly (trimethylene terephthalate) blend nanocomposites with multiwalled carbon nanotubes. *New Journal of Chemistry* **2018**;42(16):13915-26.

- [37] Li J-X, Chan C-M. Effect of the size of the dispersed NBR phase in PVC/NBR blends on the stability of PVC to electron irradiation. *Polymer* **2001**;42(16):6833-9.
- [38] Le HH, Parsekar M, Ilisch S, Henning S, Das A, Stöckelhuber KW, et al. Effect of non-rubber components of NR on the carbon nanotube (CNT) localization in SBR/ NR blends. *Macromol Mater Eng* **2014**;299(5):569-82.
- [39] Kunjappan AM, Ramachandran AA, Padmanabhan M, Mathew LP, Thomas S. Selective localization of MWCNT in poly (trimethylene terephthalate)/poly ethylene blends: theoretical analysis, morphology, and mechanical properties. *Macromol Symp* **2018**:1800104. Wiley Online Library.
- [40] Chandra R, Mishra S, Parida T. Studies on dynamic behaviour and flow properties of HDPE/EPDM blends by torque rheometer. *Polym Int* **1995**;37(2):141-7.
- [41] Essawy HA, Tawfik ME, El-Sabbagh SH. Rubber nanocomposites based on compatibilized NBR/SBR blends using a series of amphiphilic montmorillonites. *J Elastomers Plast* **2014**;46(2):113-31
- [42] Fel E, Khrouz L, Massardier V, Cassagnau P, Bonneviot L. Comparative study of gamma-irradiated PP and PE polyolefins part 2: properties of PP/PE blends obtained by reactive processing with radicals obtained by high shear or gamma-irradiation. *Polymer* **2016**;82:217-27.
- [43] Nair ST, Vijayan PP, Xavier P, Bose S, George SC, Thomas S. Selective localization of multi walled carbon nanotubes in polypropylene/natural rubber blends to reduce the percolation threshold. *Compos Sci Technol* **2015**;116:9-17.
- [44] Maria HJ, Lyczko N, Nzihou A, Joseph K, Mathew C, Thomas S. Stress relaxation behavior of organically modified montmorillonite filled natural rubber/nitrile rubber nanocomposites. *Appl Clay Sci* **2014**;87:120-8.

- [45] Friedrich K, Evstatiev M, Fakirov S, Evstatiev O, Ishii M, Harrass M. Microfibrillar reinforced composites from PET/PP blends: processing, morphology and mechanical properties. *Compos Sci Technol* **2005**;65(1):107-16.
- [46] Wang J, Pan S, Zhang Y, Guo S. Crosslink network evolution of BIIR/EPDM blends during peroxide vulcanization. *Polym Test* **2017**;59:253-61.
- [47] Ding X, Wang J, Zhang S, Wang J, Li S. Composites based on CB/CF/Ag filled EPDM/NBR rubber blends with high conductivity. *J Appl Polym Sci* **2015**;132(4).
- [48] Ray SS, Pouliot S, Bousmina M, Utracki LA. Role of organically modified layered silicate as an active interfacial modifier in immiscible polystyrene/polypropylene blends. *Polymer* **2004**;45(25):8403-13.
- [49] Uthaipan N, Jarntong M, Peng Z, Junhasavasdikul B, Nakason C, Thitithammawong A. Effects of crosslinked elastomer particles on heterogeneous nucleation of isotactic PP in dynamically vulcanized EPDM/PP and EOC/PP blends. *J Polym Res* **2017**;24(8):118.
- [50] Gögelein C, Beelen HJH, van Duin M. Morphological explanation of high tear resistance of EPDM/NR rubber blends. *Soft Matter* **2017**;13(23):4241-51.
- [51] Li H, Wang J, Li G, Lu Y, Wang N, Zhang Q, et al. Preparation of core-shell structured particle and its application in toughening PA6/PBT blends. *Polym Adv Technol* **2017**;28(6):699-707.
- [52] Abd-El-Messieh S, Mansour S, El-Nashar D, Ikladios N. Evaluation of polyester resin as a new compatibilizer for SBR/PVC blends. *Can J Chem Eng* **2004**;82(2):358-70.
- [53] Setua D, Nando G. High-performance oil/fuel-resistant blends of ethylene propylene diene monomer (EPDM) and epoxidized natural rubber (ENR). In: *High performance polymers and their nanocomposites*; **2018**. p. 315-46.
- [54] Mural PKS, Madras G, Bose S. Positive temperature coefficient and structural relaxations in selectively localized MWNTs in PE/PEO blends. *RSC Adv* **2014**;4(10):4943-54.

- [55] Ahmed K. Stress-strain and diffusion behavior of industrial waste-filled acrylonitrile-butadiene rubber/high density polyethylene blends. *Chem Lett* **2014**;43(5):690-2.
- [56] El-Nashar D. The compatibilization of EPDM/SBR blends by EPDM-graft-styrene copolymer. *Polym Plast Technol Eng* **2005**;43(5):1425-41.
- [57] Lu X, Weiss R. Relationship between the glass transition temperature and the interaction parameter of miscible binary polymer blends. *Macromolecules* **1992**;25(12):3242-6.
- [58] Brostow W, Chiu R, Kalogeras IM, Vassilikou-Dova A. Prediction of glass transition temperatures: binary blends and copolymers. *Mater Lett* **2008**;62(17e18):3152-5.
- [59] An L, He D, Jing J, Wang Z, Yu D, Jiang B, et al. Effects of molecular weight and interaction parameter on the glass transition temperature of polystyrene mixtures and its blends with polystyrene/poly (2, 6-dimethyl-p-phenylene oxide). *Eur Polym J* **1997**;33(9):1523-8.
- [60] Kalogeras IM, Brostow W. Glass transition temperatures in binary polymer blends. *J Polym Sci B Polym Phys* **2009**;47(1):80-95.
- [61] Tjong S, Meng Y. Effect of reactive compatibilizers on the mechanical properties of polycarbonate/poly (acrylonitrile-butadiene-styrene) blends. *Eur Polym J* **2000**;36(1):123-9.
- [62] Mathew L, Saha P, Kalarikkal N, Thomas S, Strankowski M. Tuning of microstructure in engineered poly (trimethylene terephthalate) based blends with nano inclusion as multifunctional additive. *Polym Test* **2018**;68:395-404.
- [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 affecting 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 phase morphology and poor interfacial adhesion between the blend phases. This may be so, as most polymers are immiscible. When the viscoelastic behavior of polymer blends is observed, the melt viscosity of immiscible polymer blends are found to depend on the interfacial interactions and phase morphology. Hence compatibilization by addition of an interfacial agent is needed to attain synergistic effect for making it most useful. There are several methods for the compatibilization of polymer blends, but the principle of all techniques is the homogenization of mixture of the polymer by adding a compatibilizing agent.

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

III.2 Strategies for compatibilization of polymer blends

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

Some of the general strategies involve the following:

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

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

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

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

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

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

III.3 Why do we need compatibilizers?

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

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

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

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

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

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

III.4 Theoretical aspects of compatibilisation

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

A successfully compatibilized blend of moderate composition (up to 30 wt% minority component) exhibits spherical dispersed phases with consistent diameters, averaging on the micron and submicron scale. Such consistent morphologies can be achieved when the compatibilizing agent provides a steric hindrance to the dispersed phase coalescence. Compatibilizers which provide steric hindrances act as anchors for minority phase droplets in the matrix, (Figure III.1) and also serve as repulsive “springs” when two droplets are in proximity.

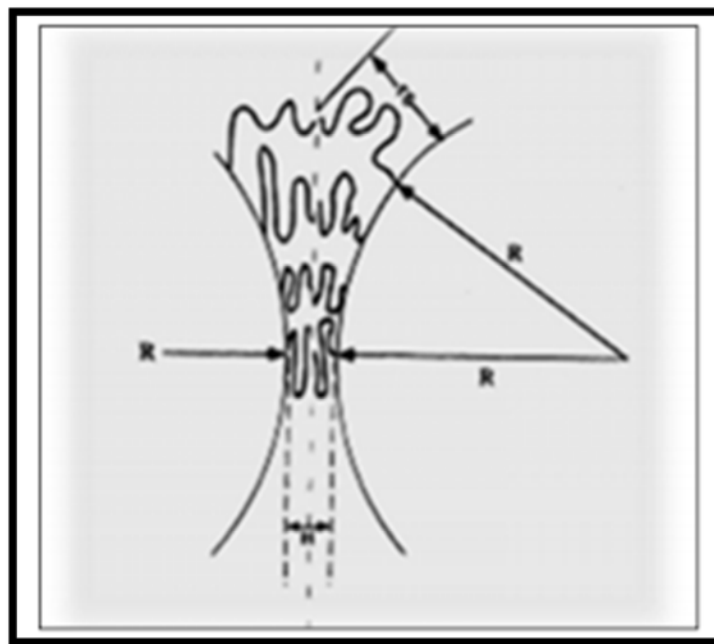


Figure III.1 Steric hindrance by compatibilizers. Compatibilizers acting as both anchors and repulsive springs ensuring the stability and prevention to coalescence[16].

From a commercial point of view, it can say that compatibilization is the method of converting a multiphase polymer mixture into a commercially useful product. In principle, a molecule can

act as a compatibilizer if it has a segment that is miscible in one phase and another segment that is miscible in the other phase. And this will lead to the positioning of the compatibilizer across the interface.

So a good compatibilizer will

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

III.5 Blending with a compatibilizer, a third component

III.5.1 Compatibilizer immiscible in both Blended Polymers

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

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

thermal conductivity at volume fraction of graphene as low as 0.53% [18]. PP blends with poly(ethylene terephthalate) (PET) have been prepared with graphene mostly in the PET phase of the co-continuous or double percolated blend that exhibited increased electrical conductivity and electromotive force shielding in the GHz frequency range [19].

III.5.2 Compatibilizer mutually miscible

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

III.5.3 Compatibilizer miscible with one of the Blended Polymers

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

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

III.6 Role of compatibilizers in Blending processes

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

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

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

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

III.7 Properties of polymer Blends influenced by compatibilization

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

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

III.8 New challenges in compatibilized Blends

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

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

III.9 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 is the most important issue worldwide and scientists endeavor to enhance the level of people's health, so various strategies have been developed so far to meet health requirements. Nowadays polymers are known as the building blocks of both commodity and modern stuff ranging from general purpose to sophisticated applications. In particular, polymers have been vital elements of advanced materials and systems in medical landscapes [31].

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

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

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

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

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

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

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

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

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

References

- [1] Utracki LA, Favis B. Polymer alloys and blends. New York: Marcel Dekker; **1989**.
- [2] Blends P, Paul DR, Newman S, vol. 2. NY: Academic Press; **1978**. p.391.
- [3] Xanthos M. Interfacial agents for multiphase polymer systems: recent advances. 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, Pagnouille Christophe, Jérôme Robert, Strategies For Compatibilization Of Polymer Blends, *Progress in polymer science* **1998**, vol. 23, iss. 4, pp. 707-757
- [22] Anastasiadis SH, Gancarz I, Koberstein JT. Interfacial tension of immiscible polymer blends: temperature and molecular weight dependence. *Macromolecules* **1988**;21(10):2980-7.
- [23] Majumdar B, Keskkula H, Paul D, Harvey N. Control of the morphology of polyamide/styrene-acrylonitrile copolymer blends via reactive compatibilizers. *Polymer* **1994**:4263-79.
- [24] Koning C, Van Duin M, Pagnouille C, Jerome R. Strategies for compatibilization of polymer blends. *Prog Polym Sci* **1998**;23(4):707-57.
- [25] Van Puyvelde P, Velankar S, Moldenaers P. Rheology and morphology of compatibilized polymer blends. *Curr Opin Colloid Interface Sci* **2001**;6(5e6):457-63.

- [26] La Mantia FP, Ceraulo M, Mistretta MC, Botta L, Morreale M. Compatibilization of polypropylene/polyamide 6 blend fibers using photo-oxidized polypropylene. *Materials* **2018**;12(1):81.
- [27] Rigoussen A, Raquez J-M, Dubois P, Verge P. A dual approach to compatibilize PLA/ABS immiscible blends with epoxidized cardanol derivatives. *Eur Polym J* **2019**;114:118-26.
- [28] Rastin H, Saeb MR, Jafari SH, Khonakdar HA, Kritschmar B, Wagenknecht U. Reactive compatibilization of ternary polymer blends with core-shell type morphology. *Macromol Mater Eng* **2015**;300(1):86-98.
- [29] Kim S, Kim JK, Park C. Effect of molecular architecture of in situ reactive compatibilizer on the morphology and interfacial activity of an immiscible polyolefin/polystyrene blend. *Polymer* **1997**;38(8):1809-15.
- [30] Jazani OM, Arefazar A, Peymanfar MR, Saeb MR, Talaei A, Bahadori B. The influence of NBR-g-GMA compatibilizer on the morphology and mechanical properties of poly (ethylene terephthalate)/polycarbonate/NBR ternary blends. *Polym Plast Technol Eng* **2013**;52(13):1295-302.

- [31] Bakhshandeh B, Zarrintaj P, Oftadeh MO, Keramati F, Fouladiha H, Sohrabijahromi S, et al. Tissue engineering; strategies, tissues, and biomaterials. *Biotechnol Genet Eng Rev* **2017**;33:144-72.
- [32] Zarrintaj P, Moghaddam AS, Manouchehri S, Atoufi Z, Amiri A, Amirkhani MA, et al. Can regenerative medicine and nanotechnology combine to heal wounds? The search for the ideal wound dressing. *Nanomedicine* **2017**;12:2403-22.
- [33] Nilforoushzadeh MA, Amirkhani MA, Zarrintaj P, Salehi Moghaddam A, Mehrabi T, Alavi S, et al. Skin care and rejuvenation by cosmeceutical facial mask. *J Cosmet Dermatol* **2018**;17(5):693-702.
- [34] Nilforoushzadeh MA, Zare M, Zarrintaj P, Alizadeh E, Taghiabadi E, 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

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, **M. Xanthos et al [1]** have studied the compatibilization of Polypropylene/Polyethylene Terephthalate (PP/PET) thermoplastic polymer Blends through functionalization of PP phase. In attempts to improve the compatibility of polypropylene with polyethylene terephthalate, an acrylic acid functionalized polypropylene (PP-g-AA) was evaluated as the blend component in polyblends containing 40 percent by weight polyethylene terephthalate and compared with an unmodified polypropylene. Uncompatibilized samples as well as compatibilized blends were prepared by compounding in a co-rotating twin-screw extruder. Morphological examination, thermal as well as mechanical properties were also investigated by means of scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and tensile test, respectively. They have found that the functionalized polypropylene promotes fine dispersed phase morphology, improves processability and mechanical properties, and modifies the crystallization behavior of the polyester component. These effects are attributed to enhance the interfacial interactions resulting in reduced the interfacial tension between the two polymer phases (i.e: PP and PET).

In another study, Compatibilization of Polyethylene Terephthalate /Polypropylene (PET/PP) Blends with Styrene – Ethylene / Butylene – Styrene (SEBS) Block Copolymers have reported by **M.Heino and co-workers [2]**. Blends of PET and PP at compositions 20/80 and 80/20 were modified with three different SEBS triblock copolymers with the aim of improving the compatibility and in particular the toughness of the systems. The compatibilizers involved an unfunctionalized SEBS and two functionalized grades containing either maleic anhydride (SEBS-g-MAH) or glycidyl methacrylate (SEBS-g-GMA) grafted to the midblock. The effects of the compatibilizers were evaluated by studies on morphology and mechanical, thermal and rheological properties of the blends by means of scanning electron microscope (SEM); Tensile and flexural tests; Dynamic-mechanical thermal analysis (DMTA); capillary viscosimeter, respectively. They have found that the addition of 5 wt % of a SEBS copolymer was found to stabilize the blend morphology and to improve the tensile properties (i.e: increased the tensile strength, young's modulus, and decreased the elongation at break) as well as the impact strength. The effect was, however, far more pronounced with the functionalized copolymers. Particularly high toughness combined with rather high

stiffness was achieved with SEBS-g-GMA for the PET-rich composition. Addition of the functionalized SEBS copolymers resulted in a finer dispersion of the minor phase and clearly improved interfacial adhesion. Shifts in the glass transition temperature of the PET phase and increase in the melt viscosity of the compatibilized blends indicated enhanced interactions between the discrete PET and PP phases induced by the functionalized compatibilizer, in particular SEBS-g-GMA. These effects could be attributed to improve the interfacial adhesion between the two polymer phases (i.e: PET, and PP) imparted by functionalized compatibilizers.

J.C. Lepers et al [3] have studied the relative role of coalescence and interfacial tension in controlling dispersed phase size reduction during the compatibilization of polyethylene terephthalate / polypropylene blends. The breaking thread and the sessile drop methods have been used to evaluate the interfacial tension between a polypropylene (PP) and a polyethylene-terephthalate (PET). An excellent correlation was found between the two polymers. The breaking thread technique was then used to evaluate the interfacial tension of these blends at various levels of a styrene-ethylene butylene-styrene grafted with maleic anhydride (SEBS-g-MA) as a compatibilizer. In order to evaluate the relative roles of coalescence and interfacial tension in controlling dispersed phase size reduction during compatibilization, the morphology of PP/PET 1/99 and 10/90 blends compatibilized by a SEBS-g-MA were studied and compared. The samples were prepared in a Brabender mixer. For the 10/90 blend, the addition of the compatibilizer leads to a typical emulsification curve, and a decrease in dispersed phase size of 3.4 times is observed. For the 1/99 blend, a 1.7 times reduction in particle size is observed. In the latter case, this decrease can only be attributed to the decrease of the interfacial tension. It is evident from these results that the drop in particle size for the 10/90 PP/PET blend after compatibilization is almost equally due to diminished coalescence and interfacial tension reduction. These results were corroborated with the interfacial tension data in the presence of the copolymer. A direct relationship between the drop in dispersed phase size for the 1/99 PP/PET blend and the interfacial tension reduction was found for this predominantly shear mixing device. These effects could be attributed to increase the interfacial adhesion and reduce the interfacial tension between the two polymer phases (i.e: PP, and PET) imparted by the compatibilizing agent.

In another publication, **J.C. Lepers and coworkers [4]**, have reported the influence of partial emulsification on coalescence suppression and interfacial tension reduction in PP/PET systems. Their study examines how the relative role of coalescence suppression and

interfacial tension reduction influence the particle size at various levels of in situ compatibilization. The polymers studied are polyethylene terephthalate (PET) as matrix and a polypropylene (PP) as dispersed phase compatibilized by a triblock copolymer of poly(styrene– hydrogenated butadiene–styrene) (SEBS) grafted with maleic anhydride. The interfacial tension was studied by the breaking-thread method, and it was used along with the morphology to characterize the emulsification efficacy of the copolymers. By modifying the concentration of MA grafted on the SEBS, different levels of emulsification of the blends were obtained. A comparison of 1/99 and 10/90 PP/PET blends compatibilized by SEBS-g-MA allows one to distinguish the relative role of interfacial tension and coalescence suppression in diminishing particle size. It is shown that varying degrees of residual coalescence remain, depending on the level of %MA in the copolymer. A detailed study of the 2% MA system below interfacial saturation was carried out to shed further light on the dependence of coalescence suppression on emulsification level and interfacial coverage. After separating out the contribution of interfacial tension on particle size reduction, it is shown that coalescence suppression for this system increases gradually with areal density of modifier at the interface right up to the region of interfacial saturation.

In another article, **Y.X. Pang et al [5]** have studied the effects of a compatibilizing agent on the morphology, interface and mechanical behaviour of polypropylene/poly(ethylene terephthalate) samples. Three maleic anhydride-grafted-polypropylene (PP) derivatives [N,N-dihydroxyethyl monomaleic amide (C-2A), octodecyl monomaleate (C-3), and 2-(N, N-dihydroxyethylamino)ethyl monomaleate (C-4)] were prepared by melt grafting and utilized to compatibilize polypropylene/poly(ethylene terephthalate) (PP/PET) blends. The resulting blends were characterized by means of scanning electron microscopy (SEM), thermal analysis (M-TDSC) and testing of mechanical properties such as tensile test, impact strength as well as flexural test. The results show the compatibilizing effects of the three PP grafts are very different and strongly dependent on the functional groups present. Compatibilizer C-4 produced the finest dispersed phase morphology, whereas C-3 showed little compatibilizing effect. Substitution of 40 wt % of C-2A with a tert-butyl phenolic resin further improved the compatibilizing effect and resulted in much finer domains of the dispersed phase.

M-TDSC measurements revealed that the T_g , T_c , T_m , ΔC_p , and ΔH_c of the PET component in the blends were all to some extent lower than those in neat PET. However, only T_c , T_m , and ΔC_p displayed obvious differences before and after compatibilization. The movement of T_c to higher temperatures by compatibilization is evidence of enhanced interfacial interaction.

In addition, the change of T_m with compatibilization, which is related to the domain sizes, is also an indication of improvement of interfacial interaction. However, the most sensitive and important parameter to compatibilization obtained from M-TDSC measurements is found to be ΔC_p , the increment of heat capacity at the glass transition. This is because ΔC_p is directly related to the interface content of the blend. The fact that the varying tendency of ΔC_p with compatibilization is entirely consistent with those of morphology and mechanical properties provides good evidence. This result suggests that ΔC_p can be used as a quantitative measure of compatibilization. Mechanical determinations showed the improvements in tensile, impact and flexural properties by compatibilization. These are a result of finely dispersed morphology and strengthened adhesion of interfaces. It is believed that these compatibilizing effects may result from the enhanced interaction between the two phases, owing to the introduction of polar functional groups carried by the compatibilizers.

In another article, **Michel F. Champagn and coworkers [6]** have studied the effect of reactive compatibilization on the morphological examination and mechanical properties of PP/PET blends. The reactive compatibilization of polypropylene/polyethylene terephthalate (PP/PET) blends by addition of glycidyl methacrylate grafted PP (PP-g-GMA) was studied. Two PP-g-GMA copolymers, containing either 0.2 or 1.2 wt% of GMA, were used as inter face modifiers. These were incorporated into PP blends (with either 70 or 90 wt% PET), replacing 1/5 of PP in the system. The use of these modifiers changed the blends' tensile mechanical behavior from fragile to ductile. Blend tensile strength was improved by 10 % and elongation at break showed 10 to 20-fold increases while stiffness remained constant. Scanning electron micrographs showed the PP average domain size in injection molded specimens to decrease to the micron/sub-micron size upon addition of the GMA modified resins, while the unmodified blends exhibited heterogeneous morphology comprising large lamellae 10-20 μm wide. The low-GMA graft content PP seemed slightly more efficient than the high GMA content PP in emulsifying PP/PET blends. The GMA grafting level on PP had very limited effects on the blends' mechanical behavior in the range of GMA graft density provided by the two modified resins.

In another article, Comparison of the effects of compatibilizers effectiveness for the PET/PP blends in their mechanical, thermal and morphological behavior were studied by **C.P. Papadopoulou et al [7]**. The compatibilizing efficiency for PET/PP blends was examined by means of tensile testing, dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) of crycro-

fractured surfaces before and after etching. Compatibilizers used were maleic anhydride modified, PP (PP-g-MA), LLDPE (LLDPE-g-MA) and hydrogenated SBS block copolymer (SEBS-g-MA). From their results, the large deformation behavior of aged blends indicated that SEBS-g-MA performed best by far. However, the addition of a thermoplastic polyolefin alloy (TPO), PP/ethylene-propylene copolymer, increased the compatibilizing efficiency of PP-g-MA to a level comparable to that of SEBS-g-MA. Improved efficiency of SEBS-g-MA and PP-g-MA+TPO compared to PP-g-MA or LLDPE-g-MA is attributed to better emulsification of the former at the interface, reduced migration of PP-g-MA into the PP phase and retardation of PET crystallization in the presence of the elastomeric additive. In addition, the elastomeric compatibilizers absorb more efficiently, the stresses developed at the PET/PP interface. Over all, A comparison of the compatibilizers used for the PET/PP blend, classifies them in the following order of decreasing efficiency: SEBS-g-MA \approx PP-g-MA+TPO \gg LLDPE-g-MA \gg PP-g-MA.

In another interest paper, **Mariano Pracella et al [8]** have investigated the reactive mixing of PET and PET/PP Blends with Glycidyl Methacrylate-Modified Styrene-b-(Ethylene-co-Olefin) Block Copolymers. Styrene-b-(ethylene-co-butylene)-b-styrene (SEBS) and styrene-b-(ethylene-co-propylene) (SEP, SEPSEP) block copolymers with different styrene contents and different numbers of blocks in the copolymer chain were functionalized by melt radical grafting with glycidyl methacrylate (GMA) and employed as compatibilizers for PET-based blends. Binary blends of PET with both functionalized (SEBS-g-GMA, SEP-g-GMA, SEPSEP-g-GMA) and neat (SEBS, SEP, SEPSEP) copolymers (75 : 25 w/w) and ternary blends of PET and PP (75 : 25 w/w) with various amounts (2.5–10 phr) of both modified and unmodified copolymers were prepared in an internal mixer, and their properties were evaluated by SEM, DSC, melt viscosimetry, tensile and impact tests. The roles of the chemical structure, grafting degree, and concentration of the various copolymers on blend compatibilization were investigated. The blends with the grafted copolymers showed a neat improvement of phase dispersion and interfacial adhesion compared to the blends with non-functionalized copolymers. The addition of grafted copolymers resulted in a marked increase in melt viscosity, which was accounted for by the occurrence of chemical reactions between the epoxide groups of GMA and the carboxyl/hydroxyl end groups of PET during melt mixing. Blends with SEPSEP-g-GMA and SEBS-g-GMA, at concentrations of 5–10 phr, showed a higher compatibilizing effect with enhanced elongation at break and impact

resistance. The effectiveness of GMA-functionalized SEBS was then compared to that of maleic anhydride– grafted SEBS.

In another paper, **Hsien-Tang Chiu and Yao-Kuei Hsiao [9]**, have studied the compatibilization of Poly(ethylene terephthalate)/Polypropylene Blends with Maleic Anhydride Grafted Polyethylene-Octene Elastomer. Blends of poly(ethylene terephthalate) (PET) and polypropylene (PP) at composition 80/20 with and without a compatibilizing agent were studied. Both materials are widely used in the soft drink bottle industry. The compatibilizing agent was a maleic anhydride grafted polyethylene-octene elastomer (POE-g-MA). The olefinic segment of POE is compatible with PP, whereas the maleic anhydride is affined with PET carbonyl groups. The effectiveness of the compatibilizing agent was evaluated using different techniques, such as Fourier transform IR spectroscopy, mechanical analysis, scanning electron microscopy, dynamic mechanical analysis, and rheological analysis. POE-g-MA was evaluated as a potential compatibilizer for PET/PP blends. Incorporation of POE-g-MA in PET/PP blends enhanced considerably mechanical properties such as the elongation at break and the impact strength. Owing to the softness of the elastomeric compatibilizer, the tensile strength, flexural strength, and modulus of the blends were, however, slightly lowered. Toughening was based on a stabilized morphology consisting of a very fine dispersion of the minor phase with droplets well embedded in the matrix. Hence, not only the small particle size, but also the improved adhesion between the PET and PP phases caused by the compatibilizer was of great importance in toughening. It was also found that POE-g-MA plays a dual interfacial function that enhances the interfacial adhesion through the formation of micro-bridges. The function of POE-g-MA was related to good mixing of its olefinic segment with the PP phase and strong interaction of the functional group with the end-group of PET. The shifts in the T_g of the PET phase towards that of PP found by DMA and the high apparent viscosity of the PET/PP/POE-g-MA blends are further indications of such interactions. The interaction with PET probably occurs owing to a dipole-dipole interaction involving the carbonyl group of the PET and the anhydride group of the POE-g-MA. The results thus indicate that highly incompatible PET/PP blends can be effectively compatibilized with the addition of POE-g-MA.

In another publication; **M. Akbari et al [10]** have studied the compatibilization of PP/PET thermoplastic polymer material using PP-g-MA as a compatibilizing agent. In attempts to improve the compatibility of polypropylene (PP) with polyethylene terephthalate (PET), a maleic anhydride grafted PP (PP-g-MA) was evaluated as a compatibilizer in a blend of

30/70 wt % PP/PET. PP-g-MA was produced from isotactic homopolymer PP utilizing the technique of solid phase graft copolymerization. Qualitative confirmations of the grafting were made by Fourier transform infrared spectroscopy (FTIR). Three different weight percent of compatibilizer, PP-g-MA, i.e., 5, 10, and 15 wt % have been used in PP/PET blends. The compatibilizing efficiency for PP/PET blend was examined using differential scanning calorimetry (DSC), optical microscopy (OM), scanning electron microscopy (SEM) of cryo-fractured surfaces, and energy dispersive X-ray spectrum (EDAX). The results show that the grafted PP promotes a fine dispersed phase morphology, improves processability, and modifies the crystallization behavior of the polyester component. These effects are attributed to enhance phase interaction resulting in reduced interfacial tension. Also, the results show that the compatibilizing effects of the three amounts of grafted PP in blend are different and dependent on the amount used. Adding 10 wt % of compatibilizer into blend produced the finest dispersed morphology. Elemental analysis results show that PP is matrix. DSC determination revealed that the melting temperature (T_m) of the PET component declined to some extent by comparison with neat PET.

In another studies, **Wenjing Li et al [11]** have studied the Effect of Viscosity Ratio on the Morphology of PET Microfibrils in Uncompatibilized and Compatibilized Drawn PET/PP/TiO₂ Blends. Uncompatibilized and compatibilized (polypropylene-grafted maleic anhydride (PP-g-MA) as compatibilizer) PET (polyethylene terephthalate)/PP (polypropylene)/TiO₂ drawn strands were prepared by extrusion of the blends and cold drawing of the extrudates. In the uncompatibilized drawn strand, the generated PET microfibrils show large aspect ratio and wide distribution in diameter; whereas in the compatibilized drawn strand numbers of short needle-like PET formations appear and demonstrate uniform diameter distribution. Derived from PET droplets, the microfibril morphology is greatly influenced by the size of PET droplets in the extrudates: small droplet deforms into needle-like shape and large one becomes microfibril. In the compatibilized PET/PP/TiO₂ extrudate, the size of PET droplet is much smaller than that in the uncompatibilized one. The reduction of droplet size is attributed to the low viscosity ratio between dispersed phase and matrix, which facilitates the breakup of the dispersed PET droplets.

In another publication, **Mohammad Asgari and Mahmood Masoomi [12]** have studied Thermal and impact study of PP/PET fibre composites compatibilized with Glycidyl Methacrylate and Maleic Anhydride. Two grafted copolymers, Glycidyl Methacrylate grafted polypropylene (PP) (PP-g-GMA) and Maleic Anhydride grafted PP (PP-g-MA) were used in

PP reinforced with short poly(ethylene terephthalate) (PET) fibre composites. Transcrystallization (TC) of PP on PET fibres was investigated using a polarized optical microscope, which revealed no TC for either of the modified composites at the fibre–matrix interface. Heat deflection temperature (HDT) results of GMA modified composites revealed more enhancement than HDT of MA modified samples. The composite strength results showed enhancement for both modified composites up to 10 wt.%, and this growth was bigger for GMA modified composites. The morphological analysis of GMA modified PP/PET composites pointed out a marked improvement of fibre dispersion and interfacial adhesion as compared to non compatibilized PP/PET composites. The results of impact strength showed about 43% enhancement for 15 wt.% PET fibre composites. It was found that at low fibre percentages, using either of the modifiers reduces the impact strength a little in comparison to impact strength of the unmodified samples. According to linear elastic fracture mechanics LEFM, impact fracture toughness (G_c) and critical stress intensity factor (K_{Ic}) were evaluated for these composites based on the fracture energy obtained from impact tests.

In another paper, **Hossein Ali Khonakdar et al [13]** have studied the Rheology-Morphology Correlation in PET/PP Blends: Influence of Type of Compatibilizer Rheological and morphological properties of melt processed poly(ethylene terephthalate) (PET)/polypropylene (PP) blends are presented. Two types of compatibilizer namely, PP-g-MA <MA5 maleic anhydride> and Elvaloy PTW, an n-butyl acrylate glycidyl methacrylate ethylene terpolymers, were incorporated at different levels to the PET/PP blend system. Scanning electron microscopy revealed that the dispersed particle sizes were smaller in PET-rich blends than PP-rich blends. With increasing compatibilizer level, the refinement of morphology was observed in both the systems. However, the blends compatibilized with PTW showed a more refined (smaller) particle size, and at high PTW content (10 wt%), the morphology changed towards monophasic. The significant changes in morphology were attributed to the highly reactive nature of PTW. Investigation of rheological properties revealed that the viscosity of the PET/PP blends followed typical trends based on mixing rule, which calculates the properties of blends based on a linear average. Incorporation of PP-g-MA into the blends resulted in a negative deviation in the viscosity of the system with respect to that of the neat blend. With increasing PP-g-MA level, the deviation became more pronounced. Although incorporation of the compatibilizer into the PET/PP blends refined the morphology, it led to a drastic drop of viscosity, which could be attributed to inherently lower molecular weight of the compatibilizer. In the case of the blends compatibilized by PTW, a strong positive

deviation in rheological properties was observed that confirmed the stronger interaction between the blend components due to reactive compatibilization process, which led to the more refined morphology in this series of blends.

In another studies, **N.C. Abdul Razak et al [14]** have studied the Effects of compatibilizers on mechanical properties of PET/PP blend. Polyethylene terephthalate (PET) and polypropylene (PP) are incompatible thermoplastics due to differences in chemical structure and polarity hence their blends possess inferior mechanical properties. Compatibilization with a suitable block/graft copolymer is one way to improve the mechanical properties especially impact strength of such a blend. In this work, the effects of two compatibilizers, maleic anhydride grafted polypropylene (PP-g-MAH) and maleic anhydride grafted styrene-ethylene/butylene-styrene (SEBS-g-MAH), were investigated for compatibilization of PET/PP blends and the results were compared. PET, PP, and compatibilizers were melt blended in a single step using a counter-rotating twin screw extruder with compatibilizer concentrations 0, 2, 4, 6, 8, and 10 phr, respectively. Standard test samples were prepared by injection molding process. The resulting compatibilized blends were characterized by tensile, flexural, and impact tests. The results showed improvements in mechanical properties of the blends due to the in situ polymerization reaction between the ester groups of PET and the maleic anhydride (MAH) during melt extrusion. The incorporation of 4 phr PP-g-MAH in the blends resulted in the highest tensile and flexural strength, while no significant improvements in Young's modulus were observed for both compatibilized blends. The maximum impact strength of the blends was obtained at 8 phr of SEBS-g-MAH. Improvement of impact strength of the blends may be attributed to the elastomeric nature of the SEBS-g-MAH while greater improvement recorded for tensile and flexural strength is likely to be due to the affinity between PP-g-MAH with PP of the blend. Scanning electron microscopy shows the addition of PP-g-MAH and SEBS-g-MAH compatibilizers into the blends promote a better dispersion of PP into PET matrix.

In another publication, **Yeling Zhu et al [15]** have studied the Compatibilization of polypropylene/recycled polyethylene terephthalate blends with maleic anhydride grafted polypropylene in the presence of diallyl phthalate. Bi-functional co-agent, diallyl phthalate (DAP), assisted melting free-radical grafting of maleic anhydride (MAH) on polypropylene (PP) is carried out by reactive extrusion. The PP/recycled polyethylene terephthalate (rPET) blends with and without PP-g-MAH/DAP (PP grafted with both MAH and DAP) are conducted on a twin-screw extruder. It reveals that the introduction of DAP can significantly

enhance the grafting degree of MAH and decrease the chain scission of PP. The maximum extent of MAH grafting (1.5 wt. %) is obtained when DCP and MAH contents are 0.5 and 6.0 wt. %, respectively, and the DAP/MAH molar ratio is 0.3. Besides, differential scanning calorimetry (DSC) analysis shows that the crystallization temperature of grafted PP is higher than that of pure PP due to the nucleation of grafted groups. Fourier transform infrared spectroscopy (FTIR) analysis proves that chemical reactions take place between PP-g-MAH/DAP and rPET. In particular, scanning electron microscopy (SEM) observations demonstrate that, the PP/rPET blends compatibilized with PP-g-MAH/DAP show enhanced adhesion at the interface comparing with the binary PP/rPET blend, which is also proved by DSC measurements, dynamic mechanical analysis (DMA) and mechanical properties.

In Another paper, **Ibrahim M. Inuwa et al [16]** have studied the Interface Modification of Compatibilized Polyethylene Terephthalate/Polypropylene Blends: Effect of Compatibilization on Thermomechanical Properties and Thermal Stability. Polyethylene terephthalate (PET) and polypropylene (PP) are incompatible thermoplastics because of differences in chemical structure and polarity, hence their blends possess inferior mechanical and thermal properties. Compatibilization with a suitable block/graft copolymer is one way to improve the mechanical and thermal properties of the PET/PP blend. In this study, the toughness, dynamic mechanical analysis (DMA), and thermogravimetric analysis (TGA) of PET/PP blends were investigated as a function of different content of styrene-ethylene-butylene-styrene-g-maleic anhydride (SEBS-g-MAH) compatibilizer. PET, PP, and SEBS-g-MAH were melt-blended in a single step using the counter rotating twin screw extruder with compatibilizer concentrations of 0, 5, 10, and 15 phr, respectively. The impact strength of compatibilized blend with 10 phr SEBS-g-MAH increased by 300% compared to the uncompatibilized blend. Scanning electron microscope (SEM) micrographs show that the addition of 10 phr SEBS-g-MAH compatibilizer into the PET/PP blends decreased the particle size of the dispersed PP phase to the minimum level. The improvement of the storage modulus and the decrease in the glass transition temperature of the PET phase indicated an interaction among the blend components. Thermal stability of the PET/PP blends was significantly improved because of the addition of SEBS-g-MAH.

In another publication, **Ibrahim Mohammed Inuwa et al [17]** have studied the Effect of Compatibilizer Content on the Mechanical and Morphological Properties of PET/PP (70/30) Blends. This work investigates the effect of compatibilizer concentration on the mechanical properties of compatibilized polyethylene terephthalate (PET) /polypropylene (PP) blends. A

blend containing 70 % (wt) PET, 30 % (wt) PP and 5- 15 phr compatibilizers were compounded using counter rotating twin screw extruder and fabricated into standard test samples using injection molding. The compatibilizer used is styrene- ethylene-butylene styrene grafted maleic anhydride triblock copolymer (SEBS-g-MAH). Morphological studies show that the particle size of the dispersed PP phase is dependent on the compatibilizer content up to 10 phr. Impact strength and elongation at break showed maximum values with the addition of 10 phr SEBS-g-MAH and a corresponding decrease in flexural and young's moduli; and strengths. Overall the mechanical properties of PET/PP blends depend on the control of the morphology of the blend and can be achieved by effective compatibilization using 10 phr SEBS-g-MAH.

In other work, **Ibrahim M. Inuwa et al [18]** have studied the Interface Modification of Compatibilized Polyethylene Terephthalate /Polypropylene Blends: Effect of Compatibilization on Thermomechanical Properties and Thermal Stability. Polyethylene terephthalate (PET) and polypropylene (PP) are incompatible thermoplastics because of differences in chemical structure and polarity, hence their blends possess inferior mechanical and thermal properties. Compatibilization with a suitable block/graft copolymer is one way to improve the mechanical and thermal properties of the PET/PP blend. In this study, the toughness, dynamic mechanical analysis (DMA), and thermogravimetric analysis (TGA) of PET/PP blends were investigated as a function of different content of styrene-ethylene-butylene-styrene-g-maleic anhydride (SEBS-g-MAH) compatibilizer. PET, PP, and SEBS-g-MAH were melt-blended in a single step using the counter rotating twin screw extruder with compatibilizer concentrations of 0, 5, 10, and 15 phr, respectively. The impact strength of compatibilized blend with 10 phr SEBS-g-MAH increased by 300% compared to the uncompatibilized blend. Scanning electron microscope (SEM) micrographs show that the addition of 10 phr SEBS-g-MAH compatibilizer into the PET/PP blends decreased the particle size of the dispersed PP phase to the minimum level. The improvement of the storage modulus and the decrease in the glass transition temperature of the PET phase indicated an interaction among the blend components. Thermal stability of the PET/PP blends was significantly improved because of the addition of SEBS-g-MAH.

In other studies , **E. P. A. van Bruggen et al [19]** have studied Influence of Processing Parameters and Composition on the Effective Compatibilization of Polypropylene–Poly(ethylene terephthalate) Blends .The effects of the addition of different functionalized compatibilizers on toughness, morphology and rheological properties of a polypropylene (PP)

– poly(ethylene terephthalate) (PET) (85–15 wt%) blend were studied. The three compatibilizers compared were: (Styrene Ethylene Butylene Styrene)-grafted- (glycidyl methacrylate); (Styrene Ethylene Butylene Styrene) – grafted – (maleic anhydride); (polyolefin) – grafted - (glycidyl methacrylate), abbreviated to: SEBS-g-GMA, SEBS-g-MA and POE-g-GMA respectively. The effective grafting content was the same for all three compatibilizers. Before the comparison of the different compatibilizers was done, first the effects of three different processing temperatures and three different compatibilizer contents were investigated, based on the addition of SEBS-g-GMA. The compatibilization effect was significantly improved with an increase in processing temperature from 250 to 300 8C. The toughness was increased with almost a factor two and a decrease in the average domain size of the dispersed phase was observed. An increase in compatibilizer content from 0.25 to 2.5 wt% resulted in a finer dispersity as well as in a steep increase in toughness, which was noted to approach the brittle-to-ductile transition. The comparison of the three compatibilizers was subsequently done at the most promising processing temperature and content: 300 8C and 2.5 wt%. The results showed that the addition of SEBS-g-MA and POE-g-GMA had a less significant positive effect on the compatibilization compared to SEBS-g-GMA. The difference is attributed to a higher reactivity for GMA compared to MA and a higher possibility for migration towards the PP-PET interface for the SEBS chain compared to the POE chain.

In another paper , **Z. Baccouch et al [20]** have studied the Experimental investigation of the effects of a compatibilizing agent on the properties of a recycled poly(ethylene terephthalate)/polypropylene blend. This study deals with the behavior of a recycled polyethylene terephthalate (PET)/polypropylene (PP) blends. The compatibilizing effect has been investigated to examine the recycling feasibility in industrial production. The compatibilizing efficiency of olefinic copolymers containing epoxy groups for a/polypropylene (PET/PP) blends was examined using scanning electron microscopy (SEM), differential scanning calorimetry (DSC), mechanical testing and rheological one. The effect of ethylene-glycidyl methacrylate (E-GMA, 92/8 wt%, Lotader AX8840) and ethylene–methyl acrylate-glycidyl methacrylate (E-MA GMA, 68/24/8 wt%, Lotader AX8900) copolymers was investigated. The blends of PET/PP/compatibilizer at compositions 80/15/5, 85/11.25/3.75, 90/7.5/2.5 and 95/3.75/1.25 (wt%) were prepared by melt mixing in a single-screw extruder. Test specimens were prepared by compression moulding at processing temperatures of 250°C. The incorporation of the compatibilizers has a large effect on the dispersion of the PP phase.

Moreover, the copolymer was more efficient than the terpolymer. Especially, E-GMA was found to improve the elongation at break of the blends containing 80 % PET.

In other studies, **Omid Moini Jazani et al [21]**, An investigation on the role of GMA grafting degree on the efficiency of PET/PP-g-GMA reactive blending: morphology and mechanical properties. Glycidyl methacrylate (GMA) has been grafted on polypropylene (PP) with the aid of styrene (St) comonomer, by changing dicumyl peroxide initiator content, GMA level, and St concentration. The performance of the resulting PP-g-GMA reactive material towards static and dynamic mechanical properties of poly(ethylene terephthalate) (PET) was monitored in terms of grafting reaction variables and compatibilizer content. Fourier transform infrared spectroscopy, scanning electron microscopy, mechanical properties, melt flow rate, and impact strength analyses were applied to correlate structural changes due to grafting (or undesired chain scission) with blends' properties. The competition between the desired reaction, i.e., GMA grafting onto PP chain, and undesired chain scission of PP macroradicals due to thermal degradation, was discussed based on torque–time curves and mechanical properties. Manipulation of grafting variables was responsible for a special behavior over properties, means that optimal or ascending/ descending trends, which noticed high sensitivity of PET toughening to GMA grafting efficiency.

In another publication, **Luciana Maria Guadagnini Araujo et al [22]** have studied the Compatibilization of recycled polypropylene and recycled poly (ethylene terephthalate) blends with SEBS-g-MA. The compatibilization of recycled PP/PET blend with high and low concentration (20 and 5 phr) of elastomer functionalized by maleic anhydride (SEBS-g-MA) was achieved. Recycled polypropylene from plastic industry and recycled PET from post-consumer bottles was used. PP/PET blends: 80:20 w/w, 50:50 w/w and 20:80 w/w were prepared in an internal mixer for mechanical properties, thermal properties, morphology and rheological properties. SEBS-g-MA promoted compatibilization of the PP/PET blends and improved their properties. With an increasing compatibilization level, the refinement of morphology was observed in the PET rich blend. Compatibilized blends showed negative deviation in the PET glass transition temperature related to neat PET, demonstrating that compatibilization was very successful. PET crystallization was accelerated in the blends due to PP presence that enhanced nucleation. It was found that the 50/50/20 blend showed huge potential for textile fiber application and that of 80/20/20 showed more intermediary properties than neat polymers.

In another work, **Mafalda S. Lima et al [23]** have studied Glycidyl methacrylate-based copolymers as new compatibilizers for polypropylene/ polyethylene terephthalate blends. The improvement of flexural properties of polypropylene (PP) could be achieved by blending it with a stiffer polymer like poly (ethylene terephthalate) (PET). The main problem is the compatibilization between a saturated, a polar structure with a polar polyester. Copolymers of glycidyl methacrylate (GMA) and 2-ethylhexyl acrylate (EHA) were prepared, characterized and used as compatibilizers in PP/PET (70/30 wt %) blends at different feed ratios. The effects of compatibilization of these polymers were analyzed by SEM, which shows reduction of the size of PET granules, and by TGA, with an increase in the thermal stability of the compatibilized blends. Thermal properties corresponding to melting and crystallization events were also changed by the introduction of the compatibilizers. The DMTA shows that the Tg of the PET domain is affected by compatibilization, contrary to the Tg of PP domain. The compatibilization efficiency was further confirmed by an increase in flexural strain at flexural strength (ϵ_{FM}).

In another publication, **Karen Van Kets et al [24]** have studied the Structural stabilizing effect of SEBS-g-MAH on a PP-PET blend for multiple mechanical recycling. The stabilizing effect of a compatibiliser for long term mechanical recycling of polymer blends is assessed. A polypropylene (PP)/poly(ethylene terephthalate) (PET) blend and their mono-materials were multiple extruded (5 times). A fourth set was made with the addition of a compatibiliser block copolymer poly(styrene-co-(ethylene-butylene)- styrene) grafted with maleic anhydride (SEBS-g-MAH) in order to evaluate the (lack of) progressive degradation effects and the morphology stabilization of adding the compatibiliser. After the third reprocessing cycle Scanning Electron Microscopy (SEM) showed a severe destabilization of the PP-PET blends while there was only minor destabilization observed for the compatibilized mix. Differential Scanning Calorimetry (DSC) highlighted an increase in PET's crystallinity enthalpy for every set. This increase was less prominent for the compatibilised blend because fractionated crystallization occurred. Fourier Transformed Infrared (FTIR) and rotational rheology confirmed that the degradation was less severe for the compatibilised blend. The demixing and degradation resulted in changed mechanical properties shown by a decreased strain at break and strain at yield. This decrease was more pronounced in the uncompatibilised blend than in the compatibilised blend over the five extrusions, thus confirming the stabilization of the ternary blend.

In another paper, **Majid Ahmad louydarab et al [25]** have studied the Compatibilization of immiscible polymer blends (R-PET/ PP) by adding PP-g-MA as compatibilizer: analysis of phase morphology and mechanical properties. In the current study, the compatibilization of polypropylene/recycled polyethylene terephthalate (PP/r-PET) blends with different percentages of maleic anhydride (PP-g-MA) was examined. Exploited resource for r-PET was used as water bottles. Specimens of PP/r-PET blends in different percentages, i.e., 90/10, 70/30, and 50/50 were prepared in a corotating twin-screw extruder to evaluate the mechanical properties. Results indicated that PP-g-MA improved compatibilization of the PP/r-PET blends (modulus of elasticity and yield stress were enhanced to about 1450 MPa and 30 MPa) and also enhanced the morphological and mechanical properties. By adding about 2% of the compatibilizer into specimens containing 10% of r-PET, the highest enhancement in mechanical properties was achieved. Besides, both yield strength and the impact of energy were improved 8.3% and 24.6% by increasing the amount of 50% and 10% r-PET in the system. Also, results showed that specimens have higher yield stress and modulus of elasticity after 10 days compared to those specimens without aging due to the presence of stronger interaction after a period of time.

In another work, **Zishou Zhang et al [26]** have studied the Reinforcement of Recycled PET for Mechanical Properties of Isotactic Polypropylene .For high-value use of recycled polyethylene terephthalate (r-PET) resource and simultaneous development of high performance isotactic polypropylene (PP) materials, the blends of r-PET with PP and its compatibilized versions were prepared. PP-g-MA, POE-g-MA and EVA-g-MA with same functional group, as well as their mixtures, were used as compatibilizer. The crystallization behavior, mechanical properties and microphotographs of r-PET/compatibilizer, r-PET/PP blends and its compatibilized versions were characterized. The results indicated that addition of compatibilizer decreased the tensile and flexural strength of r-PET and slightly improve its impact strength. The introduction of r-PET to PP matrix increased the tensile and flexural strength of PP. The tensile and flexural strength of compatibilized r-PET/PP are dependent on the kinds of compatibilizers. Addition of PP-g-MA improved the tensile and flexural strength of r-PET/PP blends and introduction of POE-g-MA or EVA-g-MA increased the impact strength of r-PET/PP blends. Effect of compatibilizer and its mixtures and r-PET content on the mechanical properties of compatibilized r-PET/PP blends is discussed. The r-PET/PP blends with high strength and toughness can be obtained by compatibilization of the mixtures

of PP-g-MA and POE-g-MA (or EVA-g-MA). This investigation provides an effective method to use the r-PET to prepare high performance PP blends with low cost and high-value.

In another studies, **Akshaya E Ma et al [27]** have studied the Properties of Blends from Polypropylene and Recycled Polyethylene Terephthalate using a Compatibilizer. Polyethylene Terephthalate (PET) is a major constituent of the plastic waste generated on a day-to-day basis. Replacing a proportion of the virgin Polypropylene (PP) with recycled Polyethylene Terephthalate (r-PET) through polymer blending is cost effective and sustainable method to increase the mechanical characteristics of PP. A compatibilizer namely Polypropylene grafted maleic anhydride (PP-g-MAH) is utilized to reduce immiscibility between them through chemical reactions involving the maleic anhydride group. In this study, PP/r-PET blend ratio is maintained at 80/20. The polymer blends prepared by twin screw extrusion are converted to test specimens by injection moulding. The mechanical and thermal properties of the blends are studied by performing characterization techniques like Tensile Tests and Differential Scanning Calorimetry (DSC). Fourier Transform Infrared Spectroscopy (FTIR) analysis shows the reaction occurring at the interface during compatibilization. Scanning Electron Microscopy (SEM) suggests the significance of compatibilizer in the microstructure development of the blend for the effective dispersion of the r-PET in PP. The crystallization temperature of PP is moved to higher temperatures in the presence of both the r-PET and the compatibilizer as evident from the DSC analysis. The addition of the compatibilizer improved the tensile strength, elongation at break and the modulus of elasticity of the blend. The blend containing 4% PP-g-MAH exhibited the optimum set of properties.

In another publication, **P. Bataille et al [28]** have studied Mechanical Properties and Permeability of Polypropylene and Poly(ethylene terephthalate) Mixtures. The synthetic membranes currently used for soil stabilization and road construction are mainly made of polypropylene and of polyesters. They are used separately for each application. The polymer used has an effect on the wettability and the permeability of the membrane. The polypropylene membranes, for instance, have a zero wettability, whereas it is high for polyester membranes. This paper reports on the mechanical properties and the permeability of mixtures of polypropylene (PP) and poly(ethylene terephthalate) (PET). The elastic modulus of the mixture was at a minimum for a **50/50** mixture. For the other compositions, the moduli gave a positive deviation as compared with the additivity equation results. This is probably due to the fact that pure PET has a fragile behavior at the temperature at which the mechanical tests were run. This **50/50** composition corresponds to the domain where a phase inversion

occurs. The permeability to water vapor gave an S-shape curve that is typical of a “mixture” of immiscible polymers. The diffusion of the water molecules is controlled by the continuous phase. To compatibilize the two homopolymers, a **94/6** copolymer of PP and of polyacrylic acid was added, at various levels, to a **60/40** mixture of PET and PP: This did not affect markedly the elastic modulus. The yield stress increased, however, indicating that we had a better adhesion and that the copolymer seems to have a certain emulsifier effect, increasing the quality of the dispersion.

References

- [1] Xanthos, M.; Young, M.W.; Biesenberger, J.A. Polypropylene/Polyethylene Terephthalate Blends Compatibilized through Functionalization. *Polym. Eng. Sci.* **1990**, *30*, 355–365, [doi:10.1002/pen.760300607](https://doi.org/10.1002/pen.760300607).
- [2] Heino, M.; Kirjava, J.; Hietaoja, P.; A Seppala, J. Compatibilization of Polyethylene Terephthalate/Polypropylene Blends with Styrene-Ethylene/Butylene-Styrene (SEBS) Block Copolymers. *J. Appl. Polym. Sci.* **1997**, *65*, 241–249, [doi:10.1002/\(SICI\)1097-4628\(19970711\)65:2<241::AID-APP4>3.0.CO;2-O](https://doi.org/10.1002/(SICI)1097-4628(19970711)65:2<241::AID-APP4>3.0.CO;2-O).
- [3] Lepers, J.-C.; Favis, B.D.; Tabar, R.J. The Relative Role of Coalescence and Interfacial Tension in Controlling Dispersed Phase Size Reduction during the Compatibilization of Polyethylene Terephthalate/Polypropylene Blends. *J. Polym. Sci. B Polym. Phys.* **1997**, *35*, 2271–2280, [doi:10.1002/\(SICI\)1099-0488\(199710\)35:14<2271::AID-POLB7>3.0.CO;2-Z](https://doi.org/10.1002/(SICI)1099-0488(199710)35:14<2271::AID-POLB7>3.0.CO;2-Z).
- [4] Lepers, J.-C.; Favis, B.D.; Lacroix, C. The Influence of Partial Emulsification on Coalescence Suppression and Interfacial Tension Reduction in PP/PET Blends. *J. Polym. Sci. B Polym. Phys.* **1999**, *37*, 939–951, [doi:10.1002/\(SICI\)1099-0488\(19990501\)37:9<939::AID-POLB6>3.0.CO;2-O](https://doi.org/10.1002/(SICI)1099-0488(19990501)37:9<939::AID-POLB6>3.0.CO;2-O).
- [5] Pang, Y.X.; Jia, D.M.; Hu, H.J.; Hourston, D.J.; Song, M. Effects of a Compatibilizing Agent on the Morphology, Interface and Mechanical Behaviour of Polypropylene/Poly(Ethylene Terephthalate) Blends. *Polymer* **2000**, *41*, 357–365, [doi:10.1016/S0032-3861\(99\)00123-8](https://doi.org/10.1016/S0032-3861(99)00123-8).

- [6] Champagne, M.F.; Huneault, M.A.; Roux, C.; Peyrel, W. Reactive Compatibilization of Polypropylene/Polyethylene Terephthalate Blends. *Polym. Eng. Sci.* **1999**, *39*, 976–984, [doi:10.1002/pen.11487](https://doi.org/10.1002/pen.11487).
- [7] Papadopoulou, C.P.; Kalfoglou, N.K. Comparison of Compatibilizer Effectiveness for PET/PP Blends: Their Mechanical, Thermal and Morphology Characterization. *Polymer* **2000**, *41*, 2543–2555, [doi:10.1016/S0032-3861\(99\)00442-5](https://doi.org/10.1016/S0032-3861(99)00442-5).
- [8] Pracella, M.; Chionna, D.; Pawlak, A.; Galeski, A. Reactive Mixing of PET and PET/PP Blends with Glycidyl Methacrylate-Modified Styrene-b-(Ethylene-Co-Olefin) Block Copolymers. *J. Appl. Polym. Sci.* **2005**, *98*, 2201–2211, [doi:10.1002/app.22413](https://doi.org/10.1002/app.22413).
- [9] **Chiu, H.-T.; Hsiao, Y.-K.** Compatibilization of Poly(Ethylene Terephthalate)/Polypropylene Blends with Maleic Anhydride Grafted Polyethylene-Octene Elastomer. *J Polym Res* **2006**, *13*, 153–160, [doi:10.1007/s10965-005-9020-z](https://doi.org/10.1007/s10965-005-9020-z).
- [10] Akbari, M.; Zadhoush, A.; Haghghat, M. PET/PP Blending by Using PP-g-MA Synthesized by Solid Phase. *J. Appl. Polym. Sci.* **2007**, *104*, 3986–3993, [doi:10.1002/app.26253](https://doi.org/10.1002/app.26253).
- [11] Li, W.; Schlarb, A.K.; Evstatiev, M. Effect of Viscosity Ratio on the Morphology of PET Microfibrils in Uncompatibilized and Compatibilized Drawn PET/PP/TiO₂ Blends. *J. Polym. Sci. B Polym. Phys.* **2009**, *47*, 555–562, [doi:10.1002/polb.21658](https://doi.org/10.1002/polb.21658).
- [12] Asgari, M.; Masoomi, M. Thermal and Impact Study of PP/PET Fibre Composites Compatibilized with Glycidyl Methacrylate and Maleic Anhydride. *Composites Part B: Engineering* **2012**, *43*, 1164–1170, [doi:10.1016/j.compositesb.2011.11.035](https://doi.org/10.1016/j.compositesb.2011.11.035).

- [13] Khonakdar, H.A.; Jafari, S.H.; Mirzadeh, S.; Kalae, M.R.; Zare, D.; Saeb, M.R. Rheology-Morphology Correlation in PET/PP Blends: Influence of Type of Compatibilizer. *J Vinyl Addit Technol* **2013**, *19*, 25–30, [doi:10.1002/vnl.20318](https://doi.org/10.1002/vnl.20318).
- [14] Abdul Razak, N.C.; Inuwa, I.M.; Hassan, A.; Samsudin, S.A. Effects of Compatibilizers on Mechanical Properties of PET/PP Blend. *Composite Interfaces* **2013**, *20*, 507–515, [doi:10.1080/15685543.2013.811176](https://doi.org/10.1080/15685543.2013.811176).
- [15] Zhu, Y.; Liang, C.; Bo, Y.; Xu, S. Compatibilization of Polypropylene/Recycled Polyethylene Terephthalate Blends with Maleic Anhydride Grafted Polypropylene in the Presence of Diallyl Phthalate. *J Polym Res* **2015**, *22*, 35, [doi:10.1007/s10965-014-0591-4](https://doi.org/10.1007/s10965-014-0591-4)
- [16] Inuwa, I.M.; Hassan, A.; Samsudin, S.A.; Haafiz, M.K.M.; Jawaid, M. Interface Modification of Compatibilized Polyethylene Terephthalate/Polypropylene Blends: Effect of Compatibilization on Thermomechanical Properties and Thermal Stability. *J Vinyl Addit Technol* **2017**, *23*, 45–54, [doi:10.1002/vnl.21484](https://doi.org/10.1002/vnl.21484).
- [17] Inuwa, I.M.; Hassan, A.; Samsudin, S.A. Effect of Compatibilizer Content on the Mechanical and Morphological Properties of PET/PP (70/30) Blends. *AMM* **2015**, *735*, 70–74, [doi:10.4028/www.scientific.net/AMM.735.70](https://doi.org/10.4028/www.scientific.net/AMM.735.70).
- [18] Inuwa, I.M.; Hassan, A.; Samsudin, S.A.; Haafiz, M.K.M.; Jawaid, M. Interface Modification of Compatibilized Polyethylene Terephthalate/Polypropylene Blends: Effect of Compatibilization on Thermomechanical Properties and Thermal Stability. *J Vinyl Addit Technol* **2017**, *23*, 45–54, [doi:10.1002/vnl.21484](https://doi.org/10.1002/vnl.21484).

- [19] Van Bruggen, E.P.A.; Koster, R.P.; Picken, S.J.; Ragaert, K. Influence of Processing Parameters and Composition on the Effective Compatibilization of Polypropylene–Poly(Ethylene Terephthalate) Blends. *International Polymer Processing* **2016**, *31*, 179–187, [doi:10.3139/217.3124](https://doi.org/10.3139/217.3124).
- [20] Baccouch, Z.; Mbarek, S.; Jaziri, M. Experimental Investigation of the Effects of a Compatibilizing Agent on the Properties of a Recycled Poly(Ethylene Terephthalate)/Polypropylene Blend. *Polym. Bull.* **2017**, *74*, 839–856, [doi:10.1007/s00289-016-1748-6](https://doi.org/10.1007/s00289-016-1748-6).
- [21] Jazani, O.M.; Rastin, H.; Formela, K.; Hejna, A.; Shahbazi, M.; Farkiani, B.; Saeb, M.R. An Investigation on the Role of GMA Grafting Degree on the Efficiency of PET/PP-g-GMA Reactive Blending: Morphology and Mechanical Properties. *Polym. Bull.* **2017**, *74*, 4483–4497, [doi:10.1007/s00289-017-1962-x](https://doi.org/10.1007/s00289-017-1962-x).
- [22] Araujo, L.M.G.; Morales, A.R. Compatibilization of Recycled Polypropylene and Recycled Poly(Ethylene Terephthalate) Blends with SEBS-g-MA. *Polímeros* **2018**, *28*, 84–91, [doi:10.1590/0104-1428.03016](https://doi.org/10.1590/0104-1428.03016).
- [23] Lima, M.S.; Matias, Á.A.; Costa, J.R.C.; Fonseca, A.C.; Coelho, J.F.J.; Serra, A.C. Glycidyl Methacrylate-Based Copolymers as New Compatibilizers for Polypropylene/ Polyethylene Terephthalate Blends. *J Polym Res* **2019**, *26*, 127, [doi:10.1007/s10965-019-1784-7](https://doi.org/10.1007/s10965-019-1784-7).
- [24] Van Kets, K.; Delva, L.; Ragaert, K. Structural Stabilizing Effect of SEBSgMAH on a PP-PET Blend for Multiple Mechanical Recycling. *Polymer Degradation and Stability* **2019**, *166*, 60–72, [doi:10.1016/j.polymdegradstab.2019.05.012](https://doi.org/10.1016/j.polymdegradstab.2019.05.012).

- [25] Ahmadlouydarab, M.; Chamkouri, M.; Chamkouri, H. Compatibilization of Immiscible Polymer Blends (R-PET/PP) by Adding PP-g-MA as Compatibilizer: Analysis of Phase Morphology and Mechanical Properties. *Polym. Bull.* **2020**, *77*, 5753–5766, [doi:10.1007/s00289-019-03054-w](https://doi.org/10.1007/s00289-019-03054-w).
- [26] Zhang, Z.; Wang, C.; Mai, K. Reinforcement of Recycled PET for Mechanical Properties of Isotactic Polypropylene. *Advanced Industrial and Engineering Polymer Research* **2019**, *2*, 69–76, [doi:10.1016/j.aiepr.2019.02.001](https://doi.org/10.1016/j.aiepr.2019.02.001).
- [27] Akshaya, E.M.; Palaniappan, R.; Sowmya, C.F.; Rasana, N.; Jayanarayanan, K. Properties of Blends from Polypropylene and Recycled Polyethylene Terephthalate Using a Compatibilizer. *Materials Today: Proceedings* **2020**, *24*, 359–368, [doi:10.1016/j.matpr.2020.04.287](https://doi.org/10.1016/j.matpr.2020.04.287).
- [28] Bataille, P.; Boissé, S.; Schreiber, H.P. Mechanical Properties and Permeability of Polypropylene and Poly(Ethylene Terephthalate) Mixtures: Mechanical Properties and Permeability of PP and PET Mixtures. *Polym Eng Sci* **1987**, *27*, 622–626, [doi:10.1002/pen.760270904](https://doi.org/10.1002/pen.760270904).

Conclusion

Conclusion

Conclusion

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

Polyethylene Terephthalate (PET), thermoplastic polyester, is widely used in industrial applications such as packaging, beverage bottles, power tools, sporting goods and textile fibers. It has good mechanical, physical, chemical and gas barrier properties. It has been reported that the worldwide production of PET has increased phenomenally over the recent years. Owing to its large consumption, PET is one of the major constituents of the plastic wastes generated. The amount of plastic wastes produced is growing at a faster rate and it is mainly treated by burning or through discharge in landfills. This eventually leads to environmental degradation, making it necessary to develop new strategies for recycling and deriving maximum benefit.

Polymer blending provides an attractive route for the recycling and reuse of plastic wastes. It also provides an effective and an economical method for the incorporation of the desired properties of the individual polymers into the blend, thus resulting in a high-performance polymer. Polyethylene Terephthalate (PET) can be effectively utilized by blending with the versatile polymer Polypropylene. Polypropylene (PP) is the lightest thermoplastic polymer which can be easily processed. PP has remarkable properties like heat resistance, high stiffness and chemical inertness. PP has applications in the fields of household appliances, automobile manufacturing and electrical manufacturing.

However, blending PP and PET results in a thermodynamically immiscible blend. The immiscibility of the blend components results in phase separation resulting in inferior properties. To improve the miscibility of the blend components, a compatibilizer can be introduced. The compatibilizer moderates the interfacial tension and enhances adhesion across the immiscible phases.

Conclusion

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 is significant and may exceed specific interactions. Such polymer blends are never thermodynamically stable; the metastable morphology is maintained by interfacial interactions and solidification of the blend. Polymer blending is particularly favorable to broaden the properties and applications of commodity polymers. Creation of new materials by combining existing polymers is often more appealing than synthesis of new copolymers; hence obtaining the required combination of characteristics and properties from each polymer.

Abstract

The compatibilization of polymer blends, such as Polypropylene (PP) and polyethylene terephthalate (PET), is a process that aims to improve the compatibility and the properties of the blend. PP/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: Polypropylene, Polyethylene Terephthalate, Immiscible Blend Phase Separation, Physical Compatibilization, Chemical Compatibilization.

Résumé

La compatibilisation des mélanges de polymères, tels que le Polypropylène (PP) et le polyéthylène téréphtalate (PET).est un procédé qui vise à améliorer la compatibilité et les propriétés du mélange. Le PP/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: Polypropylène, Polyéthylène téréphtalate, Mélanges Immiscible, Séparation de phase, Compatibilization Physique, Compatibilization Chimique.

ملخص

إن توافق خلائط البوليمر، مثل البولي بروبيلين والبولي إيثيلين تيريفثاليت هي عملية تهدف إلى تحسين توافق و خصائص المزيج. يتميز البولي بروبيلين والبولي إيثيلين تيريفثاليت باختلاط منخفض بسبب الاختلافات في التركيب الكيميائي والقطبية. وهذا ما يؤدي إلى فصل الطور و التفاعلات البينية الضعيفة بين البوليمرات، مما يؤدي ذلك أيضا إلى 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 بروبيلين ، بولي إيثيلين تيريفثاليت ، فصل طور المزيج غير القابل للامتزاج ، التوافق الفيزيائي ، التوافق الكيميائي.