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Compatibilization of Acrylonitrile Butadiene Styrene and Polycarbonate (ABS/PC) Thermoplastic Polymer Blends: Effect of Compatibilizers on the Rheological, Mechanical, Morphological, and Thermal properties.

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Dedications

We would like to dedicate our Master-thesis:

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

-To all our brothers and sisters;

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

-To all our best friends;

- To anyone who has ever taught us anything.

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

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List of Notations and Abbreviations

Abbreviations	**Description**
ASTM	American Society for Testing and Materials
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared
AFM	Atomic force microscopy
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

A polymer blend is a mixture of two or more polymers that have been blended together to create a new material with different physical properties. Generally, there are five main types of polymer blend: thermoplastic–thermoplastic blends; thermoplastic–rubber blends; thermoplastic–thermosetting blends; rubber–thermosetting blends; and polymer–filler blends, all of which have been extensively studied. Polymer blending has attracted much attention as an easy and cost-effective method of developing polymeric materials that have versatility for commercial applications. In other words, the properties of the blends can be manipulated according to their end use by correct selection of the component polymers **[1].** Today, the market pressure is so high that producers of plastics need to provide better and more economic materials with superior combinations of properties as a replacement for the traditional metals and polymers. Although, plastic raw materials are more costly than metals in terms of weight, they are more economical in terms of the product cost. Moreover, polymers are corrosion-resistant, possess a light weight with good toughness (which is important for good fuel economy in automobiles and aerospace applications), and are used for creating a wide range of goods that include household plastic products, automotive interior and exterior components, biomedical devices, and aerospace applications **[2].**

The development and commercialization of new polymer usually requires many years and is also extremely costly. However, by employing a polymer blending process–which is also very cheap to operate – it is often possible to reduce the time to commercialization to perhaps two to three years **[2].** As part of the replacement of traditional polymers, the production of polymer blends represents half of all plastics produced in 2010. Today, the polymer industry is becoming increasingly sophisticated, with ultra-high-performance injection molding machines and extruders available that allow phase-separations and viscosity changes to be effectively detected or manipulated during the processing stages **[3].** Whilst this modern blending technology can also greatly extend the performance capabilities of polymer blends, increasing market pressure now determines that, for specific applications, polymer blends must perform under some specific conditions (e.g., mechanical, chemical, thermal, electrical). This presents a major challenge as the materials must often function at the limit of the properties that can be achieved; consequently, in-depth studies of the properties and performance of polymer blends are essential.

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

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

A novel approach to the modification of interfaces in incompatible blends which has been recently receiving much attention is reactive compatibilization, in which compatibilizers are formed in-situ at the interfaces. Homopolymer blend components which have reactive groups incorporated along the chains are utilized. Functional pendant or end groups are inherent to many types of polymers and may be added to others though relatively cost efficient processes such as small-molecule grafting, conversion of existing moieties or copolymerization. The functional groups come in contact during mixing of the two polymers and react, forming bonds between the homopolymers at the interfaces. Recent studies have concentrated on the control of blend morphology which may be achieved through this type of reactive compatibilization scheme. It has been demonstrated that the dispersion of the minor polymer blend component decreases in average size with increasing concentration of functional groups, and that a homogenous material may be achieved at sufficiently high functional group concentrations.

Polycarbonate (PC) is an amorphous, transparent, engineering thermoplastic material. It is known for its good dimensional stability and impact strength. The other properties include optical clarity, heat deflection temperature, electrical properties and flame retardancy. The main drawbacks are its high notch sensitivity and difficulty in processibility. Acrylonitrile butadiene styrene (ABS) is copolymers of three monomers namely, acrylonitrile, butadiene and styrene. ABS is stiff, flexible and tough material and exhibits very good resistance to chemicals. At elevated temperatures it shows high dimensional stability, good stress crack resistance and excellent surface quality.

The draw backs include lack of transparency, poor weathering and flame retardancy. Polycarbonate /acrylonitrile butadiene styrene (PC/ABS) is the fastest growing PC alloy today in which ABS allows to balance the high impact strength, surface finish and high flow for better processing. The thermodynamic affinity of PC and styrene acrylonitrile (SAN) copolymer matrix of the ABS is good enough to lead to adequate adhesion for the required mechanical strength. However, due to incomplete miscibility between PC and SAN, the blend often experiences significant changes in its phase morphology during compounding and injection moulding, which results in phase coalescence and deterioration of mechanical properties. This large difference in solubility parameter (12.7 %) indicates immiscible nature of PC and ABS. In view of this, PC/ABS blends are generally classified under immiscible blends. Interestingly several researches have reported that ABS can be well dispersed in PC without the aid of compatibilizers and that co-continuous structure in PC/ABS blends is usual **[4, 5].** The PC behaves in a relatively Newtonian manner, but ABS exhibits significant shear thinning **[6].** The ABS rich blends show a trend that is similar to that of ABS, while PC-rich blends, exhibit a nearly Newtonian behaviour. Reactive compatibilization between PC and maleic anhydride grafted ABS (ABS-g-MAH) has been found to be beneficial in making the blend more ductile as compared to unmodified PC/ABS blend **[7-8].** Small quantity of ABS-g-MAH in PC/ABS blend is found to have very good influence on the notched Izod impact strength without compromising other mechanical properties **[9].** Tjong and Meng reported that ABS-g-MAH improves compatibility between ABS and PC and solid epoxy resin (bisphenol type-A) have been reported to be effective compatibilizers for the PC/ABS blends containing ABS content up to 30 wt% **[10].** Jin et al **[11]** has reported the enhancement of compatibility of PC/ABS in ABS rich compositions using polymethyl methacrylate (PMMA) as compatibilizer. The improved adhesion of the ABS/PC interface by PMMA changes the fracture mechanism and reduces the notch sensitivity of blend. The compatibilization of PC/ABS using a novel secondary amine functional SAN polymer (SAN-amine) has been reported by Wildes et al **[12].**

This Master-Thesis is composed of four chapters. The first chapter presents a theoretical background of Polycarbonate and Acrylonitrile butadiene styrene, their properties and their applications in industrial fields, the second chapter presents a theoretical background on thermodynamics principles of polymer blends, and the third chapter presents the strategies for compatibilization of polymer blends. The fourth chapter presents a brief presentation of some of the works that have been published and which covered different aspects of the subject.

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

References

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

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

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

[4] G. Wildes, H. Keskkula and D.R. Paul, Polymer, 40, 7089-7107, **1999**.

[5] J.P.F. Inberg and R.J. Gaymans, Polymer, 43, 2425-2434 ,**2001**.

[6] M.M.K. Khan, R.F. Liang, R.K. Gupta and S.Agarwal, Korea-Australia Rheology Journal, 17(1), 1-7 ,**2001**.

[7] S.Bala Krishnan and N.R. Neelakantan, Journal of Materials Science, 34, 1581-5185, **1999**.

[8] S.Balakrishnan, N.R.Neelakantan, S.N.Jaisankar, Journal of Applied Polymer Science, 74, 2102-2110, **1999**

[9] X. Zhang, Y. Chen, Y. Zhang, Z. Peng, Yinxi Zhang, Wen, Journal of Applied Polymer Science, 81, 831-836 ,**2001**.

[10] S.C. Tjong and Y.Z. Meng, European Polymer Journal, 36, 123-129, **2000**.

[11] D.W.Jin, K.H.Shon, H.M.Jeong, B.K.Kim, Journal of Applied Polymer Science, 69, 533-542,**1998**

[12] G.S. Wildes, T. Harada, H.Keskkula, D.R. Paul, Janarthanan and A.R. Padwa, Polymer, 40(11), 3069-3082, **1999**.

Chapter I

Theoretical Background

I.1 Introduction

Plastic substances are usually plated in order to bring about merits of the metals to the polymer substrate **[1–6].** resistance, electrical conductivity, and a variety of decorative lusters, high wear and corrosion resistances, electromagnetic shielding, weight reduction, formability enhancements, high impact resistance and weatherproofing, lower cost, flexibility in parts design, and reduced weight compared to its metal counterparts **[7–17].** Metallized plastics become useful in electronic industry, petroleum industry, national defense field, toys manufacturing industry, automotive and computer body parts, electronic housings, wheel covers, lamp housings, ventilation, air conditioning parts, pipes and fittings, and many more things **[18–31].**

I.2 Acrylonitrile Butadiene Styrene

I.2.1 History of ABS

The ABS is the third member of a family of high impact composite materials based on a thermoplastic matrix and a particulate rubber phase, being preceded by high impact polystyrene (HIPS) and PVC/nitrile rubber blends. The best of these materials have an excellent balance of properties~, due in part to their two phase nature, and may be considered as engineering plastics. The most significant advantage gained by the incorporation of the rubber is the transformation of a brittle organic gloss into a ductile thermoplastic with high impact strength. ABS stands for Acrylonitrile Butadiene Styrene **[32]**

ABS is an impact-resistant engineering thermoplastic & amorphous polymer. ABS is made up of three monomers: acrylonitrile, butadiene and styrene **(Figure I.1)**:

- **Acrylonitrile:** It is a synthetic monomer produced from propylene and ammonia. This component contributes to ABS chemical resistance & heat stability
- **Butadiene:** It is produced as a by-product of ethylene production from steam crackers. This component delivers toughness & impact strength to ABS polymer
- **Styrene:** It is manufactured by dehydrogenation of ethyl benzene. It provides rigidity & processability to ABS plastic

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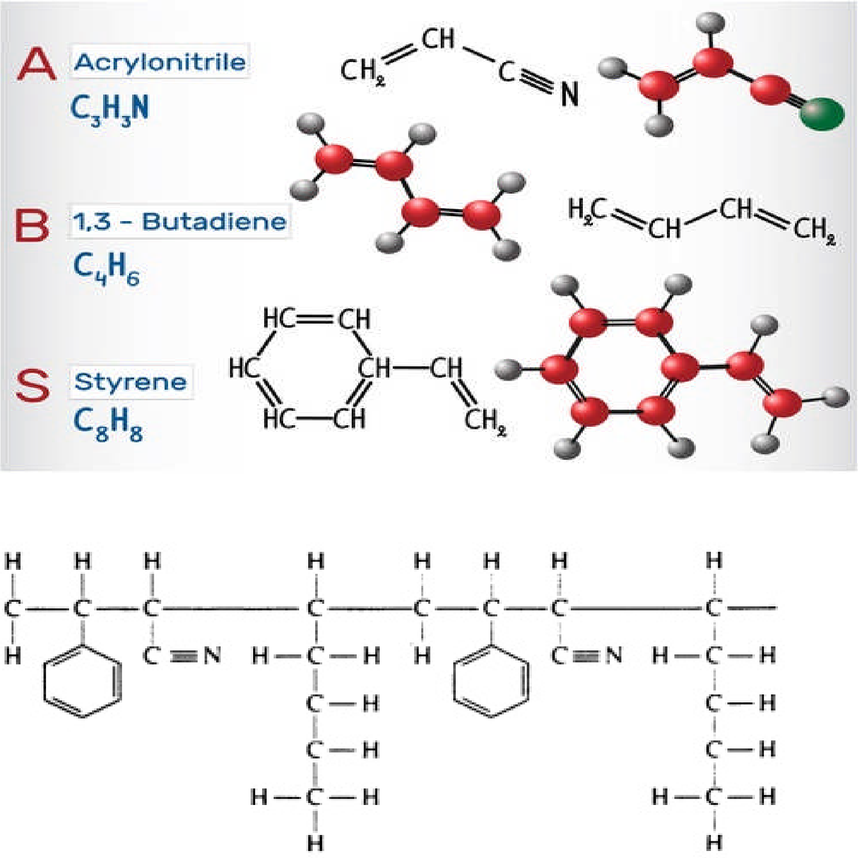

Figure I.1 Chemical Structure of Acrylonitrile Butadiene Styrene

The chemical formula of Acrylonitrile Butadiene Styrene is $(C_8H_8{\cdot}C_4H_6{\cdot}C_3H_3N)_n$. The natural material is an opaque ivory color and is readily colored with pigments or dyes.

I.2.2 Properties of ABS

ABS is a strong and durable polymer. It is a chemically resistant resin. It gets easily attacked by polar solvents. It offers greater impact properties and slightly higher heat distortion temperature than HIPS. Acrylonitrile Butadiene Styrene has a broad processing window. It can be processed on most standard machinery. It can be injection-molded, blow-molded, or extruded. It has a low melting temperature making it suitable for processing by 3D printing on an FDM machine. ABS falls between standard resins (PVC, polyethylene, polystyrene, etc.) and engineering resins (acrylic, nylon acetal, etc.). It often meets the property requirements at a reasonable price-cost effectiveness. It is an ideal material of choice for various structural applications. This is because of its several physical properties such as:

- High rigidity, good weldability, and insulating properties
- Good impact resistance, even at low temperatures

- Good abrasion and strain resistance
- High dimensional stability (Mechanically strong and stable over time)
- High surface brightness and excellent surface aspect

ABS shows excellent mechanical properties. It is hard and tough in nature and thus delivers good impact strength. It offers a high degree of surface quality. Apart from these characteristics, Acrylonitrile Butadiene Styrene exhibits good electrical insulating properties**.[33]**

I.2.3 Major Advantages of ABS

One of the biggest advantages of ABS is its high impact resistance. It is commonly used in the automotive industry for car bumpers and other exterior parts that require durability and toughness. ABS is also used in toys, luggage, and electronic housings because it can withstand rough handling without cracking or breaking.

Another advantage of ABS is its ability to be easily molded and machined. It can be injection molded into complex shapes and designs, making it ideal for manufacturing products with intricate details. ABS is also easy to paint and can be finished to achieve a glossy or matte appearance.

I.2.4 Drawbacks of ABS

Despite its many advantages, ABS also has some drawbacks. One of the main drawbacks is its poor weathering resistance. Over time, exposure to sunlight and UV radiation can cause the material to degrade and become brittle. This can lead to cracking and discoloration, which can affect the appearance and performance of the product.

Another drawback of ABS is its low heat resistance. While it can withstand temperatures up to 80°C, it begins to deform and lose its mechanical properties at higher temperatures. This limits its use in high-temperature applications where other materials like polycarbonate or nylon may be more suitable**. [34]**

I.2.5 Manufacturing processes of ABS plastic

Polymerization all manufacturing processes for ABS involve the polymerization of styrene and acrylonitrile monomers in the presence of an elastomer (typically polybutadiene or a butadiene copolymer) to produce SAN that has been chemically bonded or “grafted” to the rubber component termed the “substrate.”

Rubber Chemistry: The rubber substrate is typically produced by the free-radical polymerization of butadiene. The radical source can be provided by either thermal decomposition or oxidation–reduction (redox) systems. The primary product is primarily 1,4-polybutadiene with some 1,2-polybutadiene, which contains a pendent vinyl group. Cross-linking of polymer occurs at high conversion through abstraction of reactive allylic sites or by copolymerization through double bonds (especially the double bonds in the more sterically accessibly pendent vinyl groups). Rubber cross-linking is controlled by the use of chain-transfer agents and the concentration and type of the intiator used; the reaction can also be affected by chain transfer to emulsifiers **[35]**. For emulsion ABS, the rubber is typically both produced and subsequently used for grafting as latex.

Graft Chemistry: Grafting of styrene and acrylonitrile onto a rubber substrate is the essence of the ABS process. Grafting is a free-radical process initiated by the abstraction of allylic hydrogens on the rubber substrate or by copolymerization through double bonds that are pendent or internal in the rubber substrate, as illustrated in **Figure I.2 [36]**. Initiator level and type affects the extent of grafting **[36–42]** with oxyradicals yielding a higher degree of grafting than carbon radicals because of higher rates of abstraction from the rubber substrate. Chain-transfer agents are also used in controlling overall degree of grafting and graft molecular weight.

Ungrafted SAN: is formed concurrently with grafted SAN, with the ratio controlled by factors that include temperature, chain-transfer agent, and pendent vinyl content of rubber, initiator level, and initiator type **[36–44]**. As previously described, occlusions of SAN can also form within the rubber particles with the mass process leading to significantly higher occlusion levels than the emulsion process **[45,46].** In the mass process block copolymers of styrene and butadiene can be added to obtain unusual particle morphologies (eg, coil….) **[45]**.

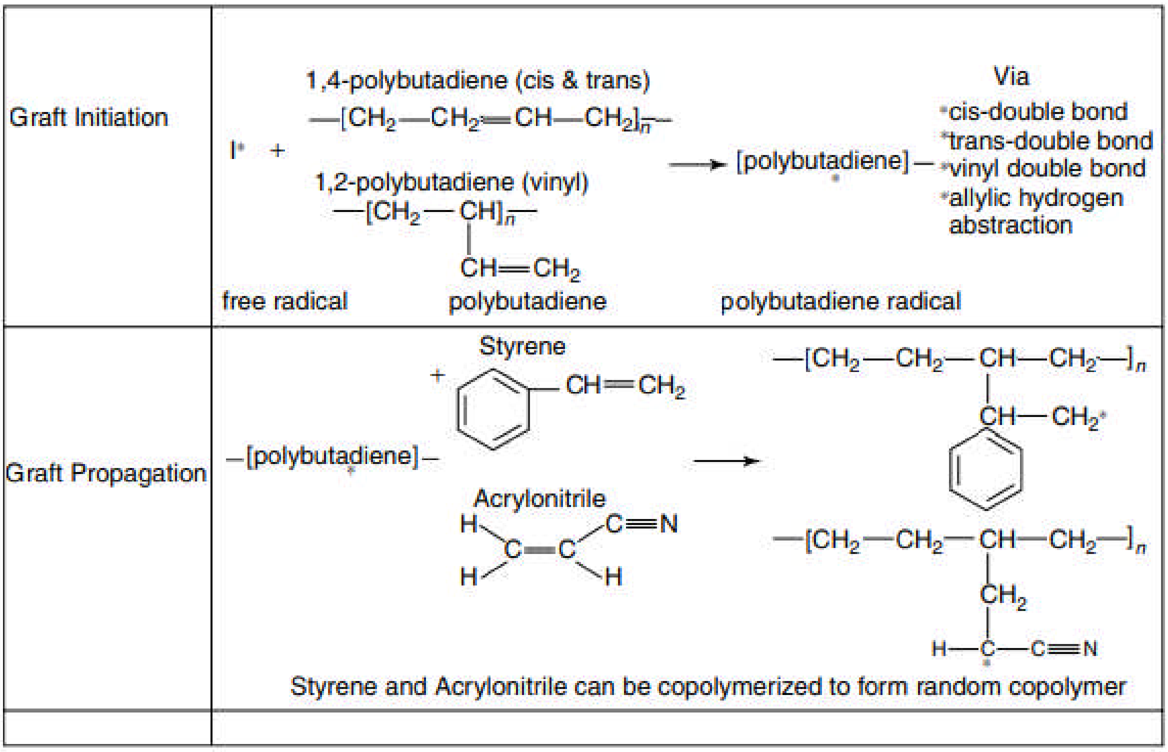

Figure I.2. Mechanisms of graft SAN formation.

Emulsion Process: The emulsion process for making ABS has been commercially practiced since the early 1950s. Its advantage is the capability of producing ABS with a wide range of compositions, particularly higher rubber contents than are possible with other processes. Mixing and transfer of the heat of reaction in an emulsion polymerization is achieved more easily than in the mass polymerization process because of the low viscosity and good thermal properties of the water phase. The energy requirements for the emulsion process are generally higher because of the energy usage in the polymer recovery area. The emulsion polymerization process is typically a two-stage reaction process **[47,52]**, as illustrated in **Figure I.3**.

In the first stage, a rubber substrate, primarily composed of polybutadiene, is made using an emulsion polymerization process. The desired particle size of the rubber is either obtained by direct growth during polymerization or by an agglomeration process subsequent to polymerization. In a second-stage reaction, styrene and acrylonitrile are grafted onto the rubber substrate by emulsion polymerization. After the graft reaction is complete, the polymer can be recovered from the graft latex and compounded into a final pellet product **[47–52].**

Rubber Substrate Process: The rubber substrate can be made by a variety of different reaction processes including batch, semi-batch, and continuous **[53].** Butadiene monomer is primarily used in the substrate reaction, but comonomers such as styrene and acrylonitrile are common **[50, 51].** The amount and type of comonomer employed will affect the glass transition of the rubber substrate and, thereby, influence the impact properties of the ABS polymer. Oxidation–reduction systems (eg, hydrogen peroxide and iron) or thermal initiators (eg, potassium persulfate or azobisisobutyronitrile) are used to initiate polymerization. Cross-link density is controlled by type and level of initiator, type and level of chain-transfer agent, reaction temperature, degree of conversion, or by the addition of comonomers. It is important to note that the graft process also can affect the cross-link density of the rubber. Various surfactant types can be employed to emulsify the monomer and stabilize the latex particles. Standard fatty acid soaps and derivatives are the most common emulsifiers employed; however, detergents such as sodium dobenzyl sulfonate and sodium lauryl sulfate can also be used. The use of non-ionic surfactants has been reported **[54].** The "soap-free" emulsion polymerization of butadiene is possible using reactive surfactants **[55],** functional monomers such as acrylic acid **[56],** or high levels of potassium persulfate **[57].**

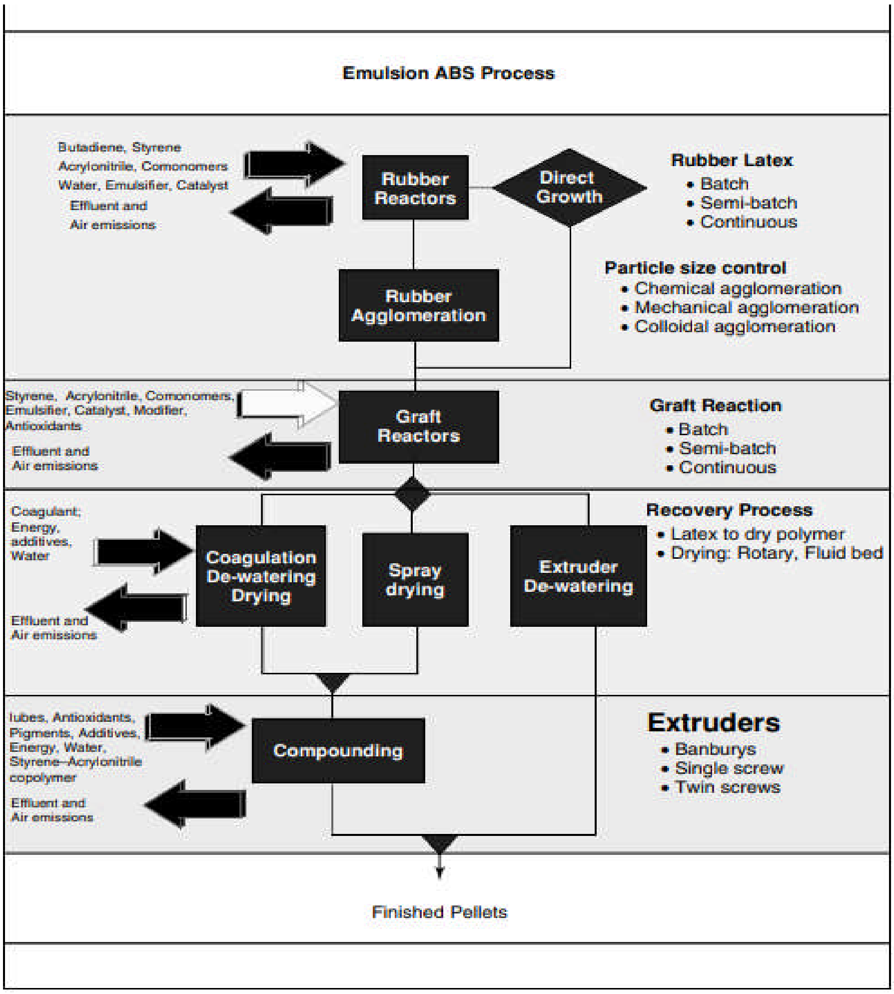

Figure I.3. Emulsion ABS process.

The incorporation of surfactants into the polymer backbone provides the advantage of minimizing low molecular by-products in the final polymer that could result in mold buildup or juicing. The incorporation of comonomers into the rubber substrate can be useful in achieving specialized performance of the final ABS polymer, such as adjusting the refractive index of the rubber phase to better match the continuous SAN phase to achieve a clear or more translucent ABS product **[58].** The incorporation of polymerizable antioxidants or uv stabilizers has also been reported **[59].** Typically, these modifications increase the cost of ABS and are only employed for specialized applications.

Reactor productivity can be affected by various factors including initiator type, latex particle size, monomer purity, chain-transfer agents, and reaction temperature **[53].** As previously described, rubber particle size and distribution are important factors controlling the final properties of the ABS polymer. Large particles can be obtained by direct growth in the reactor, but much longer reaction times are needed. Comonomers such as AN can be added to speed the reaction rate and achieve relatively large particles in less time **[60, 61].** Productivity can also be improved by the use of antifouling agents to minimize buildup of polymer on reactor heat-transfer surfaces **[62–64].** These antifouling agents improve heat transfer and minimize the time the reactor is down for cleaning

Graft Process: Grafted SAN is critical to achieving effective dispersion of the rubber in the matrix phase, with key factors being SAN composition and rubber particle surface coverage. The composition of the grafted SAN depends on the monomer-feed composition and the monomer reactivity ratio. The composition of the polymer formed will equal the feed at the azeotropic composition, which occurs at ∼3/1 mass ratio of styrene-to-acrylonitrile **[47,54],** and compositional drift will occur at monomer feed compositions other than the azeotropic concentration. Note that in aqueous systems, the difference in water phase solubility of acrylonitrile vs styrene can also perturb monomer concentrations at the reaction site and, thus, affect compositional drift. Polymerization techniques such as continuous vs batch processes and controlling pump rates can be used to control compositional drift **[65–71].** Surface coverage is controlled by rubber particle surface area and is effected by factors including initiator type, monomer feed to rubber level, and chain-transfer agents.

Resin Recovery Process Typically, the polymer is recovered by the addition of coagulants which destabilize the ABS latex. Different coagulants are used depending on the surfactant. Thus, strong and weak acids work well with fatty acid soaps, and metal salts are used with acid stable soaps **[72].** The use of nonionic coagulants has also been reported **[73,74].** Acrylic latices have been used to control the coagulation process and obtain a narrow resin particle-size distribution **[75].**

Once coagulated, the resulting slurry can then be filtered or centrifuged to recover wet ABS resin, which is then dried to a low moisture content. A variety of dryers can be used for ABS, including tray, fluid bed, and rotary kiln-type dryers. Other methods of recovery have been employed such as spray drying **[78]** and extruder dewatering **[79].** Spray drying allows for good control of the final particle size of the resin, but uses a significant amount of energy in the drying process. In extruder dewatering, the latex is either directly fed into the extruder or is first coagulated and then fed into the extruder. Extruder dewatering allows for more efficient stripping and recovery of unreacted monomer than standard drying processes.

Air and Water Treatment: The emulsion process exerts a greater demand on wastewater treatment than other processes (suspension or mass) because of the quantity of water used, and air emissions may be higher because of the types of process equipment employed. Recent federal and state EPA regulations governing air emission from ABS facilities affect the level of styrene, acrylonitrile, butadiene, and other volatile organic compounds that can be emitted into the air or sent to wastewater treatment facilities. In some cases, effluent water can be recycled and reused, but ultimately the water must be discharged, requiring treatment of the water prior to discharge. Air emissions from an emulsion ABS process can be reduced by improving the conversion of the monomers **[80],** the installation of equipment to strip and recover monomers, or the installation of end-of-pipe controls. End-of-pipe controls such as regenerative catalytic oxidation, regenerative thermal oxidation, fixed and fluid bed carbon absorption, and biofiltration are viable means of addressing air emission issues **[81].**

Mass Polymerization Process: In the mass **[82–90]** ABS process, the polymerization is conducted in a monomer medium rather than in water, usually employing a series of two or more continuous reactors. The rubber used in this process is most commonly a solution polymerized linear polybutadiene (or copolymer containing sytrene), although some mass processes utilize emulsion-polymerized ABS with a high rubber content for the rubber component **[91].** If a linear rubber is used, a solution of the rubber in the monomers is prepared for feeding to the reactor system. If emulsion ABS is used as the source of rubber, a dispersion of the ABS in the monomers is usually prepared after the water has been removed from the ABS latex.

In the mass process **[92]** using linear rubber, the rubber initially dissolved in the monomer mixture will phase separate, forming discrete rubber particles as SAN polymerization procedes. This process is referred to as phase inversion since the continuous phase shifts from rubber to SAN during the course of polymerization. Special reactor designs are used to control the phase inversion portion of the reaction **[83,85–89].** By controlling the shear rate in the reactor, the rubber particle size can be modified to optimize properties. Grafting of some of the SAN onto the rubber particles occurs as in the emulsion process. Typically, the mass-produced rubber particles are larger than those of emulsion-based ABS and contain much larger internal occlusions of SAN. The reaction recipe can include polymerization initiators, chain-transfer agents, and other additives. Diluents are sometimes used to reduce the viscosity of the monomer and polymer mixture to facilitate processing at high conversion. The product from the reactor system is devolatilized to remove the unreacted monomers and is then pelletized. Equipment used for devolatilization includes single- and twin-screw extruders and flash and thin film/strand evaporators. Unreacted monomers are recovered and recycled back to the reactors to improve the process yield.

The mass ABS process was originally adapted from the mass polystyrene process **[93].** Mass produced ABS typically has very good unpigmented color and is usually somewhat more translucent because of the large rubber phase particle size and low rubber content. Increased translucency can reduce the concentration of colorants required. The extent of rubber incorporation is limited to approximately 20% because of viscosity limitations in the process; however, the massproduced grafted rubber can be more efficient (on an equal percent rubber basis) at impact modification than emulsion-grafted rubber because of the presence of high occlusion levels in the rubber phase. The surface gloss of the mass-produced ABS is generally lower than that of emulsion ABS because of the presence of the larger rubber particles, but recent advances provide additional flexibility to achieve higher gloss **[83–86].**

Suspension Process: The suspension process utilizes a mass **[94]** or emulsion reaction **[95,96]** to produce a partially converted mixture of polymer and monomer and then employs a batch suspension process **[97]** to complete the polymerization. When the conversion of the monomers is approximately 15–30% complete, the mixture of polymer and unreacted monomers is suspended in water with the introduction of a suspending agent. The reaction is continued until a high degree of monomer conversion is attained and then unreacted monomers are stripped from the product before the slurry is centrifuged and dried, producing product in the form of small beads. The morphology and properties of the mass suspension product are similar to those of the mass-polymerized product. The suspension process retains some of the process advantages of the water-based emulsion process, such as lower viscosity in the reactor and good heat removal capability.

Compounding: ABS either is sold as an unpigmented product, in which case the customer may add pigments during the forming process, or it is colored by the manufacturer prior to sale. Much of the ABS produced by the mass process is sold unpigmented; however, precolored resins provide advantages in color consistency. If colorants, lubricants, fire retardants, glass fibers, stabilizers, or alloying resins are added to the product, a compounding operation is required. ABS can be compounded on a range of equipment, including batch and continuous melt mixers, and both single- and twin-screw extruders. The device must provide sufficient dispersive and distributive mixing dependent on formulation ingredients for successful compounding, and low work or low shear counterrotating twin-screw extruders as used in PVC are not recommended. In the compounding step, more than one type of ABS may be employed (ie, emulsion and mass-produced) to obtain an optimum balance of properties for a specific application. Products can also be made in the compounding process by combining emulsion ABS having a high rubber content with mass- or suspension-polymerized SAN.

Analysis: Analytical investigations may be undertaken to identify the presence of an ABS polymer, characterize the polymer, or identify nonpolymeric ingredients. Fourier transform infrared (ftir) spectroscopy is the method of choice to identify the presence of an ABS polymer and determine the ABS ratio of the composite polymer **[98,99].** Confirmation of the presence of rubber domains is achieved by electron microscopy. Comparison with available physical property data serves to increase confidence in the identification or indicate the presence of unexpected structural features. Identification of ABS by pyrolysis gas chromatography **[100]** and dsc **[101]** has also been reported. Detailed compositional and molecular weight analyses involve determining the percentage of grafted rubber; determining the molecular weight and distribution of the grafted SAN and the ungrafted SAN; and determining compositional data on the grafted rubber, the grafted SAN, and the ungrafted SAN. This information is provided by a combination of phase-separation and instrumental techniques. Separation of the ungrafted SAN from the graft rubber is accomplished by ultracentrifugation of ABS dispersions **[102,103],** which causes sedimentation of the grafted rubber. Cleavage of the grafted SAN from the elastomer is achieved using oxidizing agents such as ozone [10028-15-6] **[103,104],** potassium permanganate [7722-64-7] **[105],** or osmium tetroxide [20816-12-0] with tert-butyl-hydroperoxide **[106].** Chromatographic and spectroscopic analyses of the isolated fractions provide structural data on the grafted and ungrafted SAN components **[107].** Information on the microstructure of the rubber is provided by analysis of the cleavage products derived from the substrate **[103,105].** The extraction of ungrafted rubber has also been reported **[108].** Additional information on elastomer and SAN microstructure is provided by 13C NMR analysis **[109].** Rubber particle composition may be inferred from glass-transition data provided by thermal or mechano-chemical analysis. Rubber particle morphology as obtained by transmission or scanning electron microscopy **[110]** is indicative of the ABS manufacturing process.

The isolation and/or identification of nonpolymeric has been described, including analyses for residual monomers **[99,111,112]** and additives **[99,113– 115].** The determination of localized concentrations of additives within the phases of ABS has been reported; the partitioning of various additives between the elastomeric and thermoplastic phases of ABS has been shown to correlate with solubility parameter values **[116].**

I.2.6 Applications of ABS

Acrylonitrile butadiene styrene (ABS) is a thermoplastic polymer that is commonly used in various applications due to its desirable properties, such as high impact resistance, toughness, and durability. Some of the applications of ABS include:

1. Automotive Industry: ABS is widely used in the automotive industry to manufacture components such as bumper fascia, instrument panels, and interior trim. Its high impact resistance and toughness make it ideal for use in these applications.

2. Electronics Industry: ABS is also used in the electronics industry to manufacture components such as computer keyboard keys, printer housings, and telephone casings. Its high dimensional stability and ability to withstand heat make it ideal for use in these applications.

3. Toy Industry: ABS is a popular material for manufacturing toys due to its impact resistance and durability. It is commonly used to make toys such as building blocks, action figures, and puzzle pieces.

4. Construction Industry: ABS is used in the construction industry to manufacture various components such as drain pipes, gutters, and roofing tiles. Its resistance to chemicals and weather makes it ideal for use in these applications.

5. Medical Industry: ABS is also used in the medical industry to manufacture components such as medical device housings and laboratory equipment. Its ability to withstand heat and chemicals makes it ideal for use in these applications. **[117].**

I.3 Polycarbonate PC

Polycarbonate is a typical thermoplastic polymer whose molecular chains are associated with intermolecular attractive forces (Ward and Hadley 1993). These forces weaken rapidly when the temperature increases, which causes the solid polycarbonate to turn into a viscous liquid. Thus, polycarbonate can be reshaped by heating it and it is typically used to produce products through various processing techniques such as injection molding, compression molding, calendaring and extrusion **[118]**

I.3.1 Chemical structure of PC

Polycarbonate is a thermoplastic polymer that is composed of repeating units of bisphenol A and carbonate groups. The chemical formula of polycarbonate is $(C_{16}H_{14}O_3)n$, where n represents the number of repeating units in the polymer chain **[119]. Figure I.4**

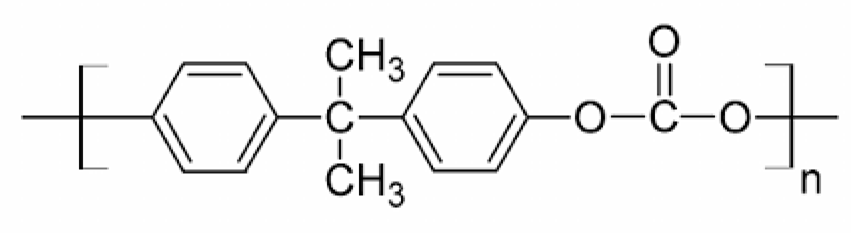

Figure I.4 Molecular structure of Polycarbonate

I.3.2 Properties of Polycarbonate

Polycarbonate is a versatile thermoplastic polymer that possesses several unique properties, including:

1. High impact resistance: Polycarbonate is known for its exceptional impact resistance, making it suitable for use in applications that require protection against impacts, such as safety glasses, helmets, and automotive components.

2. Transparency: Polycarbonate has excellent optical clarity and transparency, making it a popular choice for applications such as windows, skylights, and lenses.
3. High heat resistance: Polycarbonate can withstand high temperatures without melting or degrading, making it suitable for use in high-temperature applications such as electrical components and automotive parts.
4. Chemical resistance: Polycarbonate is resistant to many chemicals, including acids, alkalis, and hydrocarbons, making it suitable for use in harsh environments.
5. Electrical insulation: Polycarbonate has good electrical insulation properties, making it suitable for use in electrical and electronic components.
6. Lightweight: Polycarbonate is lightweight compared to many other materials with similar properties, making it suitable for applications where weight is a concern.
7. Easy to process: Polycarbonate is easy to mold and process, making it a popular choice for manufacturers.
8. UV resistance: Polycarbonate can be formulated to have excellent UV resistance, making it suitable for outdoor applications **[120].**

I.3.3 Advantages of Polycarbonate

Polycarbonate has many advantages such as:

1. High impact resistance: Polycarbonate is highly impact-resistant, making it ideal for use in applications that require protection against impacts and high stress.
2. Optical clarity: Polycarbonate has excellent optical clarity and transparency, making it ideal for use in applications that require clear visibility.
3. High heat resistance: Polycarbonate can withstand high temperatures without melting or degrading, making it suitable for use in high-temperature applications.
4. Chemical resistance: Polycarbonate is resistant to many chemicals, making it suitable for use in harsh environments.
5. Lightweight: Polycarbonate is lighter than many other materials with similar properties, making it ideal for applications where weight is a concern.

6. Easy to process: Polycarbonate is easy to mold and process, making it a popular choice for manufacturers.

7. UV resistance: Polycarbonate can be formulated to have excellent UV resistance, making it suitable for outdoor applications.

I.3.4 Drawbacks of Polycarbonate

Polycarbonate has many drawbacks such as:

1. Scratch-prone: Polycarbonate is softer than glass, which makes it prone to scratches, especially if used in applications that involve contact with other materials.

2. Low scratch-resistance: Polycarbonate is not as scratch-resistant as some other materials, which can affect its long-term durability.

3. Poor weathering performance: Polycarbonate can degrade over time when exposed to sunlight, leading to yellowing and loss of mechanical properties.

4. High cost: Polycarbonate can be more expensive than some other materials, especially when compared to standard plastics.

5. Limited solvent resistance: Polycarbonate is not highly resistant to certain solvents, which can affect its suitability for some applications **[121].**

I.3.5 Processing of Polycarbonate

Is usually obtained in granular form as a raw material, as shown in **Figure I.5**. According to the shape of the final product, polycarbonate granules are first heated to a temperature higher than the melting point. The melted polycarbonate is then extruded or pressured into a mold to give the desired shape.**[122]**

Figure I.5. Polycarbonate granules

Extrusion: melted polycarbonate is passed through a mold to produce the final shape. Then, the melt is cooled rapidly. Long pipes and sheets are usually produced by this process.

Injection molding: melted polycarbonate is pressed into a mold with the predefined shape of the final product. The melt is then cooled inside the mold. This process is ideal for products with complex geometry. (**Figure I.6)**

Due to the capability of manufacturing products with complex geometries, injection molding has been the most commonly used processing method for polycarbonate. Figure I.5 shows a schematic of a typical injection molding machine. Granular raw material is fed through a hopper into a heated barrel with a reciprocating screw that delivers the raw material forward, and mixes and homogenizes the thermal and viscous distributions of polycarbonate. When enough materials are gathered, they are forced at a high pressure and velocity into the mold cavity. Once the screw reaches the transfer position, the packing pressure is applied on the mold to complete mold filling and to compensate for thermal shrinkage. The injection pressure is applied at the cavity entrance until the solidification is complete. The material within the mold is cooled by temperature-controlled water or oil circulating in cooling lines. Once the required mold temperature or the holding time is achieved, the mold is opened and the product is obtained **[122].**

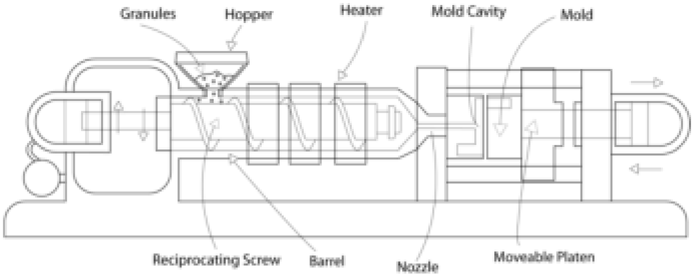

Figure I.6. Schematic of a typical injection molding machine

I.3.6 Applications of polycarbonate

Polycarbonate is a versatile material with a wide range of applications due to its unique properties. Some Common applications of polycarbonate include:

1. Safety glasses and goggles: Polycarbonate is used to make safety glasses and goggles due to its high impact resistance and optical clarity.
2. Electrical and electronic components: Polycarbonate is used to make electrical and electronic components due to its good electrical insulation properties.

3. Automotive components: Polycarbonate is used in automotive components such as headlight lenses, instrument panels, and exterior trim due to its high impact resistance and heat resistance.

4. Greenhouses: Polycarbonate is used to make greenhouse panels due to its high light transmission and resistance to impact and weathering.

5. Signage and displays: Polycarbonate is used to make signage and displays due to its high optical clarity and resistance to impact.

6. Medical devices: Polycarbonate is used in medical devices such as blood oxygenators and incubators due to its biocompatibility and sterilizability.

7. Roofing and skylights: Polycarbonate is used in roofing and skylights due to its high impact resistance and transparency.

8. DVDs and CDs: Polycarbonate is used to make DVDs and CDs due to its optical clarity and scratch resistance.

9. Sports equipment: Polycarbonate is used to make sports equipment such as helmets and visors due to its high impact resistance and lightweight.

Overall, polycarbonate is a versatile material that finds its use in a wide range of applications due to its unique properties **[123].**

References

[1] Wang W, Ji S, Lee I (2013) A facile method of nickel electroless deposition on various neutral hydrophobic polymer surfaces. Appl Surf Sci 283:309–320. doi:10.1016/j.apsusc.2013.06.108

[2] Tran V, Massardier V, Guyot A, Nguyen T (1993) Interactions in metal-polymer-metal interfaces. Polymer 34(15):3179–3183

[3] Grundmeier G, Stratmann M (2005) Adhesion and de-adhesion mechanisms at polymer/metal interfaces: mechanistic understanding based on in situ studies of buried interfaces. Annu Rev Mater Res 35:571–615

[4] Holubar P, Jilek M, Sima M (2000) Present and possible future Applications of superhard nanocomposite coatings. Surf Coat Technol 133:145–151

[5] Long DP, Blackburn JM, Watkins JJ (2000) Chemical fluid deposition: a hybrid technique for low-temperature metallization. Adv Mater 12(12):913–915

[6] Cheng K, Yang MH, Chiu WW, Huang CY, Chang J, Ying TF, Yang Y (2005) Ink-jet printing, self-assembled polyelectrolytes, and electroless plating: low cost fabrication of circuits on a flexible substrate at room temperature. Macromol Rapid Comm 26(4):247–264

[7] Garcia A (2011) Ligand induced electroless plating of polymers. PhD Dissertation, E ´ cole Polytech

[8] Arai S, Sato T, Endo M (2011) Fabrication of various electroless Ni–P alloy/multiwalled carbon nanotube composite films on an acrylonitrile butadiene styrene resin. Surf Coat Technol 205(10):3175–3181

[9] Tengsuwan S, Ohshima M (2014) Environmentally benign electroless nickel plating using supercritical carbon-dioxide on hydrophilically modified acrylonitrile–butadiene–styrene. Appl Surf Sci 311:189–200

[10] Dechasit P, Trakarnpruk W (2011) Ni electroless plating of ABS polymer by palladium and tin-free process. J Met Mater Min 21(2):19–27

[11] Wang Z, Li Z, He Y, Wang Z (2011) Study of an environmentally friendly surface etching system of ABS for improving adhesion of electroless Cu film. J Electrochem Soc 158(11):D664–D670

[12] Kim GG, Kang JA, Kim JH, K-y Lee, Kim SJ, Kim S-J (2007) Photocatalytic pretreatment of acrylonitrile–butadiene–styrene polymer for electroless plating. Scripta Mater 56(5):349–351

[13] Di L, Liu B, Song J, Shan D, Yang D-A (2011) Effect of chemical etching on the Cu/Ni metallization of poly (ether ether ketone)/carbon fiber composites. Appl Surf Sci 257(9):4272–4277

[14] Ferreira ODS, Stevens A, Schrauwen C (2009) Quantitative comparison of adhesion in metal-to-plastic systems. Thin Solid Films 517(10):3070–3074

[15] Ma Z, Tan K, Kang E (2000) Electroless plating of palladium and copper on polyaniline films. Synth Met 114(1):17–25

[16] Kulkarni MV, Elangovan K, Hemachandra RK (2013) Effects of electroplating on the mechanical properties of injection molded thermoplastics. Int J Plast Technol. doi:10.1007/s12588-013-9056-6

[17] Vander Togt RT (2011) Bumper and process to bond ionomers to plastic. US Patent 4, 999,227

[18] Teixeira LAC, Santini MC (2005) Surface conditioning of ABS for metallization without the use of chromium baths. J Mater Process Technol 170(1):37–41

[19] Shu Z, Wang X (2012) Environment-friendly Pd free surface activation technics for ABS surface. Appl Surf Sci 258(14):5328–5331

[20] Bazzaoui M, Martins J, Bazzaoui E, Albourine A (2012) Environmentally friendly process for nickel electroplating of ABS. Appl Surf Sci 258(20):7968–7975

[21] Tang X, Cao M, Bi C, Yan L, Zhang B (2008) Research on a new surface activation process for electroless plating on ABS plastic. Mater Lett 62(6):1089–1091

[22] Skelly J (2008) Decorative plating processes for common plastic resins: resin selection as well as plastic part design is critical to matching the right finishing method with the intended application. Met Finish 106(6):61–65

[23] Haba B, Sugai K, Morishige Y, Kishida S (1994) Large scale two-step selective aluminum CVD on laser patterned palladium lines. Appl Surf Sci 79:381–384

[24] Chen Y, Reisman A, Turlik I, Temple D (1995) Cu CVD from copper (II) hexafluoroacetylacetonate II. Laser-assisted selective area deposition. J Electrochem Soc 142(11):3911–3918

[25] Seebo ¨ck R, Esrom H, Charbonnier M, Romand M, Kogelschatz U (2001) Surface modification of polyimide using dielectric barrier discharge treatment. Surf Coat Technol 142:455–459

[26] To ´th Z, Szo ¨re ´nyi T, Toth A (1993) Ar? laser-induced forward transfer (LIFT): a novel method for micrometer-size surface patterning. Appl Surf Sci 69(1):317–320

[27] McCaskie JE, Tsiamis C (1985) Metal plating on plastics. US Patent 4,520,046

[28] Yang C-Y (2012) Method for preparing electronic component mounting device. US Patent App.

[29] Hooke R (2014) Method of making shaped charges and explosively formed projectiles. US Patent 8,813,651

[30] Hoyt R, Wrobel J, Cushing J, Jaster M, Voronka N, Frank S, Slostad J, Paritsky L (2014) Structures with internal microstructures to provide multifunctional capabilities. US Patent 14/462,541

[31] Nath J, Shen Y, Nealis E (2014) Systems and methods for manufacturing passive waveguide components. US Patent App. 14/453,563

[32] Chen Y, Reisman A, Turlik I, Temple D (1995) Cu CVD from copper (II) hexafluoroacetylacetonate II. Laser-assisted selective area deposition. J Electrochem Soc 142(11):3911–3918

[33] Teixeira LAC, Santini MC (2005) Surface conditioning of ABS for metallization without the use of chromium baths. J Mater Process Technol 170(1):37–41

[34] Advantages and drawbacks of ABS , with the following link line : https://chat.openai.com/c/cfddc090-d1eb-4a88-b7a9-45ca3e7835ee

[35] B. D. Gesner (1969), SPE J. 25, 73.

[36] R. A. Hayes and S. Futamura, J. Polym (1981) . Sci., Polym. Chem. Ed. 19, 985.

[37] A. Brydon, G. M. Burnett, and C. G. Cameron, J. Polym (1974) . Sci., Polym. Chem. Ed. 12, 1011 .

[38] P. W. Allen, G. Ayrey, and C. G. Moore (1959) , *J. Polym. Sci.* 36, 55.

[39] J. L. Locatelli and G. Riess(1973) , Angew. Makromol. Chem. 32, 117.

[40] N. J. Huang and D. C. Sundberg (1995), J. Polym. Sci., Polym. Chem. Ed. 33, 2551.

[41] L. V. Zamoiskaya and co-workers (1998), Vysokomol. Soedin. Ser. A 40, 557.

[42] C. S. Chern and G. W. Pehlein (1990), J. Polym. Sci., Polym. Chem. Ed. 28, 3073.

[43] G. Reiss and J. L. Locatelli, in Ref. 18, p. 186.

[44] B. Chauvel and J. C. Daniel, in Ref. 18, p. 159.

[45] A. Echte, in Ref. 48, p. 15.

[46] E. Beati, M. Pegoraro, and E. Pedemonte (1987), Angew. Makrom. Chem. 149, 55.

[47] G. Odian 1970, *Principles of Polymerization*, McGraw-Hill, Inc., New York, , Chapt. “4”.

[48] P. J. Flory 1953, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N.Y., pp. 203–217.

[49] A. M. Aerdts, S. J. Theelen, and T. M. Smith, *Polymer* **35**, 1648 (1994).

[50] R. Kuhn and co-workers (1993), *Colloid Polym. Sci.* **271**, 133.

[51] Jpn. Pat. 09286827 (Nov. 4, 1997), Y. Ii and Y. Nakai (to Mitsubishi Rayon Co.).

[52] Jpn. Pat. 01259015 (Oct. 16, 1989), J. Sugiura and co-workers (to Mitsubishi Monsanto

Chemical Co.).

[53] U.S. Pat. 2,820,773 (Jan. 21, 1958), C. W. Childers and C. F. Fisk (to United States Rubber Co.).

[54] U.S. Pat. 19970630 (1997), V. Lowry (to General Electric Co.).

[55] E. S. Daniels and co-workers (1990), J. Appl. Polym. Sci. 41, 2463.

[55] Jpn. Pat. 09296015 (Nov. 18, 1997), H. Kitayama, Y. Ishikawa, and M. Nomura (to Kao Corp.).

[56] H. S. Chung and co-workers (1993), *Komu Hakhoechi* **28**, 267.

[57] H. S. Chung and Y. J. Shin (1993), *Kongop Hwahak* **4**, 284.

[58] Eur. Pat. 712894 (Apr. 2, 1997), V. J. Kuruganti, S. K. Gaggar, and R. A. St Jean (to General Electric Co.).

[59] Eur. Pat. 479725 (Apr. 26, 1995), B. Gilg and co-workers (to Ciba Geigy).

[60] Jpn. Pat. 05017506 (Jan. 26, 1993), A. Shichizawa and S. Ozawa (to Asahi Chemical Ind.).

[61] Jpn. Pat. 05017508 (Jan. 26, 1993), A. Shichizawa and S. Ozawa (to Asahi Chemical Ind.).

[62] Jpn. Pat. 04266902 (Sept. 22, 1992), M. Watanabe and co-workers (to Shin-Etsu Chemical Ind. Co.).

[63] Eur. Pat. 496349 (Apr. 10, 1996), M. Watanabe and co-workers (to Shin-Etsu Chemical Ind. Co.).

[64] Eur. Pat. 466141 (Nov. 8, 1995), M. Watanabe, S. Ueno, and M. Usuki (to Shin-Etsu Chemical Ind. Co.).

[65] J. L. Locatelli and G. Riess (1972), *Angew. Makromol. Chem.* **27**, 201.

[66] C. F. Parsons and E. L 1971. Suck Jr., *Multicomponent Polymer Systems* (Adv. in Chem. Ser. No. 99), American Chemical Society, Washington, D.C., , p. 340.

[67] J. Stabenow and F. Haaf (1973), Angew. Makromol. Chem. 29/30, 1.

[68] J. L. Locatelli and G. Riess (1973), J. Polym. Sci., Polym. Chem. Ed. 2, 3309.

[69] P. Mathey and J. Guillot (1991), Polymer 32, 934.

[70] R. Born and co-workers, Dechema Mongr. 134, 409–418 (1998). 6th International Workshop on Polymer Reaction Engineering.

[71] Jpn. Pat. 08027306 (Jan. 30, 1996), M. Motai and co-workers (to Japan Synthetic Rubber Co.).

[72] Jpn. Pat. 03026705 (Feb. 5, 1991), M. Tsutsumi and M. Shidara (to Hitachi Chemical Co.).

[73] Jpn. Pat. 08016126 (Feb. 21, 1996), H. Hayashi, T. Maruyama, and O. Murai (to Kao Corp.).

[74] Jpn. Pat. 05163359 (June 29, 1993), F. Suzuki and co-workers (to Mitsubishi Rayon Co.).

[75] Eur. Pat. 527605 (Feb 17, 1993), M. C. Will (to Rohm and Haas Co.).

[76] A. K. Ghosh and J. Lindt (1990), J. Appl. Polym. Sci. 39, 1553.

[77] U.S. Pat. 3991136 (1976), William Dalton (to Monsanto Chemical Co.).

[78] W. P. Flanagan, V. Lowry, T. E. Ludovico, A. P. Togna, and W. J. Fucich 1998., AICHE 1998 ,Annual Meeting, Session 16: Clean Air Technologies, AICHE Publication, New York.

[79] K. R. Sharma (1997), Polym. Mater. Sci. Eng. 77, 656.

[80] U.S. Pat. 05569709 (Oct. 29, 1996), C. Y. Sue and co-workers (to General Electric Co.).

[81] U.S. Pat. 05551859 (Sep. 3, 1996), J. E. Cantrill and T. R. Doyle (to Novacor Chemicals International).

[82] U.S. Pat. 05550186 (Aug. 27, 1996), J. E. Cantrill and T. R. Doyle (to Novacor Chemicals International).

[83] U.S. Pat. 05414045 (May. 9, 1995), C. Y. Sue and co-workers (to General Electric Co.).

[84] U.S. Pat. 04415708 (Nov. 15, 1983), S. Matsumura, and co-workers (to Kanegafuchi Kagaku Kogyo Kabushiki Kaisha).

[85] U.S. Pat. 04239863 (Dec. 16, 1980), C. Bredeweg (to The Dow Chemical Company.).

[86] U.S. Pat. 03945976 (Mar. 23, 1976), J. L. McCurdy and N. Stein (to Standard Oil Co.).

[87] U.S. Pat. 3,950,455 (Apr. 13, 1976), T. Okamoto and co-workers (to Toray Industries, Inc.).

[88] U.S. Pat. 3,660,535 (May 2, 1972), C. R. Finch and J. E. Knutzsch (to The Dow Chemical Company).

[89] U.S. Pat. 2,694,692 (Nov. 16, 1954), J. L. Amos, J. L. McCurdy, and O. R. McIntire (to The Dow Chemical Company).

[90] U.S. Pat. 3,515,692 (June 2, 1970), F. E. Carrock and K. W. Doak (to Dart Industries, Inc.).

[91] U.S. Pat. 1700011 (Dec. 23, 1991), A. Z. Zumer and co-workers (to USSR).

[92] U.S. Pat. 04151128 (Apr. 24, 1979), A. J. Ackerman and F. E. Carrock (to Mobil Oil Corp.).

[93] F. Rodriguez, 1970, Principles of Polymer Systems, McGraw-Hill, Inc., New York, Chapt. “5”.

][94] J. Haslam, H. A. Willis, and D. C. M 1980. Squirrell, Identification and Analysis of Plastics,2nd ed., Heyden Book Co., Inc., Philadelphia, Pa., Chapt. “8”.

[95] J. C. Cobbler and G. E. Stobbe, in F. D. Snell and L. S 1973. Ettre, eds., Encyclopedia of Industrial Chemical Analysis, Vol. 18, Wiley-Interscience, New York, p. 332.

[96] T. Okumoto and T. Tadaoki (1972), Nippon Kagaku Kaishi 1, 71.

[97] K. Sircar and T. Lamond (1973), Thermochim. Acta 7, 287.

[98] B. D. Gesner, J. Polym. Sci., Part A 3, 3825 (1965).

[99] L. D. Moore, W. W. Moyer, and W. J. Frazer (1968), Appl. Polym. Symp. 7, 67.

[100] J. Tsurugi, T. Fukumoto, and K. Ogawa, (1968) Chem. High Polym. (Tokyo) 25, 116.

[101] H. Shuster, M. Hoffmann, and K. Dinges (1969). Angew. Makrom. Chem. 9, 35

[102] D. Kranz, K. Dinges, and P. Wendling (1976), Angew. Makrom. Chem. 51, 25.

[103] D. Kranz, H. V. Pohl, and H. Baumann (1972), *Angew. Makrom. Chem.* **26**, 67.

[104] R. R. Turner, D. W. Carlson, and A. G. Altenau, (1974) J. Elastomer Plast. 6, 94.

[105] L. W. Jelinski and co-workers, J. Polym. Sci., Polym. Chem. Ed. 20, 3285 (1982).

[106] V. G. Kampf and H. Shuster (1970), *Angew. Makrom. Chem.* **14**, 111.

[107] D. Simpson (1968) , Br. Plast. 78.

[108] L. I. Petrova and co-workers (1972) , Gig. Sanit. 37, 62.

[109] T. R. Crompton1971, Chemical Analysis of Additives in Plastics, Pergamon Press, New York.

[110] N. E. Skelly, J. D. Graham, and Z. Iskandarani (1988), Polym. Mater. Sci. Eng. 59, 23

[111] R. Yoda (1984), *Bunseki* **1**, 29.

[112] Product Bulletin Mark 2 User Manual 0-2094, Omnimark Instrument Corp., Tempe, Ariz., 1999.

[113] B. Miller (1982), Plast. World 40(3), 34.

[114] L. W. Fritch, May 1982, Paper presented at the 40th Annual Technical Conference of the Society of Plastics Engineers, p. 332.

[115] F. M. Smith1964, Manufacture of Plastics, Vol. 1, Reinhold Publishing Corp., New York, p. 443.

[116] D. M. Kulich and M. D. Wolkowicz, Rubber-Toughened Plastics (Adv. in Chem. Ser. No. 222), American Chemical Society, Washington, D.C., 1989, p. 329.

[117] Applications of acrylonitrile butadiene styrene ,with the following link line : https://chat.openai.com/c/cfddc090-d1eb-4a88-b7a9-45ca3e7835ee on

[118] Teixeira LAC, Santini MC (2005) Surface conditioning of ABS for metallization without the use of chromium baths. J Mater Process Technol 170(1):37–41

[119] Chemical structure of PC,with the following link line : https://chat.openai.com/c/1eab0e37-8318-4c4c-ba0d-a7a5d8605679 on

[120] Properties of polycarbonate, with the following link line : https://chat.openai.com/c/9bcb2fff-e786-45df-b939-c07c8a843fbf on

[121] Advantages and drawbacks of Polycarbonate, with the following link line : https://chat.openai.com/c/1eab0e37-8318-4c4c-ba0d-a7a5d8605679 on

[122] Hoyt R, Wrobel J, Cushing J, Jaster M, Voronka N, Frank S, Slostad J, Paritsky L (2014) Structures with internal microstructures to provide multifunctional capabilities. US Patent 14/462,541

[123] Applications of polycarbonate, with the following link line : https://chat.openai.com/c/1eab0e37-8318-4c4c-ba0d-a7a5d8605679

Chapter II

Thermodynamics

Of

Polymer

Blends

II.1 General Introduction

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

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

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

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

II.2 Thermodynamics of binary polymer blend systems

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

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

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

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

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

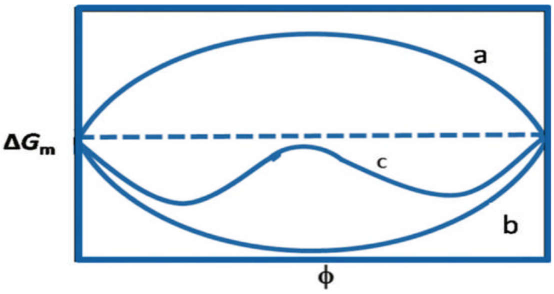

Figure II.1 Free energy of mixing for **(a)** completely immiscible, **(b)** completely miscible, and **(c)** partially miscible **[4, 21].**

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

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

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

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

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

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

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

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

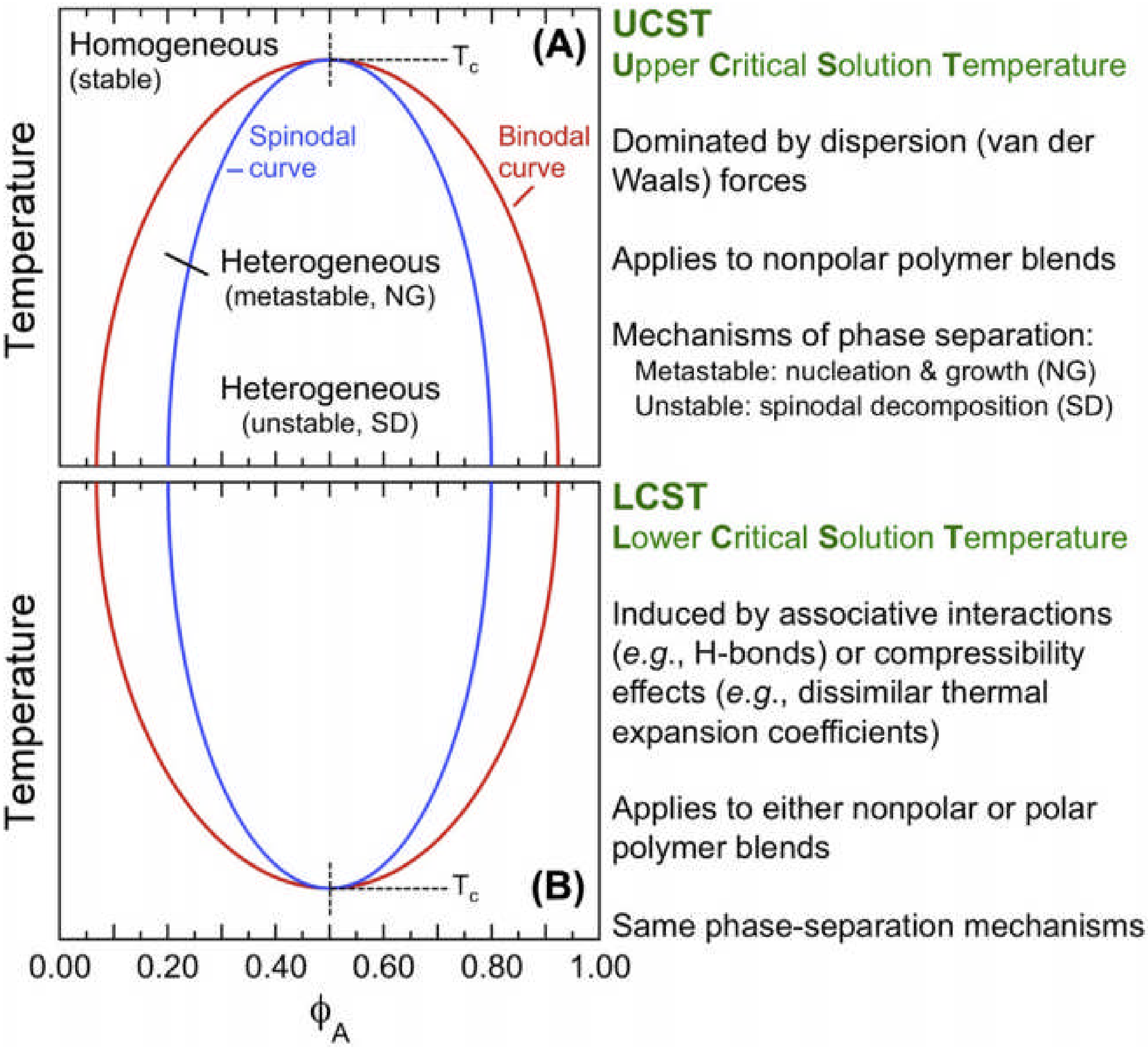

Figure II.2 Phase diagram showing the performance of polymer blends **[18].**

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

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

With the help of a phase diagram, degree of miscibility can be explained using spinodals and binodals. Three different regions in the phase diagram can be observed, that is between the two binodals there is single-phase or miscible region (highly miscible system has single phase); between binodals and spinodals there is metastable region: and phase separated or immiscible region bordered by spinodal curves. Low-molecular-weight substances show two critical points, but in the case of high-molecular-weight substances it can show either lower critical solution temperature (LCST) or upper critical solution temperature (UCST). Polymer blends normally show LCST **[18, 22-24].**

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

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

Here **R** is the universal gas constant and **T** is the absolute temperature. Ø1and Ø 2 are the volume fraction of the component 1 and 2,"**r**"represents the number of polymer segments (proportional to the degree of polymerization) and χ is the Flory-Huggins interaction parameter **[3,17,25,26].**

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

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

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

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

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

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

II.3 Classification of polymer blends

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

II.3.1 Classification based on constituents

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

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

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

II.3.2 Classification based on the miscibility

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

II.3.2.1 Miscible polymer blends

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

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

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

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

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

II.3.2.2 Compatible blends

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

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

II.3.2.3 Immiscible blends

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

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

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

References

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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.

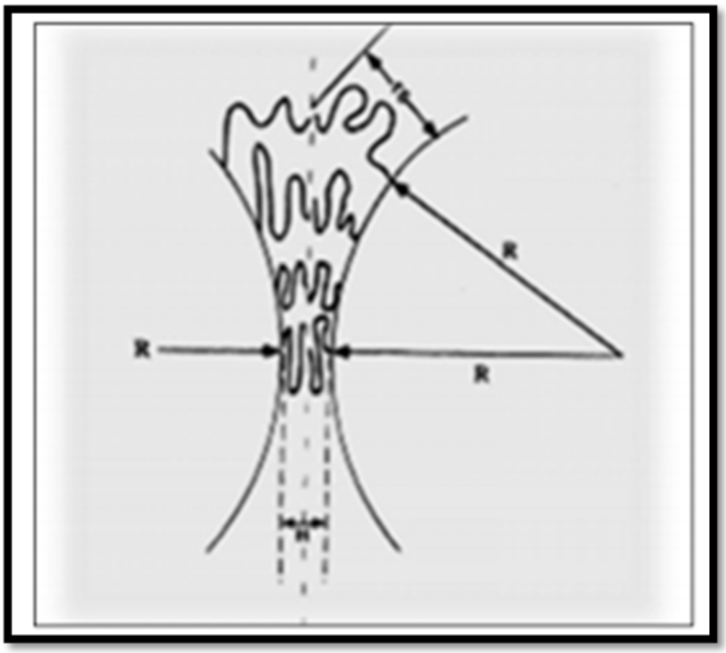

Figure III.1 Steric hinderence by compatibilizers. Compatibilizers acting as both anchors and repulsive springs ensuring the stability and prevention to coalescence **[16].**

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.

References

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Chapter IV
Literature Review

IV.1 Literature Review

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

These studies are presented in a chronological order.

Kumin Yang et al [1], have studied the effects of viscosity ratio and various compatibilizers namely (ASA, IM,MBS, and PMMA) on the rheological, morphological and mechanical properties of Polycarbonate/Acrylonitrile-Butadiene-Styrene (PC/ABS) blends. The rheological behavior was examined by means of a capillary rheometer. Scanning Electron Microscopy (SEM) was used for the morphological examination. The mechanical properties were determined by the tensile measurements. Uncompatibilized as well as compatibilized samples were prepared by twin screw extruder. They have found that the plot of the PC/ABS viscosity ratio, $\eta_{PC}/\ \eta_{ABS}$, versus the shear rate showed a gradual rise in the curve up to a critical shear rate and thereafter displayed asymptotic character. Contrary to premise, ηPC/ ηABS decreased with increasing temperature. This was elucidated by the melt viscosity of PC being thermally more sensitive than ABS over the temperature range investigated. As expected, the plot of the average domain size versus the viscosity ratio gave a concave up curve with a minimum when the viscosity ratio was close to unity. The morphology evolution along the screw of a twin screw extruder was examined. When sections of the kneading block were examined, the minor phase domains gradually showed reduction in size toward the extruder die, and the smallest domain was realized at the end of the block, namely, the flow impeding left-handed screw element. Polymethylmethacrylate (PMMA) exhibited the greatest ABS domain size reduction, and annealed samples showed that it suppressed coalescence. Contrary to expectation, the impact property of 5 wt % PMMA added to PC-rich PC/ABS blend was lower than without addition probably due to PMMA phase residing in the PC. Tensile properties showed only minimal improvement.

In another publication, the enhancement of the compatibilization of Polycarbonate/Acrylonitrile-Butadiene-Styrene thermoplastic polymer blends was studied by **D. W. Jin and co-workers [2**], using PMMA as **a** compatibilizing agents. The effects of blend composition, melt viscosity of ABS, and compatibilizing effect of PMMA on the mechanical properties, rheological properties, as well as morphological examination of ABS/ PC blends at ABS-rich compositions were studied by means of Izod impact strength, a capillary rheometer, and scanning electron microscopy (SEM), respectively. Their results indicated that, as the content of PC was increased, impact strength as well as Vicat softening temperature (VST) was increased. As the melt viscosity of ABS was increased near to that of PC, finer distribution of dispersed PC phase in the ABS matrix and consequent enhanced impact strength and VST were observed. They have also found that the PMMA was effective as the best compatibilizer to improve the viscosity as well as the interfacial adhesion between the two polymer phases (i.e: ABS, and PC), in the other words, they can clear seen that the surfaces were more smooth, more homogeneous, and regular in the ABS/PC/PMMA compared to those of the control and uncompatibilized ABS/PC blends.

S. Balakrishnan et al [3], have studied the Rheological and morphological behaviour of blends of polycarbonate with two different types of acrylonitrile-butadiene-styrene (ABS) copolymers, namely ABS and maleic anhydride grafted ABS (ABS-g-MA), prepared by melt blending using a single-screw extruder with special mixing head. The Rheological behaviour was examined by means of a capillary rheometer. Scanning Electron Microscope (SEM) was used for the morphological examination. The results showed that the melt viscosity-composition curves for both PC/ABS and PC/ABS-g-MA blends exhibited negative deviation from the rule of mixture, with minimum values occurring at PC content ranging from 25 to 65 wt.%. This means that the addition of ABS or ABS-g-MA to PC reduces the viscosity of the blend, making it easier to process. They have also found that, the morphology of unmodified blends exhibited coarse dispersion, while the morphology of modified blends showed fine and lamellar dispersion. This suggests that the addition of ABS-g-MA, which has maleic anhydride functional groups, leads to better compatibility between PC and ABS, resulting in a more homogeneous morphology. This effects could be attributed to the improve and enhance the interfacial adhesion and reduce the interfacial tension between the two polymer phases (i.e: PC, and ABS) imparted by functional group (MA) of ABS molecules.

In other study **S.C. Tjong and Y.Z. Meng [4],** have reported the effects of the incorporation of various types of compatibilizers namely: maleic anhydride (MA)-grafted polypropylene (PP-g-MA), maleic anhydride (MA)-grafted ABS, and solid epoxy resin (bisphenol type-A) on the morphological as well as mechanical properties of the PC/ABS blends. The mechanical properties of the uncompatibilized and compatibilized PC/ABS systems were studied by tensile and impact strength, respectively. The morphological examination was investigated by means of scanning electron microscope (SEM). Tensile and Izod impact tests revealed that the addition of epoxy resin at 2 phr (Part hundreds of rubber) level to the PC/ABS-g-MA 70/30 blend led to a significant increase in both tensile ductility and impact strength. The results showed also that the both functional groups (i.e. MA copolymer and epoxy) were effective to compatibilize the PC/ABS samples containing ABS content up to 30 wt%. From their results, scanning electron microscopy examination showed that the ABS tends to disperse as large domains in PC matrix of the uncompatibilized PC/ABS blends. However, the size of ABS domains of compatibilized PC/ABS blends with 30 wt% ABS was reduced dramatically owing to the incorporation of various compatilizers.

In another paper**, G. Wildes et al [5],** have the studied the effect of reactive compatibilization on the fracture behavior of polycarbonate (PC) / acrylonitrile-butadiene-styrene (ABS) blends. The study focuses on investigating the fracture behavior of thin (3.18 mm) and thick (6.35 mm) specimens made of polycarbonate (PC), acrylonitrile-butadiene-styrene (ABS), and PC/ABS blends. Were used two different test to examine the fracture, standard Izod test and single edge notch three-point bend (SEN_3PB) instrumented Dynatup test. The fracture data was analyzed by plotting the specific fracture energy (U/A) as a function of ligament length. Ligament lengths were varied for SEN_3PB samples. The results showed also that the slope of the plots of fracture energy vs, ligament length was found to be closely related to the Izod impact strength and the size of process (or stress whitened) zones surrounding the crack surface. This suggests a correlation between fracture toughness and crack propagation resistance. They have also found that, some PC/ABS (70/30) blends exhibited significant morphology coarsening in thick injection molded parts (6.35mm). However, when these blends were compatibilized with 1% of an SAN amine polymer, well-dispersed and stable morphologies were observed.

In another publication; **G. Wildes et al [6]** have studied the Synthesis method and characterization of an amine-functional SAN for the compatibilization of PC/ABS blends. An amine-functional styrene–acrylonitrile (SAN–amine) polymer is proposed as a reactive compatibilizer for bisphenol-A-polycarbonate/acrylonitrile–butadiene–styrene (PC/ABS) blends. This polymer should be miscible with the styrene/acrylonitrile (SAN) copolymer matrix of ABS materials, and the pendant secondary amine groups should react with PC at the carbonate linkage to form a SAN-g-PC copolymer. The graft copolymer molecules should reside at the PC/ABS interface and provide improved morphological stability at elevated temperatures by suppressing phase coalescence. Their describes the synthesis of this reactive compatibilizer and its reaction with carbonate moieties. Characterization of this reaction was done by nuclear magnetic resonance spectroscopy and gel permeation chromatography using model secondary amine and carbonate-containing compounds to facilitate the investigation. The morphology of compatibilized and uncompatibilized PC/SAN blends was examined by transmission electron microscopy. Morphological results showed the reduced domain sizes of minor phase (ABS) which dispersion in major phase (PC). This result confirms the chemical compatibilization of melt blended PC/ABS/SAN–amine mixtures.

In another study, **Xiangfu Zhang et al [7],** have studied the effects of a compatibilizer, namely, an acrylonitrile–butadiene–styrene copolymer (ABS) grafted with maleic anhydride (MAH) (ABS-g-MAH), on the mechanical properties and morphology of an ABS/PC thermoplastic polymer system. The Mechanical properties were determined by the Izod impact strength, Tensile Strength, Flexural Strength, and Vicat softening temperature (VST) and the degree of grafting (DG) of MAH in the ABS-g-MAH. Scanning calorimetry (DSC) analysis and Scanning Electron Microscope (SEM) were used for the thermal as well as morphological examination, respectively. The results showed that a small quantity of ABS-g-MAH which used as a compatibilizing agent has a very good influence on the mechanical properties such as a notched Izod impact strength of the ABS/PC samples. The impact strength of the ABS/PC blends increases with increasing ABS-g-MAH contents. It was also found that the DSC analysis and the SEM micrographs confirmed that ABS-g-MAH could greatly enhance the compatibility of the ABS/PC system; (i.e: The glass transition temperature (Tg) increased for the compatibilized blends with increasing ABS-g-MAH concentrations compared to those of the uncompatibilized PC/ABS blend, and the morphological aspects was developed by the increase of the interfacial adhesion between the two polymer phases imparted by the compatibilizing agent).

Munir Tas¸demir [8], have studied the compatibilization of PC/ABS blends using styrene–butadiene–styrene block copolymer (SBS), as a compatibilizing agent. The effects of blend composition, and compatibilizing effect of (SBS) on the mechanical, and thermal, morphological properties of Polycarbonate/Acrylonitrile-Butadiene-Styrene (PC/ABS) blends were also investigated. Uncompatibilized as well as compatibilized samples were prepared by twin screw extruder. The mechanical behavior was examined by means of yield strength and tensile strengths, elasticity modulus, percentage elongation, Izod impact strength, hardness; The rheological properties were determined by the melt flow index (MFI). Scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) were used for the morphological examination and thermal behavior. They have found that the addition of SBS to the ABS/PC blend resulted in a decrease in the elasticity modulus, the tensile and yield strengths, and hardness values, whereas the percentage elongation and Izod impact strength increased. From their results, When the SBS concentration was increased, the MFI value of the alloy increased. This was because SBS showed more elastomeric character, another explanation of this result, the SBS acts as a plastizer. They have also found that, the addition of SBS did not appear to alter the heating curves to any significant degree because SBS showed more elastomeric character and plastizer than the other two materials and Measurements of HDT (with the experiment started at room temperature with at a heating rate of 120°C/h and under a load of 1.8 MPa); and the Vicat softening point showed that the addition of SBS to the ABS/PC blend decreased these values. However, the addition of SBS considerably enhanced the adhesion and distribution of these phases. It was also apparent that 10% SBS markedly improved the adhesion, as evidenced by a more coherent morphology.

In other study, **Ki Heon Song et al [9],** have reported the effects of Compatibilizers called ABS-g-MAH as well as DCP. The blends were prepared by reactive extrusion with the ABS, maleic anhydride (MAH) and dicumyl peroxide (DCP) using twin screw extruder on the mechanical, rheological and morphological properties of the poly (acrylonitrile-butadiene-styrene) (ABS) and polycarbonate (PC) (70/30, wt %) blends. The mechanical properties of ABS/PC (70/30) blends were studied by tensile test. The rheological properties examination was investigated by means of Rubber Process Analyzer (RPA-2000). Scanning Electron Microscope (SEM) was used for the morphological examination. The results showed that in the uncompatibilized ABS/PC (70/30) blends, tensile strength did not change significantly, but this mechanical parameter increased from 52.25 to 55.03 MPa when the ABS-g-MAH was added in the amount of 5 phr. From the results of rheological properties, storage modulus of the compatibilized ABS/PC/ABS-g-MAH blends at low frequencies showed lager and higher value of storage modulus compared to those of the control ABS/PC (70/30) system. The morphological properties of the ABS/PC (70/30) blend, it was observed that the drop size of the PC ranged from 1.2 to 1.5 µm and did not change significantly with the addition of the ABS-g-MAH (1-10 phr). Based on the results of the storage modulus, complex viscosity, and tensile strength, it can be concluded that the ABS-g-MAH compatibilizer is effective in improving the properties of the ABS/PC (70/30) blends when added at a 5 phr amount. The compatibilizer contributes to an increase in tensile strength and enhances the stiffness of the blend at low frequencies. However, it does not significantly influence on the morphology or the size of minor phase (PC) droplets in the ABS matrix.

In another study, **Bo Zhao and co-workers [10],** have studied effect of reactive compatibilization on the Mechanical and Morphological as well as Dynamic Mechanical behavior of polycarbonate (PC) and acrylonitrile–butadiene–styrene (ABS), with a new type of reactive compatibilizer methyl methacrylate graft acrylonitrile–butadiene–styrene (MMA-g-ABS). Mechanical Properties was determined by the tensile test. Scanning Electron Microscope (SEM) was used for the morphological examination. The dynamic mechanical properties was investigated by dynamic mechanical thermal analysis (DMTA) .The results revealed that the notched impact strength and elongation at break of PC/ABS (70/30) blend increased significantly; However, the tensile strength of PC/ABS (70/30) blend decreased slightly with the increase of MMA-ABS content. The result showed also that the addition of MMA-ABS decreased the domain size of the ABS dispersed phase, making the dispersed phase well distributed, and the interfacial adhesion was enhanced between the two polymer phases. They have also found that with the addition of MMA-g-ABS, the glass transition temperature (Tg) of the PC and ABS phases were closer to each other. The addition of the MMA-g-ABS reactive compatibilizer to the PC/ABS blend resulted in improved compatibility between the two polymers, reduced domain size of the dispersed phase, enhanced interfacial cohesiveness, and improved impact resistance and elongation at break. Although there was a slight decrease in tensile strength, the overall mechanical properties of the blend were improved.

References

[1] Yang, K.; Lee, S.-H.; Oh, J.-M. Effects of Viscosity Ratio and Compatibilizers on the Morphology and Mechanical Properties of Polycarbonate/Acrylonitrile-Butadiene-Styrene Blends. *Polym. Eng. Sci.* **1999**, *39*, 1667–1677, doi:10.1002/pen.11561.

[2] Jin, D.W.; Shon, K.H.; Jeong, H.M.; Kim, B.K. Compatibility Enhancement of ABS/Polycarbonate Blends. *J. Appl. Polym. Sci.* **1998**, *69*, 533–542, doi:10.1002/(SICI)1097-4628(19980718)69:3<533::AID-APP13>3.0.CO;2-U.

[3] Balakrishnan, S.; Neelakantan, N.R.; Saheb, D.N.; Jog, J.P. Rheological and Morphological Behaviour of Blends of Polycarbonate with Unmodified and Maleic Anhydride Grafted ABS. *Polymer* 1998, *39*, 5765–5771, doi:10.1016/S0032-3861(98)00088-3.

[4] Tjong, S.C.; Meng, Y.Z. Effect of Reactive Compatibilizers on the Mechanical Properties of Polycarbonate/Poly(Acrylonitrile-Butadiene- Styrene) Blends. European Polymer Journal 2000.

[5] Wildes, G.; Keskkula, H.; Paul, D.R. Fracture Characterization of PC/ABS Blends: Effect of Reactive Compatibilization, ABS Type and Rubber Concentration. *Polymer* 1999, *40*, 7089–7107, doi:10.1016/S0032-3861(98)00865-9.

[6] Wildes, G.S.; Harada, T.; Keskkula, H.; Paul, D.R.; Janarthanan, V.; Padwa, A.R. Synthesis and Characterization of an Amine-Functional SAN for the Compatibilization of PC/ABS Blends. *Polymer* 1999, *40*, 3069–3082, doi:10.1016/S0032-3861(98)00521-7.

[7] Zhang, X.; Chen, Y.; Zhang, Y.; Peng, Z.; Zhang, Y.; Zhou, W. Effects of ABS-g-MAH on Mechanical Properties and Compatibility of ABS/PC Alloy. *J. Appl. Polym. Sci.* 2001, *81*, 831–836, doi:10.1002/app.1502.

[8] *Tas demir, M. Properties of Acrylonitrile-Butadiene-Styrene/Polycarbonate Blends with Styrene-Butadiene-Styrene Block Copolymer. J. Appl. Polym. Sci.* ***2004****, 93, 2521–2527,* doi:10.1002/app.20708.

[9] Hong, Y.; Li, H.; Ding, X.; Zhu, J.; Zhang, L.; Pan, W.; Cai, R. Effect of the Compatibilizers on Polycarbonate (PC) /Acrylonitrile-Butadiene-Styrene (ABS) Blend.

[10] Zhao, B.; Wang, Q.; Hu, G.; Wang, B.; Li, Y.; Song, J.; Wang, Z.; Li, Q. Effect of Methyl Methacrylate Graft Acrylonitrile–Butadiene-Styrene on Morphology and Properties of Polycarbonate/Acrylonitrile–Butadiene-Styrene Blend. *Journal of Macromolecular Science, Part B* 2012, *51,* 2276–2283, doi:10.1080/00222348.2012.672839.

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.

Compatibilization refers to the process of improving the compatibility between two or more immiscible polymers in a blend. In the case of ABS/PC blends (acrylonitrile-butadiene-styrene/polycarbonate), compatibilization techniques can enhance the specific properties of the blend by promoting better adhesion and interfacial interactions between the two polymers. This can result in improved mechanical, thermal, and morphological properties. Here are some effects of compatibilization on the specific properties of ABS/PC blends:

1. Mechanical properties: Compatibilization can lead to improved mechanical properties of ABS/PC blends. By promoting interfacial adhesion between the two polymers, it enhances the stress transfer across the interface, resulting in increased tensile strength, impact resistance, and elongation at break of the blend.

2. Thermal properties: Compatibilization techniques can also influence the thermal properties of ABS/PC blends. By reducing phase separation and promoting a more uniform distribution

of the polymers, it can improve the heat resistance, glass transition temperature (Tg), and thermal stability of the blend.

3. Morphological properties: The morphology of ABS/PC blends plays a crucial role in determining their properties. Compatibilization can modify the blend morphology by reducing the size and number of dispersed phases or forming a new phase at the interface. This can lead to improved dispersion of the phases, reduced particle size, and increased interfacial area, resulting in enhanced mechanical and thermal properties.

4. Impact resistance: ABS/PC blends are commonly used in applications that require high impact resistance. Compatibilization techniques can enhance the impact resistance of the blend by improving the interfacial adhesion between ABS and PC. This prevents crack propagation and improves the energy absorption capacity of the blend, making it more resistant to impact loads.

5. Processing properties: Compatibilization can also affect the processing behavior of ABS/PC blends. It can improve the melt flowability, melt strength, and processing stability of the blend, making it easier to process using common techniques such as injection molding or extrusion.

Compatibilization techniques can significantly improve the specific properties of ABS/PC blends by enhancing the interfacial adhesion, reducing phase separation, and modifying the blend morphology. These improvements can lead to better mechanical, thermal, and morphological properties, making the blend more suitable for a wide range of applications.

Abstract

Compatibilization strategies play a crucial role in improving the compatibility between different polymer systems, such as ABS (acrylonitrile butadiene styrene) and PC (polycarbonate). The ABS/PC system is known for its inherent immiscibility, which can lead to phase separation and negatively affect the mechanical, thermal, and processing properties of the blend. These compatibilization strategies can significantly improve the compatibility between ABS and PC in polymer blends, leading to enhanced mechanical properties, better thermal stability, and improved processability. The choice of strategy depends on factors such as desired properties, processing conditions, and the specific requirements of the application.

Keywords:

Acrylonitrile Butadiene Styrene, Polycarbonate, Immiscibility, Compatibilization strategies.

Résumé

Les stratégies de compatibilité jouent un rôle crucial dans l'amélioration de la compatibilité entre différents systèmes polymères, tels que l'ABS (acrylonitrile butadiène styrène) et le PC (polycarbonate). Le système ABS/PC est connu pour son immiscibilité inhérente, qui peut conduire à une séparation de phase et affecter négativement les propriétés mécaniques, thermiques et de traitement du mélange. Ces stratégies de compatibilité peuvent améliorer de manière significative la compatibilité entre l'ABS et le PC dans les mélanges de polymères, conduisant à des propriétés mécaniques améliorées, une meilleure stabilité thermique et une aptitude au traitement améliorée. Le choix de la stratégie dépend de facteurs tels que les propriétés souhaitées, les conditions de traitement et les exigences spécifiques de l'application.

Mots clés:

Acrylonitrile Butadiène Styrène, Polycarbonate, Immiscibilité, Stratégies de compatibilisation.

ملخص

تلعب استراتيجيات التوافق دورًا مهمًا في تحسين التوافق بين أنظمة البوليمر المختلفة ، مثل ABS (أكريلونيتريل بوتادين ستايرين) و PC (بولي كربونات). يُعرف نظام ABS / PC بعدم قابليته للامتزاج المتأصل ، والذي يمكن أن يؤدي إلى فصل الطور والتأثير سلبًا على الخصائص الميكانيكية والحرارية وخصائص المعالجة للمزيج. يمكن أن تحسن استراتيجيات التوافق هذه التوافق بين ABS و PC في خلطات البوليمر بشكل كبير ، مما يؤدي إلى تعزيز الخصائص الميكانيكية ، وتحسين الاستقرار الحراري ، وتحسين القدرة على المعالجة. يعتمد اختيار الاستراتيجية على عوامل مثل الخصائص المرغوبة وظروف المعالجة والمتطلبات المحددة للتطبيق.

الكلمات المفتاحية:

أكريلونيتريل بوتادين ستيرين ، بولي كاربونيت ، عدم التوافق ، استراتيجيات التوافق.