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Effects of Compatibilizers on the Interfacial Adhesion, Phase Morphology and Thermomechanical Properties in Immiscible Blend based on Styrene-co Acrylonitrile/Ethylene Propylene Diene Monomer (SAN/EPDM)

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Dedications

We would like to dedicate our Master-thesis:

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

-To all our brothers and sisters;

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

-To all our best friends;

- To anyone who has ever taught us anything.

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

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CHAPTER II

Morphology and properties of polymer blends

List Of Notations and Abbreviations

Abbreviations	Description
ASTM	American Society for Testing and Materials
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared
AFM	Atomic force microscopy
ABS	Acrylonitrile Butadiene Styrene
BR	Butadiene Rubber
CNR	Cyclic Natural Rubber
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimeter
DTG	Derivative thermogravimetry
DCP	Dicumyl peroxide
ENR	Epoxidized Natural Rubber
EPDM	Ethylene propylene diene rubber
EVA	Ethylene vinyl acetate
EPR	Ethylene propylene rubber
FTIR	Fourier transform infrared
HDPE	High density polyethylene
HNRs	Hydrogenated natural rubbers
^{1}H-NMR	Proton nuclear magnetic resonance
iPP	Isotactic polypropylene
ISO	International Standards Organization
LLDPE	Linear Low Density Polyethylene
MA	Maleic anhydride
MNR	Maleated natural rubber
MA-g-PP	Maleic anhydride grafted polypropylene
Mn	Number average molecular weight
Mw	Mass average molecular weight
NBR	Acrylonitrile butadiene rubber
NMR	Nuclear magnetic resonance
NR	Natural rubber
NR-g-PMMA	NR-graft-poly(methyl methacrylate)
NR-g-PS	NR-graft-polystyrene
PA-6	Polyamide-6
PA-12	Polyamide-12
PE	Polyethylene
PLA	Polylactide
PLLA	Poly(L-lactide)
PMMA	Poly(methyl methacrylate)
PVDF	Polyvinyl diene fluoride
PP	Polypropylene
PVC	Polyvinyl Chloride
PS	Polystyrene
Ph-PP	Phenolic modified polypropylene

SBR	Styrene Butadiene Rubber
SAN	Styrene-acrylonitrile
SEBS	Styrene Ethylene/Butylene Styrene
SEBS-g-MA	Styrene-ethylene-butylene-styrene-graft-maleic anhydride
SEM	Scanning electron microscope
TEM	Transmission electron microscope
TGA	Thermogravimetric Analysis
Tg	Glass transition temperature

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

General Introduction

I. General Introduction

Polymers are rarely used for applications in their pure form and they are often mixed with other polymers and additives to alter processability and properties. The main problem that appears when polymer blends are prepared from two immiscible and non-compatible polymers is strong phase separation due to weak adhesion resulting in poor properties of blends [**1-5**]. A huge number of interesting questions are connected with the general subject of polymer interfaces. Interfacial properties can be tailored by adding a small amount of a third substance to the blend. In particular, co-polymeric surfactant containing both types of monomers is often used as effective compatibilizer and it can reduce directly the interfacial tension; being compatible with both components, it aggregates at interfaces, thereby reducing the number of direct contacts between polymers of different types. The compatibilization aims to achieve the desired level of dispersion, to insure strong interaction between the phases for the purposes of formation of polymer blends with good properties, and maximization of the product performance. Miscible polymer blends are homogeneous at molecular level, thermodynamically associated with a negative value of the free energy of mixing, and an important feature of miscibility is thermodynamic stability **[6–8],** which is accompanied by a decrease in the Gibbs free energy.

This master thesis is composed of two chapters. The first presents a theoretical background on ethylene–propylene– diene monomer (EPDM) and poly(styrene-co-acrylonitrile) (SAN) .The Second chapter present a brief presentation of some of the works that have been published and which covered different aspects of the subject.

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

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Chapter I
Theoretical Background

I.1.Ethylene Propylene Diene Monomer

I.1.1 Synthesis method of Ethylene Propylene Diene Monomer

Ethylene Propylene Diene Monomer (EPDM) is a synthetic elastomer, which is primarily used in the production of rubber products. EPDM is made by a process called "terpolymerization", which involves the reaction of three monomers: ethylene, propylene, and a small amount of a non-conjugated diene. Here is a brief overview of the synthesis of EPDM:

1. Monomer preparation: Ethylene and propylene are produced by the steam cracking of hydrocarbons, such as natural gas or naphtha. The non-conjugated diene is usually 5-ethylidene-2-norbornene (ENB), which is synthesized from cyclopentadiene and ethylene.
2. Polymerization: The three monomers are mixed together with a catalyst, typically a transition metal complex, and a co-catalyst, such as an organoaluminum compound. The reaction is carried out in a reactor at high pressure and temperature.

3. Terpolymerization: The monomers undergo a chain-growth polymerization process, where they react to form a terpolymer with a random distribution of the three monomers along the polymer chain. The non-conjugated diene provides unsaturation in the polymer backbone, which allows for crosslinking and provides EPDM with its unique properties.

4. Stabilization: The resulting polymer is then treated with antioxidants and other stabilizers to prevent degradation during processing and use.

5. Processing: The EPDM is then processed into a variety of rubber products, such as hoses, seals, and roofing membranes, using techniques such as extrusion, injection molding, and calendaring.

The synthesis of EPDM is a complex and carefully controlled process, which requires specialized equipment and expertise to produce high-quality polymers with consistent properties **[1].**

EPDM is a synthetic rubber terpolymer consisting of ethylene (E), propylene (P) and a third monomer which is a diene (D). The letter M in EPDM rubber denotes a rubber with a saturated chain that is a polymethylene type, i.e. it has repeated (-CH_2-) units in the backbone of the polymer **[2]**

Almost 40 years ago, when it was first introduced on the market, EPDM was predominantly produced using the coordination polymerization technique in aliphatic hydrocarbon solvents

(e.g. pentane, hexane) which is based on the Ziegler Natta catalysis. Vanadium salts (VCl_4, $VOCl_3$) were used as catalyst and aluminium alkyl halide such as Et_2AlCl or $Et_3Al_2Cl_3$ as co-catalyst. Later a new technology was developed for the production of EPDM using a metallocene catalyst in solution or in agas phase reactor **[3].**This technology allows not only for the recovery of propylene and diene, but also for the recovery of the ethylene used in the process. Using this technology, polymers with uniform molecular architecture and better properties than those obtained using Ziegler Natta catalyst are obtained.

A wide variety of dienes has been studied **[4]** as a third monomer, of which nowadays only two are commercially used, 5-ethylidene-2-norbornene (ENB) and dicyclopentadiene (DCPD) as shown in **Figure 1.1**, the most common of these is ENB. The non-conjugated dienes monomers contain two olefin units. One is used in the terpolymerisation reaction with ethylene and propylene and the other, from the side chain, serves as crosslink when curing with sulphur or resin. In the peroxide vulcanisation, the diene monomer acts as coagent allowing for a faster attack of radicals on the remaining double bond. The amount of diene added is between 0.5 and 12**% [5].** In comparison with other termonomers used, ENB presents a high rate of polymerisation and is very active with respect to sulphur vulcanisation. The chemical structures of the termonomers are shown in **Figure 1.1**

in

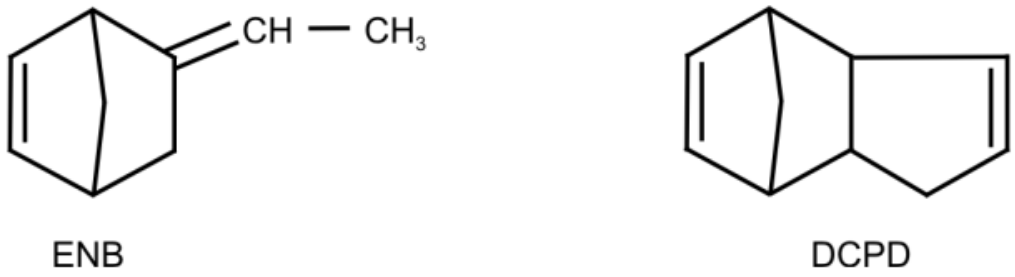

Figure I.1 Commercial dienes used as termonomer EPDM

I.1.2.Chemical structures of EPDM

EPDM (Ethylene Propylene Diene Monomer) is a type of synthetic rubber that is commonly used in a variety of applications, including automotive and construction industries. The chemical structure of EPDM can vary depending on the specific manufacturing process used, but generally, it is composed of three monomers: ethylene, propylene, and a diene.

The diene component is typically a small amount (1-5%) of the total monomer mixture and is added to introduce unsaturation into the polymer backbone, which improves its elasticity and low-temperature performance.

EPDM is the most widely used and highly developing synthetic rubber, occupying the third place in the synthetic rubber consumption after styrene butadiene and butadiene rubber **[6].**The chemical structure of EPDM with ENB as a third monomer is presented in **Figure I.2**

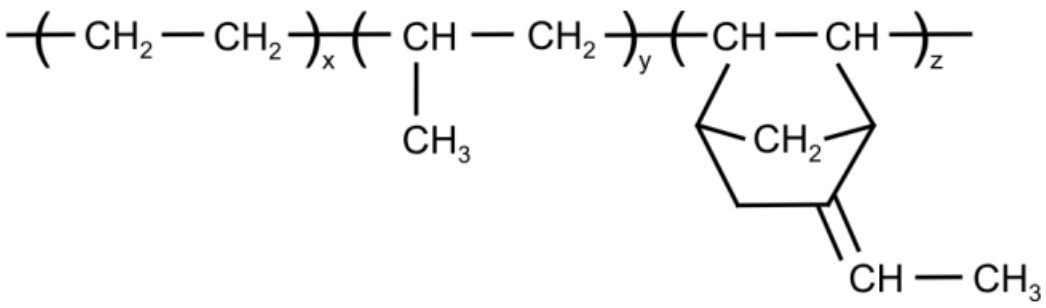

Figure I.2 Chemical structure of EPDM with ENB **[5]**

I.1.3.Properties of EPDM

I.1.3.1.Rheological properties of EPDM

EPDM (ethylene propylene diene monomer) is a synthetic rubber that is widely used in various industrial applications due to its excellent chemical and physical properties. The rheological properties of EPDM are crucial in determining its behavior under different processing and application conditions. The following are some of the important rheological properties of EPDM:

1. Viscosity: The viscosity of EPDM is a measure of its resistance to flow under a certain applied stress. It depends on factors such as molecular weight, temperature, and shear rate. Higher molecular weight EPDM has higher viscosity and is more difficult to process. The viscosity of EPDM decreases with increasing temperature and shear rate, which makes it easier to process.

2. Elasticity: EPDM exhibits high elasticity, which means it can deform under stress and then return to its original shape when the stress is removed. This property is important in applications where EPDM is subjected to repeated deformation cycles.

3. Shear modulus: The shear modulus of EPDM is a measure of its resistance to deformation under shear stress. It is related to the stiffness of the material and depends on factors such as temperature, frequency, and strain amplitude. EPDM has a low shear modulus compared to other elastomers, which makes it more flexible and easier to deform.

4. Strain rate sensitivity: The strain rate sensitivity of EPDM refers to its ability to deform under different strain rates. EPDM exhibits a strain rate sensitivity that is typical of most elastomers, meaning its deformation behavior is influenced by the rate of deformation.

5. Relaxation behavior: EPDM exhibits time-dependent relaxation behavior, meaning it will slowly relax and deform under a constant load over time. This property is important in applications where EPDM is subjected to sustained loads or stresses.

In summary, the rheological properties of EPDM play a crucial role in determining its processing and application behavior. These properties can be optimized by adjusting the molecular weight, temperature, and other processing parameters to meet specific application requirements **[7].**

I.1.3.2.Mechanical properties of EPDM

EPDM (ethylene propylene diene monomer) is a type of synthetic rubber that exhibits a range of mechanical properties. Some of the key mechanical properties of EPDM include:

1. Tensile strength: EPDM has high tensile strength, which means it can resist stretching and tearing when subjected to a load. This property makes it useful in applications where there is a risk of mechanical damage, such as seals and gaskets.

2. Elongation at break: EPDM has a high elongation at break, which means it can stretch considerably before breaking. This property makes it useful in applications where flexibility is required, such as in hoses and tubing.

3. Hardness: EPDM can be formulated to exhibit a wide range of hardness levels, from soft and pliable to hard and rigid. This property makes it suitable for a variety of applications, including automotive seals, roofing, and construction.

4. Abrasion resistance: EPDM has good resistance to abrasion, which means it can withstand wear and tear from repeated use or exposure to abrasive materials. This property makes it suitable for use in industrial applications such as conveyor belts and rollers.

5. Compression set: EPDM has low compression set, which means it can maintain its shape and properties even when subjected to a compressive load. This property makes it suitable for use in applications such as O-rings and seals, where deformation under pressure could compromise the effectiveness of the seal **[8].**

I.1.3.3.Physical properties of EPDM

EPDM, or ethylene propylene diene monomer, is a synthetic rubber that is commonly used in a variety of industrial applications. EPDM has a number of physical properties that make it useful for these applications, including:

1. Chemical resistance: EPDM is resistant to many chemicals, including acids, alkalis, and oxidizing agents. This makes it useful in applications where it will be exposed to these types of chemicals.

2. UV resistance: EPDM is highly resistant to UV radiation, making it useful in outdoor applications where it will be exposed to sunlight.

3. Heat resistance: EPDM has good heat resistance, with a maximum operating temperature of around 150°C (302°F).

4. Cold resistance: EPDM also has good cold resistance, with a minimum operating temperature of around -45°C (-49°F).

5. Water resistance: EPDM is highly resistant to water and can be used in applications where it will be exposed to water or moisture.

6. Electrical insulation: EPDM has good electrical insulation properties, making it useful in electrical applications.

7. Elasticity: EPDM is a highly elastic material, which allows it to stretch and deform without breaking. This makes it useful in applications where it will be subjected to stress or strain.

8. Low compression set: EPDM has a low compression set, which means that it can maintain its shape and elasticity even after being compressed. This makes it useful in applications where it will be subjected to repeated compression and release cycles **[9].**

I.1.3.4.Chemical properties of EPDM

EPDM, or Ethylene Propylene Diene Monomer, is a synthetic rubber material that exhibits a variety of chemical properties. Some of the important chemical properties of EPDM are:

1. Resistance to Weathering: EPDM has excellent resistance to weathering, which makes it a suitable material for outdoor applications. It can withstand exposure to sunlight, ozone, and other environmental factors without breaking down.

2. Chemical Resistance: EPDM is resistant to a wide range of chemicals, including acids, bases, and alcohols. It is also resistant to oil and other petroleum-based products.

3. Thermal Stability: EPDM has good thermal stability and can withstand high temperatures without losing its physical properties. It can withstand temperatures up to 150°C.

4. Electrical Insulation: EPDM is an excellent electrical insulator, making it useful in electrical applications.

5. Low Water Absorption: EPDM has low water absorption, which makes it suitable for use in wet environments.

6. Elasticity: EPDM has high elasticity, which allows it to recover its original shape after being stretched or compressed.

7. Adhesion: EPDM has good adhesion properties, which makes it easy to bond with other materials.

EPDM is a versatile material that exhibits a range of chemical properties that make it suitable for a variety of applications in different industries **[10].**

I.1.3.5.Thermal properties of EPDM

EPDM (ethylene propylene diene monomer) is a synthetic rubber with good thermal stability. Some of the important thermal properties of EPDM are:

1. Melting point: EPDM has a relatively low melting point of around 40-60°C (104-140°F), which means it can soften and deform at relatively low temperatures.

2. Glass transition temperature: The glass transition temperature (Tg) of EPDM is around -54°C (-65°F), which is the temperature at which the rubber transitions from a hard, glassy state to a softer, rubbery state.

3. Thermal conductivity: EPDM has a relatively low thermal conductivity, which means it is a good insulator and does not conduct heat well. The thermal conductivity of EPDM typically ranges from 0.2 to 0.4 W/mK.

4. Thermal expansion coefficient: EPDM has a relatively high coefficient of thermal expansion, which means it expands and contracts significantly with changes in temperature. The coefficient of thermal expansion of EPDM typically ranges from 100 to 200 µm/mK.

5. Heat resistance: EPDM is known for its excellent heat resistance and can withstand temperatures up to 150°C (302°F) without significant degradation. However, exposure to higher temperatures can cause thermal degradation and reduce its mechanical properties.

EPDM is a good choice of material for applications requiring good thermal stability, low thermal conductivity, and resistance to heat and weathering **[11].**

- **Effect of Ethylene/Propylene Ratio on the Mechanical Properties of EPDM**

EPDM are available in various grades depending on the ratios of ethylene, propylene and iene. The selection of particular grade of EPDM depends upon on the final required properties for applications. Different ratios of monomers grant different characteristics to EPDM **[12].** For example, green strength of EPDM increases with the increase of

ethylene content while low and medium ethylene content EPDM is comparatively soft and elastic **[13].**

Berdan and Verstrata et al**[14]** investigated the effect of the ethylene and propylene content on the glass transition temperature (Tg) and on the crystallinity of EPDM. They reported that Tg of EPDM varied with the content of the ethylene and propylene in non linear way and generally increased with increase of propylene conten **[14 ,15].**Crystallinity of the EPDM increases with increase of ethylene content and decreases with that of propylene content **[14,16].** High crystallinity associates with good mechanical properties and that why high ethylene content provides good green strength to EPDM **[13,17].**On other hand, high propylene content results low hardness EPDM with more flexibility at low temperature and more elasticity **[18].**

Allen et al has investigated that high ethylene content is very important for shape retention and processability of the EPDM. He further reports that ethylene content also enhances the cross linking efficiency of the EPDM **[19].** EPDM with high ethylene content is the best candidate for thermal insulator in space applications **[20].**

- **Effect of Ethylene/propylene Ratio on Thermal Properties of EPDM**

Clint Gamlin et al **[18]** reported in detail the effect of the ethylene contents on the thermal decomposition performance of EPDM. He investigated that high ethylene content provided thermal stability to EPDM **[18]** Furthermore, the activation energy of decomposition increased with increase of ethylene content. However, no direct correlation existed between ethylene content and activation energy required for decomposition of EPDM and there might be some other factors such as themicrostructures along with ethylene content that controlled the activation energy of decomposition **[18,21].**

- **Effect of Diene on the Properties of EPDM**

The most widely non-conjugated dienes incorporated for creating of un-saturation in EPDM are ethylidene norbonene, 1, 4 hexadiene and dicyclopetadiene. These conjugated dienes exploit one double bond during copolymerization with ethylene and propylene while reserve the other in the side chain of EPDM for sulfur vulcanization **[22].** Generally, diene content increases the vulcanization rate and the amount of diene added ranges from 0.5 to 12% weight **[19].** Because of the difference in structures, different types of dienes provide different properties to EPDM.

I.1.4.Advantages of EPDM

EPDM sheeting has excellent water resistance, both fresh and salt, as well as being very good with ozone, UV and oxidation. The temperature and weathering properties of EPDM rubber sheeting are also outstanding.

These factors make EPDM ideal for use in water and it is often the material of choice for potable water applications. There are WRAS approved materials available for use in specific applications but, in more general terms, EPDM is a good all-round commercial material. It is widely used as a lower cost polymer, with good processing abilities **[23].**

EPDM (Ethylene Propylene Diene Monomer) is a type of synthetic rubber that has a wide range of applications due to its unique properties. Here are some advantages of EPDM:

1. Weather Resistance: EPDM is highly resistant to weathering, ozone, UV rays, and extreme temperatures, making it suitable for outdoor applications.

2. Chemical Resistance: EPDM is resistant to acids, alkalis, and many other chemicals, making it suitable for use in harsh chemical environments.

3. Flexibility: EPDM is highly flexible and can stretch up to 300% of its original length without breaking, making it an ideal material for applications that require flexibility and durability.

4. Easy to Install: EPDM is lightweight and easy to install, making it a popular choice for roofing applications.

5. Longevity: EPDM is highly durable and can last up to 50 years with proper maintenance, making it a cost-effective solution in the long run.

6. Low Maintenance: EPDM requires minimal maintenance and is resistant to cracking, peeling, and fading.

7. Eco-Friendly: EPDM is a recyclable material and does not release harmful chemicals into the environment, making it an eco-friendly option.

EPDM's unique combination of properties makes it an ideal choice for a wide range of applications, from roofing to automotive and industrial applications **[24].**

I.1.5.Drawbacks of EPDM

EPDM exhibits unsatisfactory compatibility with most oils, gasoline, kerosene, aromatic and aliphatic hydrocarbons, halogenated solvents, and concentrated acids. The very inert nature of the material also means it is difficult to adhere to, and this can be a limitation **[25].**

EPDM (Ethylene Propylene Diene Monomer) is a popular synthetic rubber material that is used in a variety of applications, including roofing, automotive seals, and electrical insulation. While EPDM has many advantages, such as its excellent weather resistance and durability, it also has some drawbacks, including:

1. Limited temperature range: EPDM is not suitable for use in extremely high-temperature environments, as it can start to break down at temperatures above 150°C (302°F).

2. Poor resistance to certain chemicals: EPDM is not resistant to oils, solvents, and some other chemicals, which can cause it to degrade over time.

3. Difficult to bond: EPDM can be difficult to bond to other materials, which can limit its use in certain applications.

4. Limited color options: EPDM is typically only available in black or white, which can limit its use in certain applications where color is important.

5. Cost: EPDM can be more expensive than other rubber materials, which can make it less attractive for some applications.

While EPDM has many advantages, it is important to consider these drawbacks when selecting a material for a specific application **[26].**

I.1.6.Manufacturing of EPDM

The manufacturing process of EPDM typically involves the following steps:

1. Polymerization: The first step is the polymerization of ethylene and propylene with a diene monomer (typically 5% to 15% by weight) in the presence of a catalyst. The polymerization can take place using different methods such as suspension, solution, or emulsion polymerization.

2. Vulcanization: The EPDM polymer is then vulcanized, which involves cross-linking the polymer chains using a sulfur-based curing agent and heat. The vulcanization process improves the mechanical properties of EPDM, making it stronger and more durable.

3. Processing: The vulcanized EPDM is then processed into various shapes and forms using different methods such as extrusion, molding, or calendering. The processing method used depends on the desired final product and application.

4. Finishing: Finally, the EPDM products are finished by trimming, cutting, or coating with a release agent to prevent sticking.

The manufacturing process of EPDM is complex and requires specialized equipment and expertise to ensure consistent quality and performance of the final product **[27].**

I.1.7.Applications of EPDM in industrial fields

EPDM (ethylene propylene diene monomer) is a synthetic rubber material that has excellent resistance to weathering, ozone, UV radiation, and many chemicals. As a result, EPDM is used in various industrial applications where durability, flexibility, and chemical resistance are critical. Some of the common industrial applications of EPDM include:

1. Roofing: EPDM is widely used in the roofing industry due to its excellent weather resistance and long-term durability. It is commonly used for flat or low-slope roofs, and it can be easily installed using adhesives, ballasts, or mechanical fasteners.

2. Seals and gaskets: EPDM is used extensively for sealing and gasketing applications in the automotive, aerospace, and industrial sectors. Its excellent resistance to heat, water, and chemicals makes it an ideal material for sealing applications.

3. Electrical insulation: EPDM is used as an electrical insulator in various industrial applications due to its excellent dielectric properties. It is commonly used in the manufacture of high-voltage cables, electrical connectors, and insulating gaskets.

4. Automotive parts: EPDM is widely used in the automotive industry for making weather stripping, grommets, and seals due to its excellent resistance to heat and weathering. It is also used in engine cooling systems and other automotive components.

5. Marine applications: EPDM is used in the marine industry for making seals, gaskets, and hoses due to its excellent resistance to saltwater, UV radiation, and weathering.

6. Industrial hoses: EPDM is used for making industrial hoses that are used in various industries, including chemical processing, food and beverage, and pharmaceuticals. Its excellent chemical resistance and flexibility make it an ideal material for hoses.

In summary, EPDM is widely used in various industrial applications due to its excellent weather resistance, chemical resistance, and long-term durability **[28].**

I.2.Styrene co acrylonitrile (SAN)

I.2.1.Synthesis method of Styrene co acrylonitrile SAN

The synthesis of styrene co-acrylonitrile (SAN) is typically carried out via a copolymerization reaction between styrene and acrylonitrile monomers. There are several methods for

synthesizing SAN, but the most common industrial process is emulsion copolymerization. Here are the general steps involved in the synthesis:

1. Monomer Preparation: The monomers, styrene and acrylonitrile, are typically prepared by purification and distillation.

2. Initiator Addition: A free radical initiator is added to the reaction vessel to initiate the polymerization reaction.

3. Emulsification: The monomers are emulsified in water with the help of surfactants and stabilizers.

4. Polymerization: The emulsified monomers are heated under controlled conditions to initiate the copolymerization reaction. This typically occurs at temperatures ranging from 60°C to 80°C and under pressures ranging from 1 to 5 bar.

5. Termination: The polymerization reaction is terminated by quenching the reaction mixture with a suitable agent such as hydrogen peroxide.

6. Purification: The polymer is then isolated and purified by washing with water, followed by drying and pelletization.

7. Post-treatment: Depending on the intended application, the SAN copolymer may undergo additional post-treatment steps such as compounding with other materials, extrusion, and injection molding.

The emulsion copolymerization method is a highly efficient and cost-effective process for synthesizing SAN on an industrial scale**[29].**

The synthesis of styrene acrylonitrile copolymer follows **Figure I.3**

Figure I.3 Synthesis of styrene co -acrylonitrile copolymer **[30].**

I.2.2.Chemical structures of SAN

Styrene-co-acrylonitrile, or SAN, is a copolymer of styrene and acrylonitrile. The chemical structure of SAN can be represented by the following repeating unit:

$CH_2=CH(C_6H_5)-CH_2-CH(CN)-$

This unit contains one styrene unit and one acrylonitrile unit. The copolymerization of these two monomers results in a random distribution of styrene and acrylonitrile units along the polymer chain. The relative amounts of styrene and acrylonitrile units can be varied to modify the properties of the copolymer**[31].**

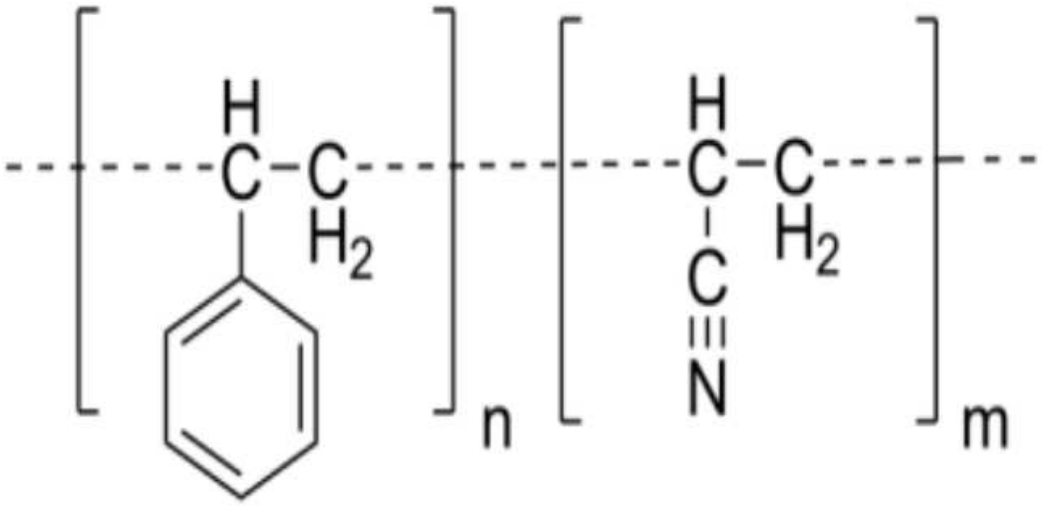

Figure I.4 Chemical structures of SAN **[32].**

I.2.3.Properties of SAN

I.2.3.1. Rheological properties of SAN

Styrene-co-acrylonitrile (SAN) is a copolymer made from a mixture of styrene and acrylonitrile monomers. The rheological properties of SAN depend on various factors such as molecular weight, composition, temperature, and processing conditions. Here are some general characteristics of the rheological properties of SAN:

1. Viscosity: SAN has a relatively low viscosity compared to other thermoplastics, which makes it easy to process. The viscosity of SAN can be adjusted by changing the monomer ratio or adding a plasticizer.

2. Shear thinning behavior: SAN exhibits shear thinning behavior, which means that the viscosity decreases as the shear rate increases. This behavior is due to the alignment of the polymer chains under high shear conditions.

3. Temperature sensitivity: The viscosity of SAN is highly dependent on temperature. As the temperature increases, the viscosity decreases. This temperature sensitivity can affect the processing conditions and properties of the final product.

4. Non-Newtonian behavior: SAN exhibits non-Newtonian behavior, which means that the viscosity is not constant over a range of shear rates. Instead, the viscosity changes depending on the shear rate, which is due to the complex molecular structure of the copolymer.

5. Elastic behavior: SAN has some degree of elasticity, which is due to the polymer chains' ability to stretch and return to their original position. This behavior can affect the mechanical properties of the final product.

The rheological properties of SAN make it suitable for various applications, including injection molding, extrusion, and blow molding **[33].**

I.2.3.2. Mechanical properties of SAN

Styrene co-acrylonitrile (SAN) is a copolymer consisting of styrene and acrylonitrile monomers. The mechanical properties of SAN can vary depending on the ratio of styrene to acrylonitrile in the copolymer.

Generally, SAN has good tensile strength and stiffness, as well as good impact resistance. It also has good dimensional stability, meaning it does not warp or change shape significantly when exposed to changes in temperature or humidity.

The specific mechanical properties of SAN can be further improved by adding fillers or reinforcing fibers. For example, adding glass fibers can significantly increase the strength and stiffness of SAN, making it a popular material for automotive and industrial applications.

SAN is a versatile engineering thermoplastic with good mechanical properties, and its specific properties can be tailored for specific applications through modifications to its composition or reinforcement **[34].**

I.2.3.3. Physical properties of SAN

Styrene co-acrylonitrile, also known as SAN, is a thermoplastic copolymer that is composed of styrene and acrylonitrile monomers. Its physical properties include:

1. Transparency: SAN is a transparent material with good optical clarity. It is commonly used in applications where transparency is important, such as in the production of consumer goods, packaging, and medical devices.

2. Hardness: SAN is a hard material with good scratch resistance, which makes it suitable for applications that require durability and resistance to wear and tear.

3. Chemical resistance: SAN is resistant to a wide range of chemicals, including acids, alkalis, and organic solvents. This makes it a suitable material for applications where chemical resistance is important.

4. Heat resistance: SAN has a relatively high melting point, which makes it suitable for use in applications that require heat resistance. However, it is not as heat-resistant as some other thermoplastics, such as polycarbonate.

5. Dimensional stability: SAN has good dimensional stability, meaning that it maintains its shape and size even when subjected to changes in temperature or humidity.

6. Electrical insulation: SAN has good electrical insulation properties, making it suitable for use in electrical applications.

SAN is a versatile thermoplastic that has a range of physical properties that make it suitable for a variety of applications **[35].**

I.2.3.4. Chemical properties of SAN

Styrene co-acrylonitrile, also known as SAN, is a thermoplastic polymer that is composed of styrene and acrylonitrile monomers. Its chemical properties include:

1. Chemical resistance: SAN has good resistance to many chemicals including acids, alkalis, and oils.

2. Thermal stability: SAN has a high melting point and can withstand high temperatures without degrading.

3. Hydrophobicity: SAN is highly hydrophobic, meaning it repels water and is resistant to moisture absorption.

4. Flammability: SAN is highly flammable and should be handled with care when exposed to fire or high temperatures.

5. Compatibility: SAN is compatible with a variety of other materials, including other thermoplastics, rubber, and some metals.

6. UV resistance: SAN has poor resistance to ultraviolet (UV) light and may degrade when exposed to prolonged sunlight.

7. Electrical properties: SAN has good electrical insulation properties and is commonly used in electrical applications.

SAN is a versatile polymer with a wide range of chemical properties that make it suitable for use in various applications, including packaging, automotive parts, and electrical equipment **[36].**

I.2.3.5.Thermal properties of SAN

Styrene co-acrylonitrile, also known as SAN, is a copolymer of styrene and acrylonitrile. The thermal properties of SAN depend on the ratio of styrene and acrylonitrile in the copolymer, as well as other factors such as molecular weight and processing conditions. Here are some general thermal properties of SAN:

1. Glass transition temperature (Tg): SAN has a relatively high glass transition temperature compared to other thermoplastics. The Tg of SAN ranges from around 100°C to 120°C, depending on the ratio of styrene and acrylonitrile.

2. Melting temperature (Tm): SAN is amorphous, so it does not have a distinct melting temperature like crystalline polymers. Instead, SAN softens and flows gradually with increasing temperature.

3. Thermal stability: SAN has good thermal stability and can withstand temperatures up to around 200°C without significant degradation.

4. Thermal conductivity: SAN has a relatively low thermal conductivity compared to metals and other materials, which makes it a good insulator.

5. Heat capacity: The specific heat capacity of SAN is relatively low, which means it does not require a lot of energy to raise its temperature.

SAN is a thermoplastic with good thermal properties, making it suitable for a variety of applications where heat resistance and dimensional stability are important **[37].**

I.2.4.Advantages of SAN

Styrene acrylonitrile (SAN) is a copolymer composed of styrene and acrylonitrile monomers. Here are some advantages of SAN:

1. Excellent transparency: SAN is a highly transparent material, making it an excellent choice for applications where clarity and visibility are essential, such as in packaging or optical components.

2. Good chemical resistance: SAN is resistant to many chemicals, making it suitable for use in a wide range of environments, including those with exposure to harsh chemicals.

3. High strength and stiffness: SAN has excellent mechanical properties, including high strength and stiffness, which make it a good material for applications that require durability and dimensional stability.

4. Good processability: SAN is easy to process using a variety of methods, including injection molding, extrusion, and blow molding, making it a versatile material for manufacturing.

5. Low water absorption: SAN has low water absorption properties, which makes it ideal for use in applications where moisture resistance is critical.

6. Cost-effective: SAN is an affordable material, making it an excellent choice for applications where cost is a significant consideration.

SAN is a versatile material that offers excellent properties, making it suitable for a wide range of applications **[38].**

I.2.5. Drawbacks of SAN

Styrene co-acrylonitrile (SAN) is a copolymer made from styrene and acrylonitrile monomers. While SAN has several benefits, such as high stiffness, excellent chemical resistance, and good dimensional stability, there are also some drawbacks to consider. Here are some of them:

1. Brittleness: SAN is a relatively brittle material, especially at low temperatures. It can crack or shatter easily under impact, making it unsuitable for some applications that require toughness and durability.

2. UV sensitivity: SAN is also sensitive to ultraviolet (UV) radiation, which can cause discoloration, cracking, and other forms of degradation over time. This makes it less suitable for outdoor applications or products that will be exposed to sunlight.

3. Flammability: SAN is a highly flammable material and can ignite easily. It is not recommended for use in applications where fire safety is a concern, unless treated with flame-retardant additives.

4. Cost: SAN can be more expensive than some other thermoplastics, such as polyethylene and polypropylene. This can make it less competitive in some applications where cost is a significant factor.

5. Recycling challenges: SAN is not easily recyclable and can be difficult to separate from other plastics. This can pose challenges for waste management and sustainability efforts.

While SAN has many useful properties, it may not be the best material for every application. Other factors such as cost, performance requirements, and sustainability considerations should be taken into account when selecting a material for a specific application **[39].**

I.2.6.Manufacturing of SAN

Styrene co-acrylonitrile (SAN) is a thermoplastic resin that is commonly used in the manufacture of a variety of products such as automotive parts, household appliances, and medical devices. The production process of SAN involves the following steps:

1. Monomer Preparation: The two monomers, styrene and acrylonitrile, are prepared separately. Styrene is derived from petroleum and is produced by the dehydrogenation of ethylbenzene. Acrylonitrile is made by the ammoxidation of propylene or propane.

2. Mixing of Monomers: The styrene and acrylonitrile monomers are mixed together in a reactor vessel along with a polymerization initiator, typically a peroxide.

3. Polymerization: The mixture of monomers is then heated and agitated, which initiates the polymerization reaction. The reaction continues until a high molecular weight polymer is formed.

4. Cooling: The polymer is then cooled to a temperature below its softening point to solidify it.

5. Pelletizing: The solid polymer is then ground into small pellets or beads, which can be used for further processing.

6. Extrusion: The pellets are melted and extruded into the desired shape or form using an extrusion machine.

7. Finishing: The finished product is then subjected to finishing processes such as cutting, trimming, and polishing to achieve the desired dimensions and surface finish.

Overall, the manufacturing of SAN involves a complex and precise process that requires strict control of various parameters such as temperature, pressure, and composition to ensure the desired properties of the final product **[40].**

I.2.7.Applications of EPDM in industrial fields

Styrene co-acrylonitrile (SAN) is a copolymer consisting of styrene and acrylonitrile monomers. It is a versatile thermoplastic material with excellent mechanical, thermal, and chemical properties, which makes it suitable for a wide range of industrial applications. Here are some of the common industrial applications of SAN:

1. Automotive: SAN is widely used in the automotive industry for manufacturing various interior and exterior parts such as dashboards, door panels, instrument panels, and grilles. SAN offers good dimensional stability, toughness, and resistance to chemicals, making it ideal for these applications.

2. Electrical and Electronic: SAN is also used in the electrical and electronic industry for manufacturing various components such as switches, connectors, and housings for electronic devices. SAN's high dielectric strength, excellent thermal stability, and resistance to flame make it an ideal choice for these applications.

3. Packaging: SAN is used in the packaging industry for manufacturing various products such as bottles, containers, and caps. SAN offers excellent clarity, toughness, and resistance to chemicals, making it ideal for packaging applications.

4. Appliances: SAN is used in the appliance industry for manufacturing various components such as refrigerator liners, washing machine tubs, and dryer drums. SAN's excellent resistance to chemicals, impact, and temperature makes it suitable for these applications.

5. Medical: SAN is also used in the medical industry for manufacturing various components such as medical devices, drug delivery systems, and diagnostic equipment. SAN offers good dimensional stability, biocompatibility, and resistance to chemicals, making it ideal for medical applications.

SAN is a versatile material that finds applications in a wide range of industrial fields, thanks to its excellent mechanical, thermal, and chemical properties **[41].**

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CHAPTER II

Morphology and Properties of Polymer Blends

II.1 General Introduction

The properties and performance of polymer blends are critically dependent on blend morphology. Morphology development is the path of morphological change, in which the material undergoes its transformation from large to small domains. Morphology depends on blend composition, melt viscosity of the components and processing history .Nielsen **[1]** showed that the phase morphology of polymer blends prepared by melt mixing changes as a function of composition. Callan et al **[2]** extensively studied the dependence of morphology on composition of the blends. Danesi and Porter **[3]** showed that under same processing conditions, the blend ratio and melt viscosity differences of the components determine the morphology. When the components have similar melt viscosities the resultant morphology shows a distribution of minor component in the major one. When the components have different melt viscosities the morphology of the resultant blends depends on whether the minor component has a lower or higher viscosity than the major one. The minor component will be finely dispersed. When it has got lower viscosity. The minor component will be dispersed as spherical domains if its viscosity is higher than the major component. Recently different studies were reported on morphology of polymer blends **[4-11].**

By the addition of suitably selected compatibiliser to immiscible blends, the interfacial tension can be reduced and finer dispersion of the dispersed phase is achieved during mixing. Above all it provides good interfacial adhesion **[12].** The physical properties of polymer blends are highly influenced by the morphology of the compatibilised blends **[13-20].**

II.2 Morphology and properties of polymer blends

As we mentioned in the previous paragraph, the properties of polymer blends directly related to its morphology **[63].** The morphology formation during processing depends on the various properties of the polymer components such as ratio of viscosities, interfacial adhesion, interfacial tension, volume fraction, and processing conditions/mixing protocols **[21, 22].**

In the case of immiscible polymer blends four basic morphologies can be expected **[23]:**

➢Dispersion of minor phase on major continuous phase (droplet morphology/domain morphology)

➢Fibers into the major phase

➢Planar alternating phases (lamellae morphology)

➢Co-continuous (bi-continuous morphology).

In the case of morphology of polymer blends, polymer having higher concentration forms the continuous phase. Morphology control is the key point behind the development of required properties of prepared blends.

Viscosity ratios between the polymer components, interfacial properties, and processing protocols have great importance in the control of morphology of polymer blends. Among the various morphologies, the domain and co-continuous morphologies are shown by many commercial polymer blends. But domain morphology is found very commonly in commercial polymer blends, since it is shown by a large range of compositions **[23, 24].**

II.2.1 Co-continuous morphology

Co-continuous structures can be defined in different way according to available literatures. For example, it can be defined as coexistence of two or more continuous structures within the same quantity **[25].** Some other reports define the co-continuous structures as structures with dual-phase continuity or co-phase continuity **[26-28].**

In a literature, co-continuous structures described as interpenetrating polymer networks, which refers to a bi-continuous structure of polymer chains **[29].** For thermoplastic blends, co-continuous morphology is termed as interpenetrating polymer blends. Its size scale is higher than that of interpenetrating networks by two orders of magnitude **[30].** Co-continuous structures are forming over a certain interval of volume fractions and centered about the phase inversion composition (phase inversion point).

According to Utracki, in co-continuous structure at least one part of each phase forms a coherent continuous structure that permeates the entire volume **[26, 28,31].**

Co-continuous structure of polymer blends forms near the phase inversion composition. Paul and Barlow suggested an equation to explain the condition for phase inversion related with viscosities of two components **[32].**

$$\frac{\varphi_1}{\varphi_2} = \frac{\eta_1}{\eta_2} \qquad \textbf{(II.1)}$$

Where φ_1 and φ_2 are the volume fractions of components 1 and 2, respectively. Similarly η_1 and η_2 denote the melt viscosities of polymer components 1 and 2, respectively.

II.2.2 Dispersed phase (domain) morphology

In the case of domain morphology minor phase is dispersed in the major continuous phase, but the size distribution of domains varies with compositions of polymer components. Normally the domain size of dispersed component increases with an increase in its concentration due to coalescence, and phase inversion can be observed after a particular composition.

Before phase inversion, at a critical volume fraction, development of co-continuous morphology can be expected and it depends on the viscosity ratio of the components.

The domain collisions lead to the coalescence (schematic given in **Figure. II.1**) and it depends on the concentration and viscosity of components and several types of interactions such as van der Waals forces between adjacent particles, capillary forces, etc. Increase in the concentration of dispersed phase leads to increase in the size of domains due to coalescence; increase in concentration makes an increase in a number of domain particles, as a result an increase in collision of particle-particle can be expected. This leads to the increased coalescence rate. Coalescence rate is higher with large interfacial tension, low shear rate, and long mixing times. If the viscosity of minor phase is lower than the major phase, the rate of coalescence decreases due to the limited diffusion of domains in the highly viscous continuous phase. Size distribution of phase domains directly depends on the composition of that minor phase and this dependence can be observed greatly at intermediate concentrations **[21, 33].**

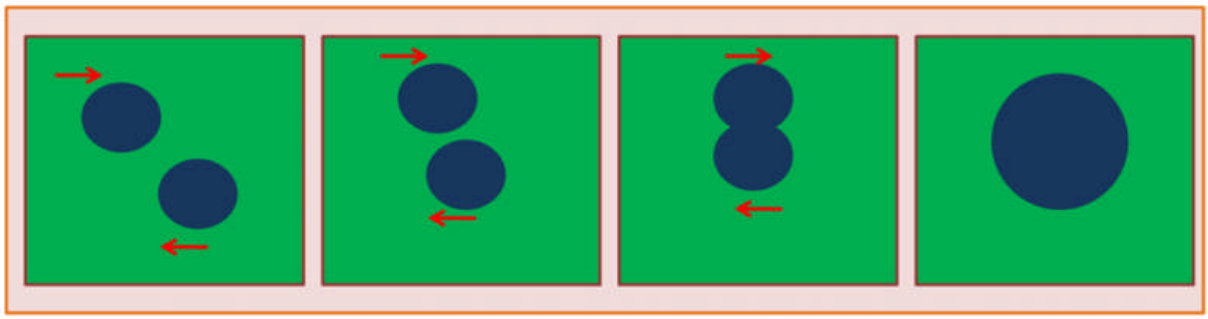

Figure II.1 Schematic representation of coalescence of nearby domains**.**

For example, **Figure. II.2** shows the size distribution of domains in PTT/PP blend system. The given graph shows the variation of number average and weight average domain diameter of PTT and PP domains as a function of PP composition. Domain diameter analyzed from the scanning electron microscopy (SEM) images of Cryo-fractured blend samples with the help of image J software. From the graph it is very clear that at lower composition of PP, PP dispersed as domains in PTT phase. With increased composition of PP, domain size of PP also increased due to the coalescence of domains. After 50/50 composition phase inversed with PTT domains.

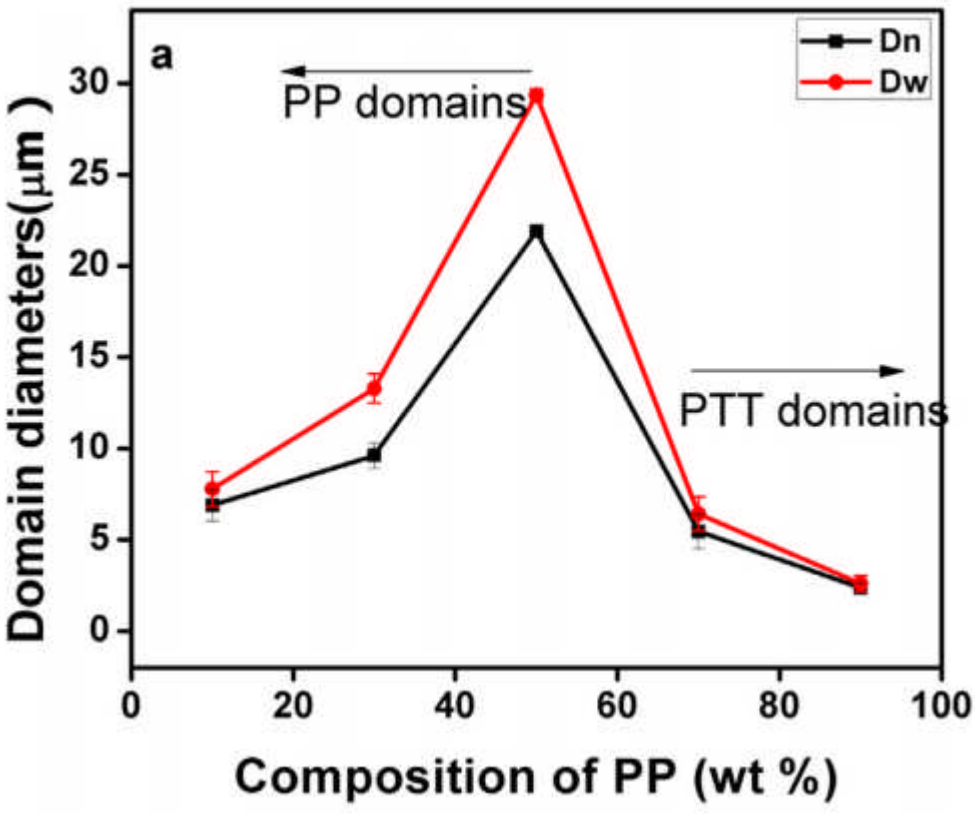

Figure II.2 Number average and weight average domain diameters of poly (trimethylene terephthalate)/polypropylene blends with various compositions of PP.

II.3 Factors affecting properties of polymer blends

Properties of polymer blends not exactly show the combined properties of individual polymer components. Overall performance and properties of polymer blends depend on several factors such as properties of the individual polymer components (which include its structure, state, and molecular weight), method of preparation, processing temperature and time, composition of polymer components, morphology and morphological parameters (size, shape, interfacial

area, uniformity, and distribution), and distance between adjacent dispersed particles and adhesion between polymer components**.[23,34,35-40].**

In the case of miscible polymer blends, its properties follow a mathematical expression as,

$$X=X_1\varphi Ø_1+X_2Ø_2+IØ_1Ø_2 \quad (2.2)$$

Where **X** is the property of interest, **Ø** is the concentration, and I is an interaction term. If **I** value is zero, the polymer blends may behave as mixtures, if **I** is negative, an anti-synergistic effect can be observed in the properties of polymer blend, and if **I** is positive synergistic effect can be observed in the overall properties of polymer blends.

The above equation is not practicable for immiscible polymer blends; its physical properties follow another semi-empirical rule and it can be expressed as,

$$P_2 = \frac{1 + AB\phi_2}{P_1 - B\psi\phi_2} \quad (2.3)$$

Where P1 represents the continuous phase, P2 represents the dispersed phase, Ø2 denotes the concentration of the dispersed phase, "A" the shape and orientation of the dispersed phase, "B" the relative values of the properties P1 ,P2, and A, and ψ represents packing fraction (concentration term) **[41].**

II.4 Preparation methods of polymer blends

Fabrication methods have great importance since they can affect the uniform mixing, morphology, and thereby final properties of the blends and composites. The methods of solution blending, melt blending, and in-situ polymerization are broadly applied to fabricate polymer blends and their composites. In addition, solid-state shear pulverization, freeze-drying, latex blending, and coagulation spinning methods also show promise **[42].**

II.4.1 Melt mixing/melt blending

Melt mixing is one of the main methods for the preparation of polymer blend in an economic and eco-friendly manner. In this method, the polymers are heated to form a melt, and mixing occurs under high shear forces. In the case of melt mixing, a large amount of mechanical energy can be supplied by the rotating screws for the uniform mixing of polymers.

Melt mixing of two or more different polymers leads to different morphologies depending on the rheological and thermodynamic properties of the components and on processing conditions. The morphology of the fabricated blends strongly influences the final properties of the system. The melt mixing can be carried out in batch or continuous operation using a melt mixer (e.g., Brabender mixer, Haake mixer) and extruder, respectively. The melt processing is considered as a feasible choice for the preparation of polymer blends toward large-scale synthesis for industrial applications **[42-45].**

II.4.2 Mill mixing

Mill mixing is a general method to prepare rubber-based polymer blends. Blending can be carried out in between two horizontally placed rotating hollow metal cylinders. The nip gap between the two rollers can be adjusted by varying the roller distances as per the compound consistency.

II.4.3 Solution mixing

In this method polymers are dissolved in common solvent, under vigorous stirring. The blend is finally recovered by solvent evaporation or by a nonsolvent. This method is only applicable to the polymers which are soluble in any solvents and is the main drawback of this technique. Also the solvent recovery is a problem for the wide use of this solution mixing **[42, 45].**

II.5 Characterization techniques: to study phase separation in blends

II.5.1 Morphological studies

From the morphological studies one can clearly get an idea regarding the type of morphology, phase separation, and degree of miscibility. The morphology of a developed polymer blend can be analyzed by various microscopic techniques such as transmission electron microscopy, SEM, atomic force microscopy, optical microscopy, fluorescence microscopy, con-focal microscopy, etc. For example **Figure.II.3** shows the morphology of PTT/PP (90/10) blends analyzed by SEM and optical microscopy. From the figure it is very clear that PTT/PP blend is immiscible and phase separated system. In the images the domains represent the PP phase and PTT is the continuous phase.

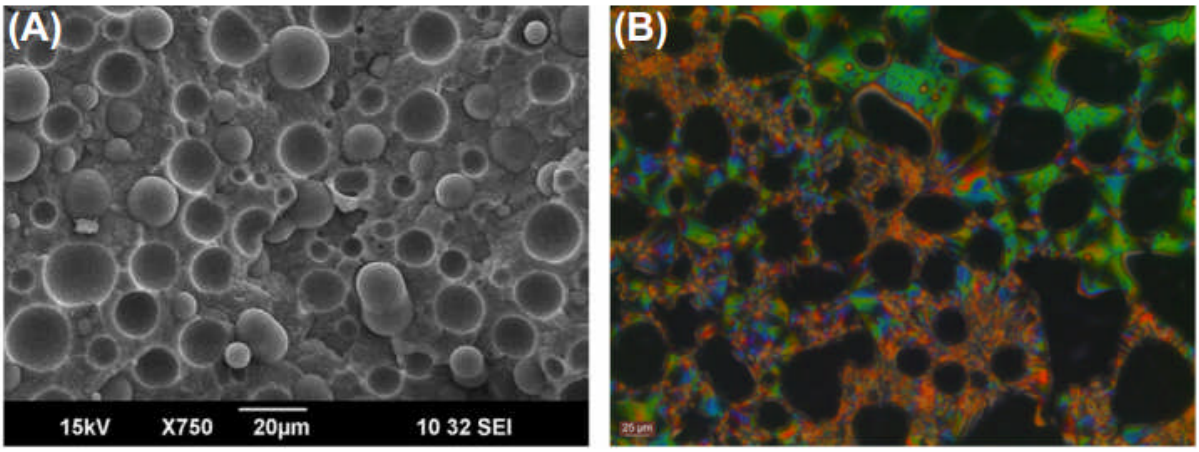

Figure II.3 (A) scanning electron microscopy image and (B) optical microscopy image of 90 poly (trimethylene terephthalate)/10 polypropylene blend.

II.5.2 Thermal properties

II.5.2.1 Analysis of glass transition temperature

Other important techniques used to check the phase separation and miscibility of blend system are DSC and DMA by the analysis of the Tg of the blend. As already discussed the analysis of Tg can be considered as a common way to evaluate the miscibility of blends. The single Tg of blend stands for a miscible blend and the possibility of two or more Tg sheds light on a phase separated blend system. The main experimental techniques generally used to measure Tg of components involve DSC and DMA.

Various characterization techniques used for polymer blend nanocomposites are given in Table **II.1**

Table II.1 Characterization techniques for polymer blends.

Characterization techniques used for polymer blends	Information
Scanning electron microscopy (SEM)	Surface roughness and morphology, particle size and distribution.
Transmission electron microscopy (TEM)	Morphology and microstructure, phase separation, structural heterogeneities.
Atomic force microscopy (AFM)	Phase separation, surface roughness, morphology and microstructure.
Infrared (IR) spectroscopy	Component identification and analysis of interfacial interactions.
Thermogravimetric analysis (TGA)	Thermal stability.

Characterization techniques used for polymer blends	Information
Differential scanning calorimetry (DSC)	Melting and crystallization behavior, local dynamics of polymer chains.
Rheometry	Flow properties, viscoelastic properties.
Mechanical test	Young's modulus, tensile strength, elongation at break, impact strength, hardness.
Dynamic mechanical analysis (DMA)	Viscoelastic properties.
Optical	Morphology, crystallization kinetics, spherulite growth rate study.
Neutron scattering	Miscibility, morphology.
Ultrasound	Composition of polymer blends, measuring extrusion flow instabilities, monitoring injection-molding processes, polymer chain modification, compatibilization of immiscible blends, dispersing nanoparticles in polymer melts, morphology.
Ellipsometry	Determination of interfacial thickness between two polymers, determination of glass transition temperature (thin films).
Light scattering	Phase separation studies, crystallization studies, cloud-point determination (to locate the phase boundary), evaluation of particle size.
X-ray scattering techniques	Structural characterization, crystallization studies (degree of crystallinity, size of crystals).
Secondary ion mass spectrometry (SIMS) techniques, time-of-flight secondary ion mass spectrometry (To FSIMS), and nano-scale secondary ion mass spectrometry (Nano SIMS)	Polymer surface characterization (focused especially on polymer blends and interfaces), molecular structural information (such as branching, saturation, functional groups, molecular weight distribution, segmental length, etc.).
Fluorescence microscopy	Structural analysis of polymer blend systems.
Solid-state nuclear magnetic resonance (NMR) spectroscopy	Microstructures, miscibility, intermolecular interactions of polymer blends.
Raman imaging	Phase morphology.
Electron paramagnetic resonance (EPR) spectroscopy and forward recoil spectrometry (FRES)	Surface and interfacial properties and processes of polymer blends (especially for polystyrene-based blends).
Dielectric relaxation spectroscopy (DRS)	Degree of miscibility of polymer blends, crystallization kinetics of amorphous/crystalline polymer blends.
Positron annihilation spectroscopy (PAS)	Free-volume distributions, miscibility.

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CHAPTER III

Compatibilization of Polymer Blends

III.1 General introduction

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

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

III.2 Strategies for compatibilization of polymer blends

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

Some of the general strategies involve the following:

➢Adding previously made grafted block copolymers.

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

➢ Addition of low-molecular-weight chemicals like peroxide activate inert polyolefins, resulting in the formation of branched copolymers, a functional chemical that forms block

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

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

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

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

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

III.3 Why do we need compatibilizers?

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

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

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

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

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

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

III.4 Theoretical aspects of compatibilisation

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

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

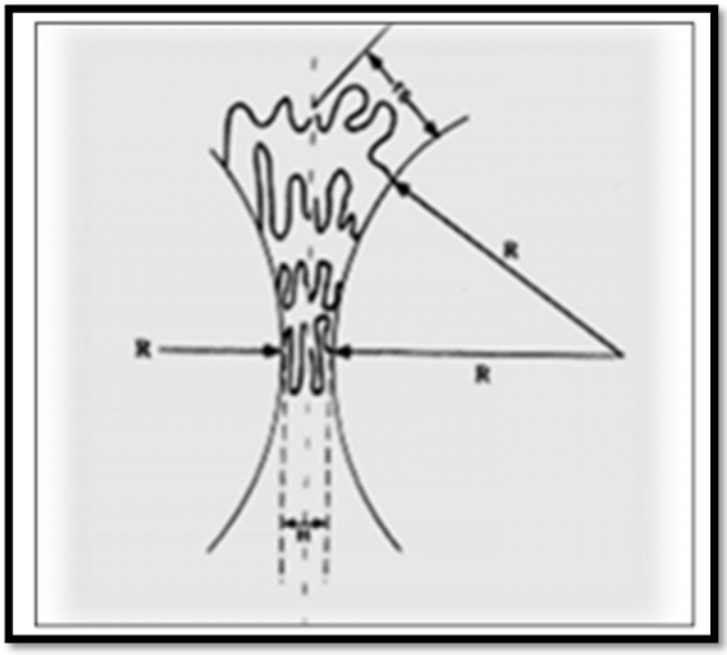

Figure III.1 Steric hinderence by compatibilizers. Compatibilizers acting as both anchors and repulsive springs ensuring the stability and prevention to coalescence **[16].**

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

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

So a booming compatibilizer will

➢Reduce interfacial tension between components,

➢Permit finer dispersion during mixing,

➢Provide a measure of stability against gross separation,

➢Produce ultimate product, and

➢Results in improved interfacial adhesion.

III.5 Blending with a compatibilizer, a third component

III.5.1 Compatibilizer immiscible in both blended polymers

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

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

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

III.5.2 Compatibilizer mutually miscible

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

III.5.3 Compatibilizer miscible with one of the blended polymers

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

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

III.6 Role of compatibilizers in blending processes

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

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

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

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

III.7 Properties of polymer blends influenced by compatibilization

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

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

III.8 New challenges in compatibilized blends

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

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

III.9 Application of compatibilized polymer blends in biomedical fields

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

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

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

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

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

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

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

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

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

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

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CHAPTER IV
Literature Review

IV.1 Literature Review

In this section, we will focus our study on the compatibility methods between EPDM and SAN. EPDM and SAN are two components which exhibited poor adhesion and interaction between the interfaces. This is attributed to the large differences in individual melt viscosity and molecular weight. This leads to inferior performance in mechanical properties. Therefore, compatibilization of the blend is necessary to enhance its useful properties. Addition of compatibilizers to polymer blends affects the flow behavior, Physical, Mechanical, Dynamic Mechanical, Morphological as well as Thermal properties because of the interactions which have been developed between the two polymer phases imparted by the different strategies of compatibilization.

For example**, O. Chiantore et al [1]** have studied the Compatibilization effects in the thermal degradation of blends containing SAN and EPDM polymers. Thermal degradation of blends containing **EPDM/SAN** was investigated by means of Thermogravimetric Analysis (TGA) and compared with that of graft EPDM-**g**-SAN copolymer molecules. Characterization of decomposition products and of degradation residues was carried out in order to reveal the differences in the degradation processes. With plain mixtures of SAN and EPDM, degradation behaviour is practically additive whereas in the case of EPDM-g-SAN lower volatile products and larger chain scissions are produced. The results can be explained by considering that the degradation process is influenced by the dispersion of the blend components. In phase segregated systems very few interactions take place between the different types of polymers, whereas in the graft copolymer molecular dispersion favors reactive interactions between the structurally different components.

In another study, **C. Pagnoulle, and R. Jerome [2]** have investigated the effect of the reactive compatibilization of EPDM/SAN Thermoplastic Elastomer blends. Poly (ethylene-co-propylene-co-diene) (EPDM) containing 50 wt% of poly(ethylene-co-propylene) grafted with maleic anhydride (EP-g-MA) has been melt blended with poly (styrene-co-acrylonitrile) (SAN) added with various amounts of reactive SAN, i.e. SAN bearing either primary amine (SAN-NH_2) or carbamate groups (SAN-carb). Carbamate groups are precursors of primary amines by thermal thermolysis during melt processing. These reactive systems are good models for studying the effect of the kinetics of the interfacial reaction on the phase morphology. Reaction of maleic anhydride with the primary amine is indeed very fast, at high

temperature, in contrast to the reaction with carbamate, which is controlled by the carbamate thermolyis into primary amine. Special attention has been paid to their experimental conditions required for the development of the particle-in-particle morphology for the dispersed phase. Depending on the mixing sequence and the grafting kinetics (NH_2/MA versus carb/MA), this particular phase morphology can be forced or occurs spontaneously. These observations emphasize the importance of the rate at which the interfacial reaction occurs with respect to the coalescence rate which governs phase inversion. The grafting rate affects not only the amount of the compatibilizer formed in situ but also its localization with direct consequence on the size and the morphology of the dispersed phase, i.e. composite morphology or not. It is essential to note that these kinetic effects can be modulated by changing the mixing sequence (or at least the order of addition) of blend components. The experimental data collected in their work indicate that the melting rate of the reactive polymers, mixed in one step, can have a strong effect on the development of the phase morphology and must be taken into account whenever the scaling up of the process is considered.

Reactive blending of the rubber EPDM (a terpolymer consisting of ethylene, propylene and a diene) and the thermoplastic material SAN (a copolymer of styrene and acrylonitrile) is reinvestigated by **Mario Vierle and coworkers [3]** with special attention to EPDM/SAN blends with a 50/50 blend ratio. A resin cure system based on a low molecular weight phenol formaldehyde condensate, which primarily consists of diméthylol-phenol and stannous dichloride, is used for compatibilization of EPDM and SAN, as well as for crosslinking of the EPDM phase. The amounts of phenolic resin and $SnCl_2$ $2H_2O$ as well as the EPDM grade and the EPDM/SAN blend ratio are varied. The blends are characterized by stress-strain measurements, transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Unreacted EPDM, unreacted SAN and gel plus graft copolymer are quantitatively determined by fractionation of the blends with a binary solvent mixture which exhibits phase separation at room temperature. Blends prepared from EPDM grades that are amorphous and have a high molar mass exhibit high levels of gel and rather poor mechanical properties. With these blends, gel formation is favored over the formation of EPDM/SAN graft copolymers. Even with low levels of the resin cure system, the formation of gel cannot be avoided. It is therefore not possible to prepare graft copolymers without some gelling. Blends prepared from an EPDM grade with high crystallinity and a low Mooney viscosity exhibit substantially better mechanical property than blends based on amorphous and higher viscosity EPDM

grades. TEM and SEM micrographs reveal good dispersion of the two polymers, as well as good interfacial adhesion between the EPDM and the SAN phase. This electron microscopic evidence, in combination with low gel contents, supports the view that the tendency towards graft copolymer formation and gelling strongly depends on the EPDM grade used. Variation of the EPDM/SAN blend ratio between 5–90 wt.-% results in blends which cover the product range from toughened thermoplastics to thermoplastic elastomers. These results indicated to improvement in the morphological and mechanical properties of the compatibilized EPDM/SAN system compared to those of the uncompatibilized ones. This could be attributed to increase of the interfacial adhesion and reduce the interfacial tension between the two polymer phases imparted be the reactive compatibilization.

Xiongwei Qu et al [4] have studied the Effect of the Addition of Acrylonitrile/Ethylene–Propylene–Diene Monomer (EPDM)/Styrene Graft Copolymer on the Morphology–Properties Relationships in Poly(styrene-co-acrylonitrile)/EPDM Rubber Blends. Blends of poly(styrene-co-acylonitrile) (SAN) with ethylene–propylene– diene monomer (EPDM) rubber were investigated. An improved toughness–stiffness balance of the SAN/EPDM blend was obtained when an appropriate amount of acrylonitrile–EPDM–styrene (AES) graft copolymer was added, prepared by grafting EPDM with styrene–acrylonitrile copolymer, and mixed thoroughly with both of the two components of the blend. Morphological observations indicated a finer dispersion of the EPDM particles in the SAN/EPDM/AES blends, and particle size distribution became narrower with increasing amounts of AES. Meanwhile, it was found that the SAN/EPDM blend having a ratio of 82.5/17.5 by weight was more effective in increasing the impact strength than that of the 90/10 blend. From dynamic mechanic analysis of the blends, the glass-transition temperature of the EPDM-rich phase increased from53.9 to46.2°C, even32.0°C, for the ratio of 82.5/17.5 blend of SAN/EPDM, whereas that of the SAN rich phase decreased from 109.2 to 108.6 and 107.5°C with the additions of 6 and 10% AES copolymer contents, respectively. It was confirmed that AES graft copolymer is an efficient compatibilizer for SAN/EPDM blend. The compatibilizer plays an important role in connecting two phases and improving the stress transfer in the blends. Certain morphological features such as thin filament connecting and even networking of the dispersed rubber phase may contribute to the overall ductility of the high impact strength of the studied blends. Moreover, its potential to induce a brittle– ductile transition of the glassy SAN matrix is considered to explain the toughening mechanism.

Mona Taheri et al [5] have studied the Reactive Compatibilization of SAN/EPDM Blend and Study of the Parameters Affecting its Properties. Most polymer blends are immiscible and need to be compatibilized. Compatibilization can be accomplished either by addition of a compatibilizer or by reactive processing. Grafting has been the most common method for compatibilizing two immiscible polymers during reactive processing. In this work, the reactive blending of EPDM (ethylene-propylene-diene monomer) rubber and SAN (styrene-acrylonitrile) copolymer was studied. The blends were prepared in an internal mixer with three types of organic peroxides as initiator. The effects of initiator type and concentration, EPDM content, and mixing sequences of components were investigated. Blends were separated to their structural components (i.e., SAN, EDPEM, SAN-g-EPDM, and gelled EPDM) which were then characterized by FTIR spectroscopy and SEM microscopy techniques. Mechanical properties including tensile and impact strength as well as elongation-at break were measured. From the three initiators used, the blends which have 2,5-dimethyl-2,5-di-(t-butyl peroxy) hexane as initiator show better mechanical properties. Also, SEM studies reveal a good compatibility for SAN/EPDM blends using this initiator. The blend using 40 wt% of EPDM of the mentioned initiator contains 16.24 wt% SAN-g-EPDM. Impact strength of the blends was affected by mixing sequences of the components. The Blends prepared by mixing sequences of SAN/initiator/EPDM show the highest impact strength of the order of 45 J/m.

A. Pticvek et al [6] have studied the Morphology and thermal behaviour of SAN/EPDM blends. Blends of styrene-acrylonitrile (SAN) with ethylene-propylene-diene (EPDM) with and without high impact polystyrene (HIPS) as a compatibilizer were studied. One series of blends was prepared in composition 95/5, 90/10, 85/15, 80/20 and 60/40; and the second series of blends was prepared with the addition of 5 wt% of HIPS. Their morphology and thermal behaviour were inspected by scanning electronic microscopy (SEM) and dynamic mechanic analysis (DMA), respectively. Further on, blends were separated to their components by Soxhlet extraction in selective solvent and characterized by Fourier Transform Infrared Spectroscopy (FTIR) and gel permeation chromatography (GPC), respectively. The results of morphological observations revealed that the addition of a small percentage of compatibilizer decreases the domain size of the dispersed phase and the compatibility of the blends was enhanced. The shifts of values of glass temperatures (Tg) in the examined blends also indicate that with addition of compatibilizer HIPS miscibility between SAN and EPDM is improved.

L. J. Kratofil et al [7] have reported the Compatibilization Effects in SAN/EPDM Blends Prepared by Reactive Extrusion. Styrene-acrylonitrile copolymer (SAN) and ethylene-propylenediene terpolymer (EPDM) are known as immiscible polymers but their blends are interesting for application because of good stability in use. The blending of SAN and EPDM by reactive extrusion under various conditions is studied. SAN/EPDM blends are investigated to obtain improved SAN/EPDM miscibility and to determine the effect of rubber (EPDM) on the polymer morphology and mechanical properties. The first series of samples is prepared with different ratios of SAN and EPDM, the second series with addition of high impact polystyrene (HIPS) as a compatibilizer, and the third series with free radical initiators a,a-di(t-butylperoxy)diisopropyl-benzene (Peroximon F40) and 2,2-azo-di-(2-acetoxy) propane (Luazo AP). The blends are characterized by determination of mechanical properties. Then the blends are separated on its components: SAN, EPDM, graft (EPDM-g-SAN), and gel to elucidate the extrusion process. The identification of extracted polymers has been made by IR spectrophotometry. Scanning electron microscopy (SEM) is used to observe the morphology. The dominant grafting reaction, which improves compatibility, is observed in blends prepared with HIPS compatibilizer and with Peroximon F40 initiator.

Mona Taheri et al [8] have studied the Compatibilization and Properties of SAN/EPDM Blends with the Addition of Coagent. SAN and EPDM are not miscible. In this work, the dry blending of SAN and EPDM using Centrex (acrylonitrile/EPDM/styrene graft copolymer) and

EPMMA (EPDM-g-Mah) as coagents was studied. Centrex content was used at 6–20 wt %. EPMMA content in the mixture was 20 wt %. The effects of coagent type and content on the mechanical properties and morphology were investigated. SEM micrographs of SAN/EPDM/Centrex and SAN/EPDM/EPMMA blends showed that both Centrex and EPMMA have an effective role in forming a finer morphology. For the ternary blends, the addition of coagent resulted in a significant reduction in the size of the dispersed phase. The mechanical properties of SAN/EPDM/coagent blends were improved significantly in comparison to the simple SAN/EPDM blends. SAN/ EPDM/Centrex blends showed higher stress-at-break and SAN/EPDM/EPMMA blends showed higher impact strength.

A.Pticˇek et al [9] have investigated the Effect of Compatibilizer on Morphology and Mechanical Properties of SAN/EPDM Blends. Miscibility of styrene-acrylonitrile (SAN) and ethylene-propylene-diene (EPDM) blends containing high impact polystyrene (HIPS) as a compatibilizer were studied. Blends were characterized by determination of mechanical

properties, glass transition temperatures and their morphology was inspected by scanning electronic microscopy. Blends were separated into components to clarify the effects of the extrusion process and the obtained components were characterized by FTIR spectroscopy and by gel permeation chromatography. It was observed that significant fraction of in situ formed graft copolymer is formed during extrusion, which contributes to the homogeneity of the studied systems. The results show finer morphology and size reduction of the dispersed phase due to enhanced interface adhesion in compatibilized blends, with enhanced mechanical properties.

Mona Taheri et al [10] have studied the Phase Morphology and Thermomechanical Analysis of Poly(styrene-co-acrylonitrile)/Ethylene–Propylene–Diene Monomer Blends: Uncompatibilized and Reactively Compatibilized Blends with Two Mixing Sequences. The phase morphology developing in immiscible poly(styrene-co-acrylonitrile) (SAN)/ethylene–propylene–diene monomer (EPDM) blends was studied with an in situ reactively generated SAN-g-EPDM compatibilizer through the introduction of a suitably chosen polymer additive (maleic anhydride) and 2,5-dimethyl-2,5-di-(tbutyl peroxy) hexane (Luperox) and dicumyl peroxide as initiators during melt blending. Special attention was paid to the experimental conditions required for changing the droplet morphology for the dispersed phase. Two different mixing sequences (simple and two-step) were used. The product of two-step blending was a major phase surrounded by rubber particles; these rubber particles contained the occluded matrix phase. Depending on the mixing sequence, this particular phase morphology could be forced or could occur spontaneously. The composition was stabilized by the formation of the SAN-g-EPDM copolymer between the elastomer and addition polymer, which was characterized with Fourier transform infrared. As for the two initiators, the blends with Luperox showed better mechanical properties. Scanning electron microscopy studies revealed good compatibility for the SAN/EPDM blends produced by two-step blending with this initiator. Dynamic mechanical thermal analysis studies showed that the two-step-prepared blend with Luperox had the best compatibility.

M. Taheri et al [11] have reported the Effect of compatibilizer on interfacial tension of SAN/ EPDM blend as measured via relaxation spectrums calculated from Palierne and Choi–Schowalter models. Morphology, interfacial tension, and stress relaxation spectra of immiscible SAN/EPDM blend and its compatibilized blend with SAN-g-EPDM (Centrex) was studied. The results showed that the morphology of the blend had a quick response to added Centrex. In the compatibilized blend with 20-wt% compatibilizer (optimized blend)

having a droplet-in-matrix type of morphology, the particle sizes were reduced by a factor of 4. The power-law index of EPDM and SAN obtained 0.33 and 0.53, respectively. With increasing of compatibilizer the power-law index decreased. It meant that at the same amount of EPDM its influence in the blend was increased. Also the cross-over point of G' and G" curves in the melt of optimized blend decreased which was attributed to increased elasticity. These observations were in good correspondence with the morphological observations. In optimized blend, the number average diameter of EPDM dispersed particles had the lowest value of about 1.8 lm. The interfacial tension of the compatibilized SAN/ EPDM blend was determined from the morphological studies and the relaxation time was calculated using the Palierne and Choi-Schowalter models. The optimized blend showed the least interfacial tension about 0.306 (N/m) which was in agreement with the morphological observations.

Anita Ptiček Siročić et al [12] have studied the Evaluation of compatibility in SAN/EPDM blends by determination of the adhesion parameters. A series of various types (different structures) of ethylene-polypropylene-diene-graft-polystyrene (EPDM-g-PS) copolymers were synthesized and their surface property variations were studied using surface analysis techniques such as surface contact angle measurement. Pre-synthesized graft copolymers were added (5 phr) in styrene-acrylonitrile (SAN)/ethylene-propylene-diene (EPDM) blends composition of 95/5 and 90/10. The adhesion parameters at the interface, that is work of adhesion, the interfacial energy and the coefficient of wetting were calculated and correlated to the differential scanning measurements and SEM micrographs in order to study the effect of graft copolymers on compatibility of SAN/EPDM blends. It is obvious that depending of the graft copolymer's structure, various interactions between the components in the blend will be established, resulting in better adhesion which implicates improvement of compatibility in blends. Also, from the results, it can be seen that differences in structures of the added compatibilizer are clearly reflected in the adhesion parameters results, making this an acceptable method to determine whether two polymers are compatible. Morphology of the blends with the graft copolymers is significantly finer and the dispersed size is more uniformly distributed in comparison to the neat SAN/EPDM blend. The conditions of the optimal adhesion parameters with compatibilizer location at the interface, predicting by the thermodynamically models, correlated well with the improvement of the morphology and thermal measurements.

Anita Ptiček Siročić et al [13] have investigated the surface energy as an indicator of miscibility of SAN/EDPM polymer blends. Surface properties of blends prepared of styrene-

acrylonitrile and ethylene-propylene-diene changing the homopolymer proportions and compatibilized by high impact polystyrene have been studied by contact angle measurement. The surface free energy of interphase of homopolymers pairs, work of adhesion, and wetting coefficient were calculated using Wu's geometric mean method and the total surface free energy and acid–base components of the blends by using van Oss, Good and Chaudhury method. Blends were also characterized by dynamic mechanical analysis and by scanning electron microscopy. The miscibility of studied blends was estimated through changes of surface free energy, energy of interface and through the shifts of glass transition temperature and changes in morphology. From the results, it can be seen that added compatibilizer reduces the interface energy and provides more homogenous system by interfacial segregation and rearrangements of molecules at the blend surface. The results of morphological observations reveal that the addition of a small percentage of compatibilizer decreases the domain size of the dispersed phase and enhances the compatibility of the blends.

Weitao Liu et al [14] have reported the Synthesis of EPDM-g-MAN by suspension graft copolymerization and its toughening effect on SAN resin. Suspension graft copolymerization of methyl methacrylate and acrylonitrile onto ethylene–propylene–diene terpolymer (EPDM) was carried out under different reaction conditions. A series of graft products of EPDM-graft-methyl methacrylate and acrylonitrile (EPDM-g-MAN), characterized by Fourier-transform infrared spectroscopy, was blended separately with styrene–acrylonitrile (SAN) resin to investigate their toughening effect on SAN matrix. The relationship between the polarity of EPDM-g-MAN and toughness of EPDM-g-MAN/SAN resin blends (AEMS) was evaluated. The compatibility and morphologies of AEMS were probed by dynamic mechanical analysis, transmission electron microscopy, and scanning electron microscopy to determine the toughing mechanism of the blends. Thermogravimetry results showed that the thermal stability of AEMS was enhanced with the incorporation of EPDM-g-MAN graft copolymer.

Mona Taheri et al [15] have studied the Effect of chlorinated polyethylene on dynamic mechanical and thermal properties of SAN/EPDM blends in dependence of mixing conditions. The effect of chlorinated polyethylene (CPE) on the compatibilization and thermal properties of styrene-acrylonitrile copolymers (SAN)/Ethylele-Propylene-Diene-polyMethylene rubber (EPDM) blends (80/20) was investigated. Two different mixing procedures were employed, that is, single- and two-step blending. In the single-step process, EPDM was melting blended with CPE and SAN simultaneously, which led to droplet

morphology. In the two-step process, first, a masterbatch of EPDM and CPE in SAN was prepared, and then mixed with further amounts of SAN and CPE in order to reach the same fixed blend ratio of 80/20 for SAN/EPDM. The morphology changed from EPDM droplets for the one-step mixing to co-continuous for the two-step blending process. This morphological change was reflected in a change of the complex modulus. The characteristics of thermogravimetric analysis (TGA) curves (T1%, T5%, T30%, and T50%) were examined, as indicators for improved thermal stability of the blends. The intermolecular interaction characterized by the Kwei equation showed higher values for the blends prepared by the two-step mixing procedure. The dynamic mechanical analysis supported the occurrence of chain scission in the SAN phase at the beginning of aging and cross-linking of SAN at higher temperatures and longer times as a result of cyclization of CN groups in SAN.

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Conclusion

Conclusion

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

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

Most polymer blends are immiscible and need to be compatibilized. The compatibilization must accomplish: (i) optimization of the interfacial tension; (ii) stabilize the morphology against high stresses during forming; and (iii) enhance adhesion between the phases in the solid-state. Compatibilization is accomplished either by the addition of a compatibilizer or by reactive processing. This review will focus on the two aspects: thermodynamics principles of polymer blends, and their strategies for compatibilization.

Keywords: Polymer blends, Immiscible polymers, Interfacial tension, Compatibilization.

Résumé

La plupart des mélanges de polymères sont immiscibles et ont besoin d'être rendus compatibles. La mise en compatibilité doit permettre : (i) l'optimisation de la tension interfaciale ; (ii) la stabilisation de la morphologie contre les fortes contraintes lors de la formation ; et (iii) l'amélioration de l'adhésion entre les phases dans l'état solide. Cette « compatibilisation » s'effectue soit par ajout d'un agent de compatibilisation ou par un processus réactif. Cette revue portera sur les deux aspects : les principes thermodynamiques et les stratégies de compatibilisation des mélanges de polymères.

Mots clés: Mélanges de polymères, Polymères non miscibles, Tension interfaciale, Compatibilisation.

ملخص

معظم خلائط البوليمر غير قابلة للامتزاج وتحتاج إلى التوافق. يجب أن يحقق التوافق ما يلي: (1) تحسين التوتر السطحي ؛ (2) تثبيت التشكل ضد الضغوط العالية أثناء التشكيل ؛ (3) و تعزيز الالتصاق بين مراحل الحالة الصلبة. يتم تحقيق التوافق إما عن طريق إضافة جهاز التوافق أو عن طريق المعالجة التفاعلية. ستركز هذه المراجعة على جانبين: مبادئ الديناميكا الحرارية لمزيج البوليمر ، وكذلك استراتيجيات التوفيق بين خلائط البوليمرات المختلفة.

الكلمات المفتاحية:
مزيج البوليمر ، البوليمرات غير القابلة للامتزاج ، التوتر البيني ، التوافق.