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The Influences of Blend Compatibilizers on the Structural, Rheological, Mechanical, Thermal, and Morphological Properties of Nitrile Rubber/ Polypropylene Thermoplastic Elastomer Blends.

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Réalisé par :

1- **BOUSBOULA Hani Chaker**
2- **SISSAOUI Aya**

Encadré par :

Dr. BELHAOUES Abderrahmane

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Dedications

Dedications

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I dedicate my graduation:

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- *To my friend's namely:*

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Dedications

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To my older sister Djouheina and my little Lyna, to my brothers Midou and Sohaib, and to my grandparents;

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Abstract

Abstract

Polymer blends emerge as one of the most important research areas in macromolecular science. The study of polymer blends structures, properties, and processing from academics and industries has been observed for decades. Due to their wide potential applications such as electronics, packaging, automotive, household appliances, etc., polymer blends have shown a growing development.

As we know that polymer blending is a mixing of at least two polymers to produce new materials with quite different properties. But unfortunately, most of the polymer pairs are thermodynamically immiscible, and the resulting blends exhibit poor mechanical performance due to the weak interfacial adhesion between the phases. Compatibilization of such polymer blends has been carried out to modify the interface and to improve their properties. The incorporation of compatibilizers as a third component in immiscible blends is effectively used to improve the phase compatibility.

Thermoplastic Elastomers (TPEs) are an important class of polymer blends that exhibit the typical advantages of conventional rubbers but can be processed with the thermoplastic processing methods. Among different kinds of thermoplastic elastomers, those based on polypropylene (PP) and nitrile rubber (NBR). Considering the commercial significance of the mentioned blends, different approaches have been used during the last few decades to improve their compatibility/or their engineering properties to expand their fields of applications.

The objective of this work was to investigate the effects of a 50/50 blend of epoxidized natural rubber (ENR)/maleic anhydride grafted polypropylene (PP-g-MA) as a compatibilizing agent (CA).The incorporation of these modified forms of NR and PP, through their functional groups would promote the interactions with NBR and PP phases. The effects were investigated through the measurements of the mechanical properties of a 50/50 NBR/PP thermoplastic elastomeric blend. The chemical structure of raw materials, as well as the compatibilizer was identified by fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (^{1}H-NMR).

FTIR analysis has confirmed the occurrence of reactions between the maleic anhydride groups of PP-g-MA and the epoxy groups in ENR and produced ENR-grafted PP with an ester and acid-based linkages. Moreover, ^{1}H-NMR results revealed that the CA was insoluble and did not dissolve in the different solvents but swelled only confirming hence the chemical reaction that took place between ENR and PP-g-MA.

The mechanical properties results confirmed the enhancement of the interphase interactions for the NBR/PP TPE blends. This was reflected by the increase of tensile strength, Young’s modulus, and a decrease of the elongation at break. This effects could be attributed to improvement of the interfacial interaction and reduce the interfacial tension between the two polymer phases.(i.e: NBR, and PP).

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List of Abbreviations

Abbreviations	Description
ABS	Acrylonitrile Butadiene Styrene
AFM	Atomic Force Microscopy
BR	Butadiene Rubber
CBS	N-Cyclohexyl-2-benzothiazole sulfenamide
CPE	Chlorinated Polyethylene
CNR	Cyclic Natural Rubber
DTDM	Dithiodimorpholine
DMTA	Dynamic Mechanical Thermal Analysis
DSC	Differential Scanning Calorimetry
DCP	Dicumyl Peroxide
ENR/PP-g-MA	Epoxidized Natural Rubber/ Polypropylene-grafted-Maleic Anhydride
ENR	Epoxidized Natural Rubber
ELNR	Epoxidized Liquid Natural Rubber
EPDM	Ethylene Propylene Diene Rubber
EPDM-g-MA	Ethylene Propylene Diene Rubber –grafted- Maleic anhydride
EVA	Ethylene Vinyl Acetate
EPR	Ethylene Propylene Rubber
HDPE	High Density Polyethylene
HBTP	Hexamethylene N, N′ Bis (Tert-Butyl Peroxy Carbamate)
ISO	International Standards Organization
LNR	Liquid Natural Rubber
LLDPE	Linear Low Density Polyethylene
MA	Maleic Anhydride
MNR	Maleated Natural Rubber
PP-g-MA	Polypropylene-grafted- Maleic Anhydride
Mn	Number Average Molecular Weight
Mw	Molecular Weight
MFI	Melt Flow Index
NR/PP	Natural Rubber/ Polypropylene
NBR	Acrylonitrile Butadiene Rubber
NMR	Nuclear Magnetic Resonance
NR	Natural Rubber

List of Abbreviations

NRL	Natural Rubber Latex
NR-g-MMA	Natural Rubber -graft-Methyl Methacrylate
NR-g-PMMA	Natural Rubber -graft-Poly(Methyl Methacrylate)
NR-g-PS	Natural Rubber -graft-Polystyrene
PA	Polyamide
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 block copolymer
SEBS-g-MA	Styrene-Ethylene-Butylene-Styrene-graft-Maleic Anhydride
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
TGA	Thermogravimetric Analysis
TPEs	Thermoplastic Elastomers
TPVs	Thermoplastic Vulcanizates
TMTD	Tetramethylthiuram Disulfide
TBBS	N-Tert-Butyl-2-Benzothiazole sulphenamides
TPNR	Thermoplastic Natural Rubber
TPO	Thermoplastic Polyolefin
Tg	Glass Transition Temperature

List of Abbreviations

Symbols	Description
E	Young’s Modulus
E'	Storage Modulus
E"	Loss Modulus
ΔHm	Melting Enthalpy of Sample
ΔH_0	Theoretical Enthalpy for 100 % Crystalline
Tan δ	Loss Tangent
Tc	Crystallization Temperature
Tm	Melting Temperature
ω	Frequency
Ɛb	Elongation at Break
TS	Tensile Strength
Xc	Degree of % Crystallinity
ε	Strain
η	Viscosity
η*	Complex Viscosity

Introduction

Introduction

Blending of two or more types of polymers such as blending nitrile rubber with polyolefins is a useful technique for the preparation and development of materials with properties superior to those of the individual constituents **[1]**. However, most polymer blends are immiscible and usually exhibit phase-separated morphologies and poor interfacial adhesion between their phases **[2]**. The interfacial adhesion can be improved by introducing a third component into the binary system that will either chemically interact with both the phases or will have specific interactions with one phase and physical interactions with the other **[3]**. This phenomenon can be explained as an improvement in the compatibilization of the blend. Commonly, compatibilization can lead to a finer phase structure and enhanced interfacial adhesion **[4]**.

A particular type of polymer blends is thermoplastic elastomers (TPEs). TPEs play an important role in the polymer industry due to their good processability and their elastomeric properties. There has been a growth of subcategories of TPEs to distinguish between different types of materials. Several examples are block copolymers, thermoplastic/rubber blends, and ionomers. Extensive studies have been carried out in the area of TPEs based on blends of elastomers with thermoplastics **[5]**. TPEs based on rubber- thermoplastic blends are classified into two distinct types. One type consists of a simple blend where the rubber known as a thermoplastic elastomer polyolefin (TPE-O) or a thermoplastic polyolefin (TPO). The rubber phase of the thermoplastic polyolefin is an unvulcanized material. In the other type, the rubber singular phase is dynamically vulcanized during melt mixing with a thermoplastic polymer, giving rise to thermoplastic vulcanizates (TPVs), dynamic vulcanizates (DVs), or elastomeric alloys (EAs) **[6]**.

The objective of the present study is to investigate the effects of the incorporation of a 50/50 blend of ENR/PP-g-MA as a compatibilizing agent (CA) on the rheological, and mechanical, properties of a 50/50 NBR/PP TPE blends.

The incorporation of a blend of ENR with PP-g-MA through the functional groups enhanced by the epoxy groups and the anhydride groups would promote the interactions with (NBR) and thermoplastic (PP) phase, respectively in the resulting TPEs.

This Master thesis is composed of four chapters. The first of which presents a theoretical background on the main polymers used in the study and a state of the art of the research carried out in the field of compatibilization of polymer blends as well as the chemical modification of NBR and PP. The second chapter describes the materials and the experimental procedures. In the third chapter, characterizations of the produced compatibilizing agents by FTIR and ^{1}H-NMR analyses as well as the rheological properties of the CA-containing blends are discussed. The results of the effect of addition of the 50/50 blend of ENR with PP-g-MA to the 50/50 NBR/PP TPE on the Rheological, as well as Mechanical properties are discussed in the last chapter.

The main results obtained are summarized in the conclusion, and recommendations for future work are also proposed.

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Chapter

I

Theoretical Background and Literature Review

I.1 Introduction

The simple blending of a crystalline thermoplastic and elastomeric polymer results in a new class of material termed a thermoplastic elastomer (TPE). The properties of the resultant TPE will be derived from the properties of each of the two polymers and dependent on the composition and the interaction between their phases. However, most TPE blends are immiscible and usually exhibit phase separated morphology and poor interfacial adhesion between the phases. The interfacial adhesion can be improved by introducing a third component into an immiscible binary system that will either interact chemically with both the phases or will have specific interaction with one phase and physical interaction with the other. This phenomenon generally results in as improvement in compatibilization of the blend.

TPEs based on PP/NBR are of particular interest for heat and oil resistance applications. However, PP and NBR are highly incompatible due to poor physical, mechanical and chemical interactions across the phase boundaries.

The increased use of acrylonitrile butadiene rubber (NBR) latex in glove manufacture has been seen over the last couple of years all over the world. The reason is its excellent resistance to punctures and tears as well as the non-existence of leachable allergeneic proteins, unlike in natural rubber latex. Similarly, nitrile gloves can be used to offer superior resistance to many types of chemical.

Nitrile gloves are currently used in many areas such as the medical and dental fields to a greater extent, food industry, automotive industry, chemical industry and so on, and as a result significant quantities of rejects are generated worldwide daily. As such, it would be of immense importance to the industry to find an appropriate method to recycle and reuse these waste materials.

In this chapter we present an overview of the polymers involved in this study. Emphasis is made on thermoplastic elastomers (TPEs) and those based on nitrile rubber (NBR) and the different strategies used for compatibilization. In the second part, a literature review concerning the research studies published in the field of NBR/PP TPEs is presented.

I.2 Nitrile Rubber

Nitrile rubber is a synthetic polymer made from 1,3-butadiene and acrylonitrile using emulsion polymerization techniques. The ASTM designation (D1418) for nitrile rubber is NBR and the Chemical Abstracts Service (CAS) registry number for poly(acrylonitrile-co-1,3-butadiene) is [9003-18-3]. Nitrile rubber was first developed in Germany during the early

1930s. Domestic production of NBR started during the 1940s. Nitrile rubber is classified as a specialty rubber and is well known for its resistance to various oils, fuels, and chemicals. After mixing with other ingredients (fillers, plasticizers, anti-degradants, and curatives) and curing, NBR compounds commonly see use in various seals, gaskets, hose, and roll applications. Nitrile rubber has been chemically modified by a solution hydrogenation process to extend its high-temperature performance. Hydrogenated nitrile rubber (HNBR) [88254-10-8] was developed and commercialized during the early 1980s. The saturated backbone of the HNBR polymer leads to the improved heat resistance of the rubber while retaining excellent oil/chemical resistance **[1].**

I.2.1 Synthesis method and chemical structure of NBR

- **Synthesis methods**

The two different methods of carrying out emulsion polymerization on a commercial scale are shown in **Figures I.1** and **I.2**. Each reactor operates independently to carry out a complete polymerization reaction in the batch process. Raw materials are charged to each reactor and the polymerization proceeds to the desired endpoint in each reactor, where it is either stopped or dropped to a “blow-down” tank and stopped. When large quantities of a single product are being made, many individual polymerizations are carried out, and the latices from them are blended. In the continuous process, several reactors are connected in series, usually three or more. Raw materials are charged to the first reactor where polymerization is started. The reacting mass then flows from one reactor to the next continuously, until it reaches the desired endpoint where polymerization is stopped.

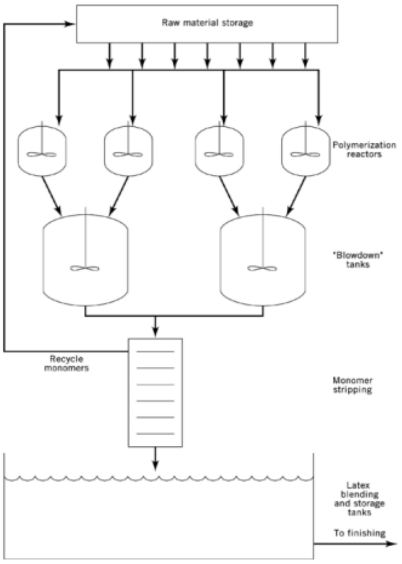


Figure I.1 Nitrile rubber polymerization, batch process **[1]**

The batch process is most useful when relatively short runs of a large number of products are planned. Several products can be made simultaneously and collected in separate storage tanks for testing and later finishing. The continuous process is more efficient when large quantities of a few products are desired. Reactors remain in operation a larger fraction of the time because no time is lost for emptying and recharging such as in the batch mode. **[1]**

In both cases, the progress of polymerization is closely monitored to follow the conversion of monomer to polymer. The conversion is important for two reasons: some recipes call for additions of ingredients at specific points during polymerization, and all recipes have a specific final conversion at which they must be stopped so that desired product properties are achieved. **[1]**

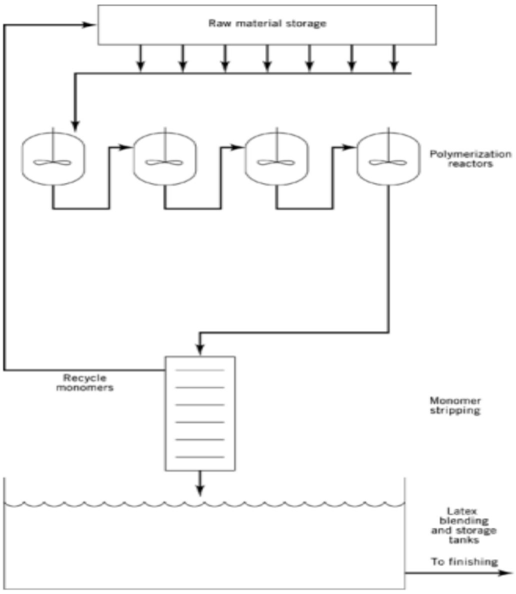


Figure I.2 Nitrile rubber polymerization, continuous process **[1].**

- **Chemical structure**

Acrylonitrile butadiene copolymer (NBR), commonly referred to as "nitrile rubber", is a synthetic rubber, random copolymer of acrylonitrile (ACN) (15-51% with a value of about 30% by weight) and butadiene (BR). Obtained by hot or cold radical emulsion polymerization in water with an emulsifier (soap) and various other products. It is characterized essentially by the resistance to solvents, in particular to aliphatic or partially aromatic hydrocarbons.

The production of nitrile rubber represents about 3% of the world’s production of synthetic elastomers.

From a molecular architecture point of view, the structure of these elastomers is quite complex. On the one hand, butadiene (BR) can be found in three distinct structures (trans, cis, and 1,2-vinyl with the predominant trans in a nitrile-type elastomer); it is the stable and non-polar part of the elastomer. On the other hand, the acrylonitrile groups (ACN) are found inserted in a statistical manner in the macromolecular chain, and represent the highly polar part of the elastomer, the nitrogen developing a strong potential for hydrogen bonds **[2].**

Figure I.3 shows the chemical structure of NBR and indicates the three possible isomers for the butadiene segments.

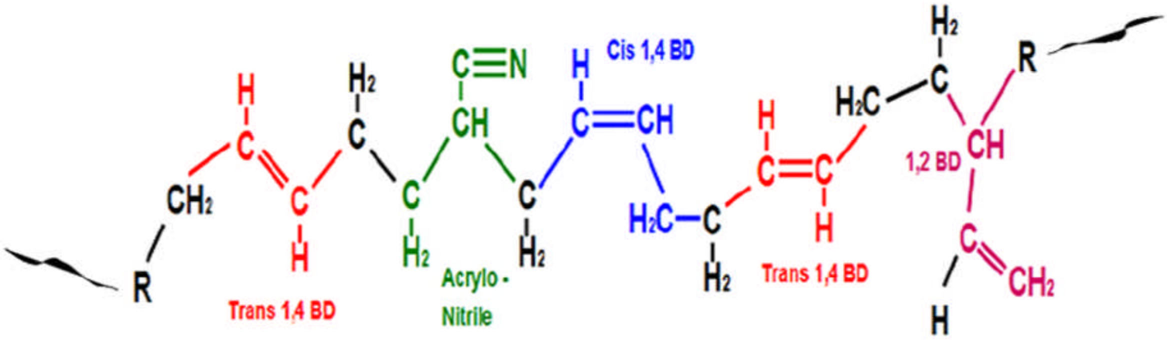


Figure I.3 Chemical structure of NBR **[2].**

I.2.2 Properties of Nitrile Rubber

Nitrile butadiene rubber is a family of unsaturated copolymers of 2-propene nitrile and different butadiene monomers (1,2-butadiene and 1,3-butadiene). Although its physical and chemical properties vary depending on the composition of the nitrile polymer (the richer the polymer in nitrile, the higher its resistance to oils but the less flexible it is), this form of synthetic rubber is generally used in the oil industry because of its chemical resistance to aliphatic hydrocarbons which is generally very satisfactory but limited in the presence of aromatic hydrocarbons, good chemical resistance to ordinary fuels (such as gasoline, diesel), good resistance to vegetable oils (unlike NR and SBR), animal fats, lubricants and alcohols, solvents, good impermeability to liquefied petroleum gases, and other inorganic chemicals.

- ✓ In addition, it has good mechanical resistance, to traction, compression, cutting, and perforation.….
- ✓ Resistance to aging, sunlight, and ozone is poor.
- ✓ The temperature limits for use of nitriles can be 130°C for heat and – 40°C for cold. It should be noted that this material hardens quickly in cold temperatures below – 20°C and that the relative softening is observed as the temperature rises.

- ✓ Nitrile rubber is resistant to a wide temperature range; it works well in areas where ordinary rubbers wear out quickly. Nitrile rubber is chemically more durable than natural rubber but less flexible and weaker.
- ✓ Adhesion to metals is very good (good adhesion to steel).
- ✓ Excellent tear resistance.
- ✓ High electrical conductivity due to its polarity **[2].**

I.2.3 Applications of Nitrile Rubber

Owing to its excellent properties, NBR is an essential component of many products used in various applications.

Nitrile rubber is generally used when excellent resistance to hydrocarbons and good mechanical properties are required, and therefore the different fields of application of NBR are:

- ✓ Petroleum tubes, petrol and fuel pipes, kerosene tanks, conveyor belts, coated fabrics.
- ✓ Automotive and aeronautical construction: which represents 65% of commercial outlets for parts intended to be in permanent or accidental contact with fuels, oils or greases, let us mention O-ring seals, hoses, agglomerated cork seals.
- ✓ Handling and transport of hydrocarbons: flexible pipes for loading and unloading tankers, flexible tanks, pipe valve seals, pipes resistant to heat, cold, gasoline, grease, and oil.
- ✓ Rollers and cylinder coatings: in the textile, paper, and printing industry.
- ✓ Safety shoe soles.
- ✓ Food and pharmaceutical products (white NBR).
- ✓ Adhesives: for bonding rubber, bonding plasticized polyvinyl chloride on various substrates **[2].**

I.3 Modified forms of Nitrile Rubber

Nitrile rubber, also known as NBR, is a synthetic rubber copolymer made by combining acrylonitrile and butadiene. It is known for its excellent resistance to oil, fuel, and chemicals, making it a popular choice in various industrial and automotive applications.

There are several modified forms of nitrile rubber that have been developed to enhance its properties or expand its range of applications. Some of these include:

I.3.1. Hydrogenated nitrile butadiene rubber (**HNBR**): This is a modified form of NBR that has been hydrogenated to improve its heat resistance and mechanical properties. HNBR is used in high-temperature applications and in the automotive industry for seals and gaskets.

I.3.2. Carboxylated nitrile rubber (**XNBR**): XNBR is a form of NBR that has been chemically modified with carboxyl groups to enhance its physical properties. XNBR is commonly used in the production of O-rings, hoses, and seals.

I.3.3. Chlorinated nitrile rubber (**CM**): CM is a form of NBR that has been modified with chlorine to improve its resistance to heat, oil, and chemicals. It is used in automotive applications, such as fuel and oil hoses.

I.3.4. Acrylonitrile-butadiene-styrene (ABS): ABS is a thermoplastic polymer made by blending nitrile rubber with styrene and butadiene. It is used in the production of automotive parts, electronic housings, and toys.

I.3.5. Styrene-butadiene rubber (SBR): SBR is a copolymer made by blending styrene and butadiene. It is used in the production of tires, conveyor belts, and footwear.

These modified forms of nitrile rubber offer improved properties and expanded applications compared to traditional NBR. **[2].**

I.4 Polypropylene

I.4.1 Chemical structure and synthesis method of polypropylene

Polypropylene is a tough, rigid, and semi-crystalline thermoplastic produced from a propane (or propylene) monomer. It is a linear hydrocarbon resin. The chemical formula of polypropylene is (C_3H_6) n. Polypropylene is a vinyl polymer in which every carbon atom is attached to a methyl group and can be expressed as shown in **Figure I.4**

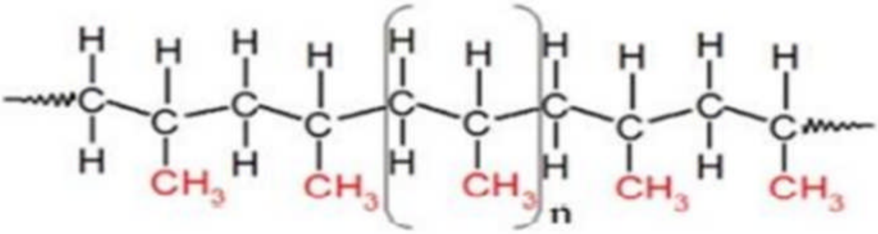
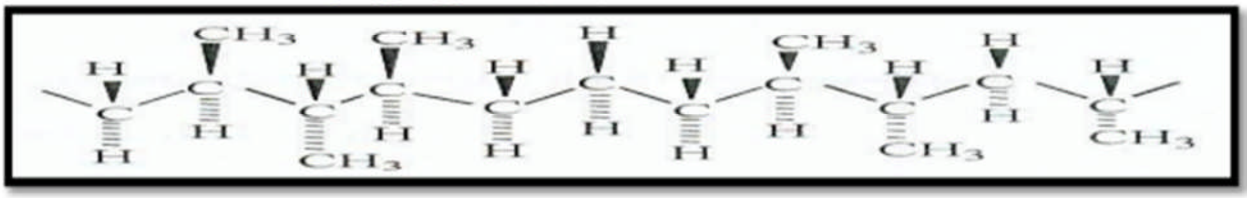


Figure I.4 Chemical structure of polypropylene. **[3]**

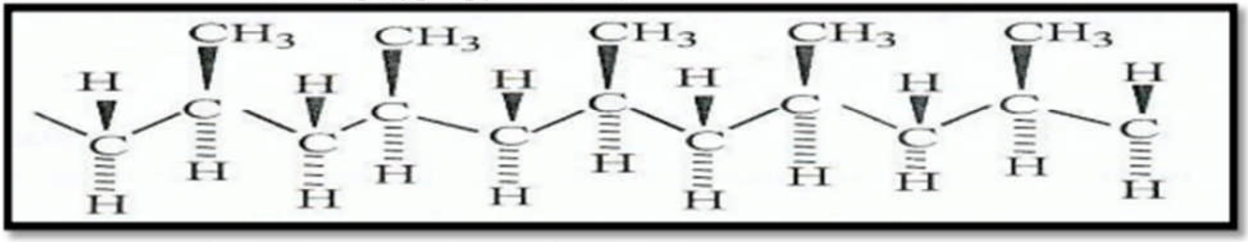
Polypropylene shows many good properties such as excellent chemical and thermal resistance, high melting point, stiffness, chemical inertness and low density, a high tensile modulus, and easy recyclability. Polypropylene offers a very attractive combination of physical and mechanical properties at a relatively low cost with continuously increasing applications. Some of the characteristics of this material are suitable for common service conditions. Due to its high transition temperature and high crystallinity, PP exhibits poor low-temperature impact resistance. Polypropylene forms very poor blends with other polymers. It has no chemical functionalities. Polypropylene is one of the most important commercial polymers; it is a highly versatile material with an outstanding combination of cost performance and excellent physical properties. The property range of PP can be broadened by physically blending it with other polymers. It has a hydrophobic, low-free-energy, chemically inert surface. Polypropylene shows brittleness, low mechanical performance, and low impact resistance at below or around glass transition temperature. Polypropylene is made from the polymerization of propene monomer by Ziegler-Natta polymerization or Metallocene catalysis polymerization.

Upon polymerization, PP can form three basic chain structures depending on the position of the methyl groups (**Figure I.5**): 1-Atactic (APP) - Irregular methyl group (CH_3) arrangement, 2-Isotactic (IPP) – Methyl groups (CH_3) arranged on one side of the carbon chain. 3- Syndiotactic (SPP) - Alternating methyl group (CH_3) arrangement **[3]**

1- Atactic polypropylene (aPP)



2- Isotactic polypropylene (iPP)



3- Syndiotactic polypropylene (sPP)

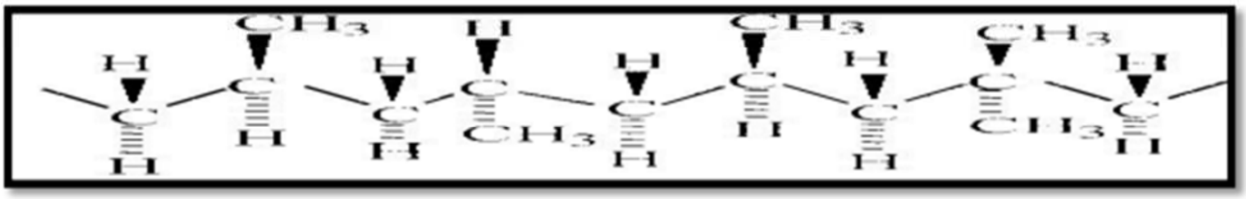


Figure I.5 The Ziegler-Natta catalytic polymerization of propene with three different stereoregular structures **[3].**

I.4.2 Advantages of polypropylene

- Polypropylene is readily available and relatively inexpensive.
- It has high flexural strength due to its semi-crystalline nature.
- It has also a relatively slippery surface.
- It is very resistant to absorbing moisture.
- Polypropylene has good chemical resistance over a wide range of bases and acids.
- It possesses good fatigue resistance.
- Polypropylene has good impact strength.
- Polypropylene is also a good electrical insulator **[3].**

I.4.3 Drawbacks of polypropylene

- Polypropylene has a high thermal expansion coefficient which limits its high-temperature applications.
- It is susceptible to UV degradation.
- Polypropylene has poor resistance to chlorinated solvents and aromatics.
- It is known to be difficult to paint as it has poor bonding properties.
- Polypropylene is highly flammable. It is susceptible to oxidation **[3].**

I.4.4 Properties of Polypropylene

Polypropylene (PP) is a thermoplastic polymer that is widely used in various applications due to its desirable properties. Some of the properties of polypropylene are:

1. Chemical resistance: PP has excellent chemical resistance, making it resistant to most acids, bases, and organic solvents. This property makes it suitable for use in chemical storage tanks, laboratory equipment, and chemical processing applications.

2. Low density: PP is a lightweight material with a density of approximately 0.9 g/cm^3. This property makes it suitable for use in applications where weight reduction is critical, such as automotive components, packaging materials, and sports equipment.

3. High tensile strength: PP has a high tensile strength, which means it can withstand high levels of stress without breaking or deforming. This property makes it suitable for use in applications that require high strength, such as ropes, automotive components, and furniture.

4. Low moisture absorption: PP has low moisture absorption, which means it is less likely to absorb water or other liquids. This property makes it suitable for use in applications where water or moisture resistance is critical, such as food packaging, medical devices, and outdoor furniture.

5. Excellent thermal resistance: PP has excellent thermal resistance and can withstand high temperatures without melting or deforming. This property makes it suitable for use in applications that require high-temperature resistance, such as hot-fill packaging, automotive components, and electronic components.

6. Good electrical insulation: PP has good electrical insulation properties, which makes it suitable for use in electrical and electronic applications, such as cable insulation, capacitor films, and battery cases.

Overall, the properties of polypropylene make it a versatile and cost-effective material for a wide range of applications. **[4,5].**

I.4.5 Chemical modification of polypropylene

The chemical modification of polymers consists of a modification of the nature of the Reactive groups carried by a polymer chain; it can take place on the groups, functional or unsaturations at the end of the chain, on the side chains or at the level of the main backbone of the polymers **[5].** The chemical modification of polypropylene can be made by several methods: modification by grafting and modification by cross-linking.

I.4.5.1 Modification by grafting

The grafting of polypropylene through the use of vinyl monomers is the major modification of polypropylene. Both chemical and irradiation means have been adopted for creation of the active site on polypropylene required for initiation of graft polymerization. However, the majority of work on the grafting of polypropylene reported has used the irradiation technique. γ radiation, radiation by electron beam, and UV radiation all have been successfully used for the creation of radicals on polypropylene surfaces. Extensive studies have been carried out on the grafting of polypropylene fiber using MAA and acrylic acid for improvement of its dyeability. As expected, acrylic acid grafted polypropylene; fiber has shown good dyeability toward basic dyes**. [6].**

I.4.5.1.1 The functionalization of polypropylene with acrylic acid

The functionalization of polypropylene with acrylic acid has been reported as early as the mid-1960s. Some of the most detailed work is reported in various patents issued to Exxon. Stein kamp and Grail (6) reported the use of a single screw extruder with a specially designed reaction zone that produces a very thin film and high surface area so that the monomer and initiator are thoroughly mixed before reacting with the polymer. The grafting of acrylic acid onto polypropylene results in various side reactions. The molecular weight of the polypropylene is reduced and the distribution is narrowed. Along with grafted polypropylene, homopolymerized acrylic acid is produced as well. Graft efficiencies are relatively high, up to about 6 wt% acrylic acid **Figure I.6**. At this level of functionalization, grafting efficiencies of _90% are obtained. Increasing the level of functionalization results in a reduction of graft efficiency **[6]**

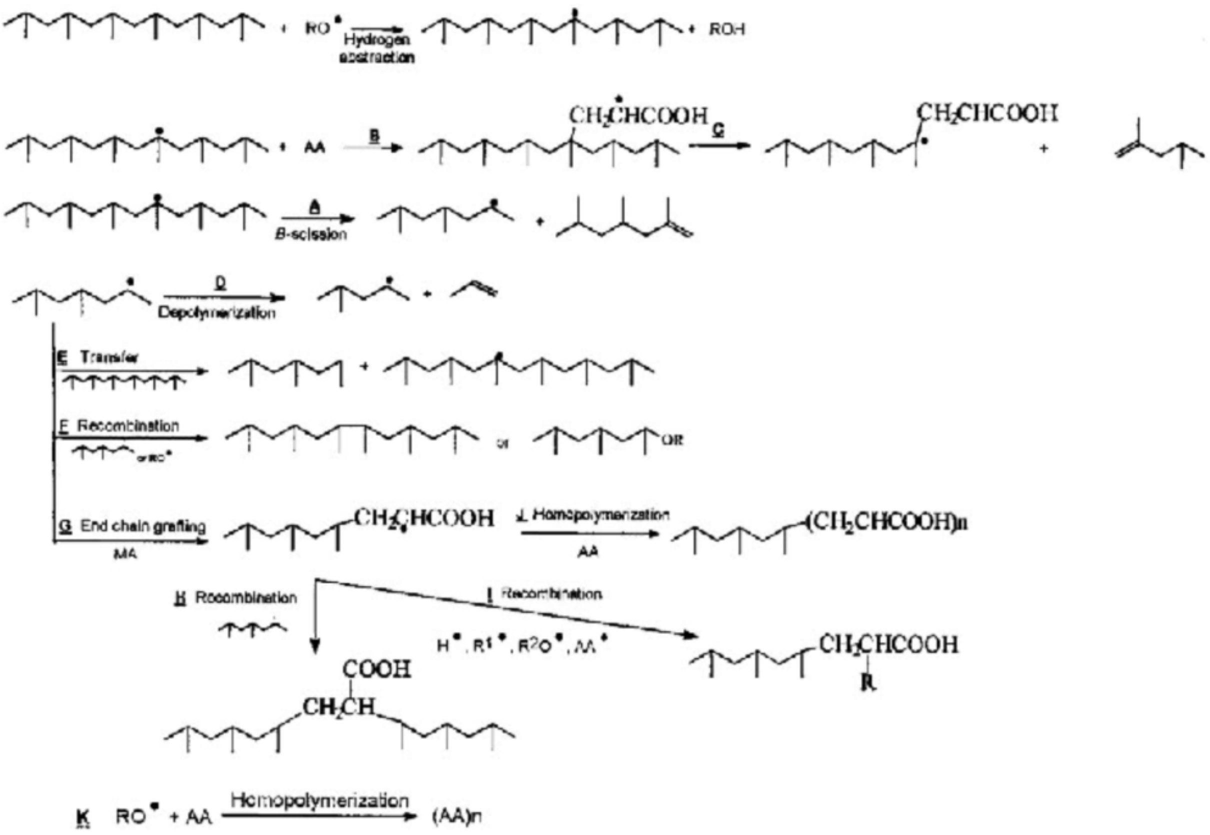


Figure I.6: Possible reaction mechanism for grafting acrylic acid onto polypropylene. **[6]**

I.4.5.1.2 The functionalization of polypropylene with maleic anhydride

There is considerable information available on the grafting of polypropylene with maleic anhydride or its analogues. The grafting can be carried out using a variety of techniques, including thermal, solution, and extrusion. Eastman Kodak Company discusses one thermal grafting process in patent 3,433,777. In this patent, low viscosity amorphous polypropylene is combined with maleic anhydride in an autoclave reactor. The material is heated to 325°C for 30 min. The resulting functional material has a high level of functionality, but it also has a drastically reduced molecular weight due to the thermal degradation of the polymer. Another method developed by Hercules Inc. (9) consisted of reacting crystalline polypropylene with maleic anhydride in the presence of organic peroxide in an inert liquid organic solvent. This process is expensive because it requires the separation of solvent and excess maleic anhydride from the modified polypropylene. **[6]**

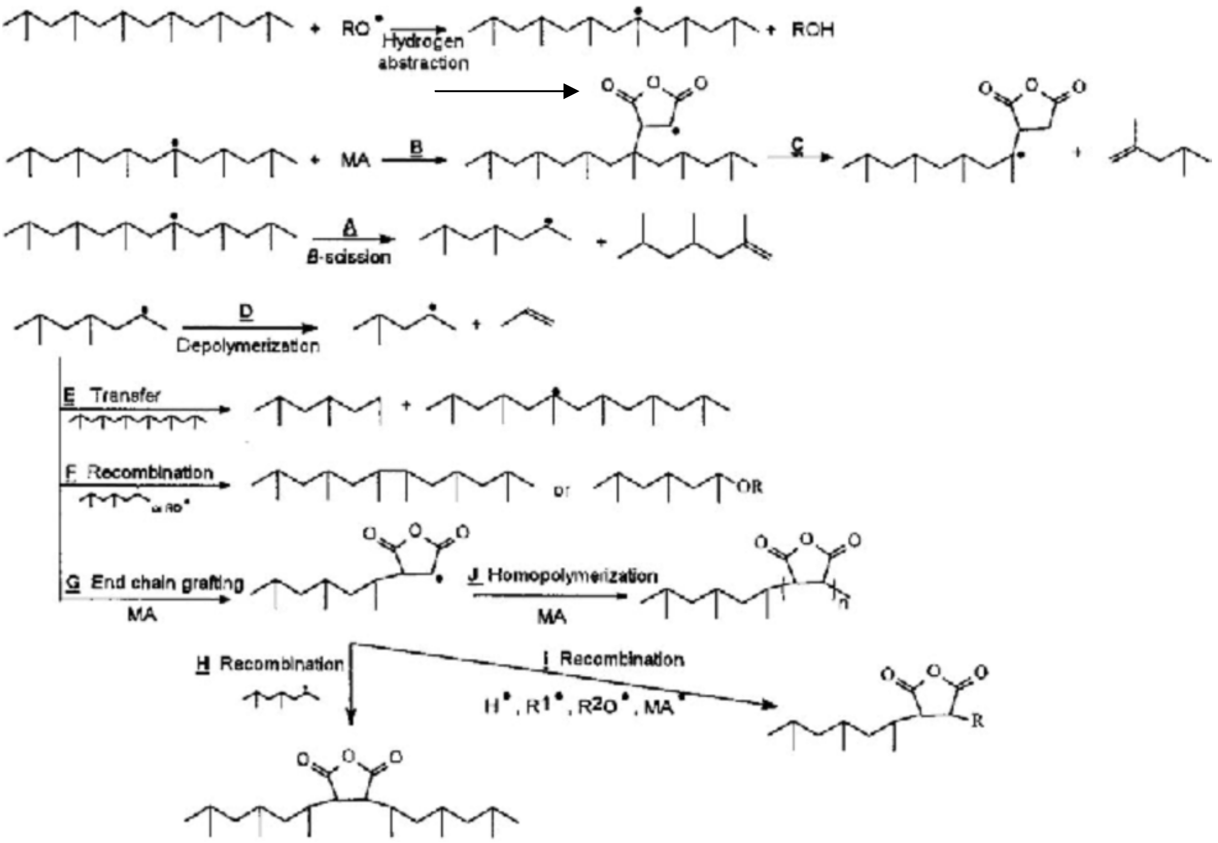


Figure I.7: Possible reaction mechanism for grafting maleic anhydride onto polypropylene according to De Roover et al. **[6]**

I.4.5.2 Modification by crosslinking

Crosslinked polymers are an important class of materials used in fiber reinforced plastics, thermosetting molding compounds, elastomers, coatings, adhesives, ion exchange resins, and many other applications. Although the use of these materials has grown rapidly, the understanding of the relationship of structure or chemical nature and properties has not progressed very well, mostly because of the difficulties in the characterization of the network structure and morphology. [**6].** PP can be crosslinked by several techniques: crosslinking by radiation, crosslinking by silanes and crosslinking by acrylates.

I.4.5.2.1 Crosslinking by radiation (radiation crosslinking)

Crosslinking by radiation transforms a linear network of polymer chains into a three-dimensional network by direct bridging of the carbon atoms between them, and causes an increase in the branching rate and therefore in the average molecular weight of the polymer. Crosslinking significantly modifies the initial technical characteristics of the polymer.

Exposure of the polymer to ionizing radiation such as electron bombardment or gamma rays (γ) creates free radicals (ionization reaction) which can generate crosslinking or grafting reactions. Indeed, the radicals can react with each other with monomers having an unsaturation of the vinyl function type. If the monomer has only one unsaturation, this leads to grafting or to crosslinking if it is multifunctional. Grafting is carried out in two stages (**Figure I.8**), which occur simultaneously or consecutively, depending on whether or not the monomer is present at the time of treatment with ionizing radiation. Since polypropylene is a semi-crystalline polymer, in this case, the crosslinking occurs essentially at the level of the amorphous zone because the fixed structure of the crystalline zones limits the probability of association of two free radicals **[3-5].**

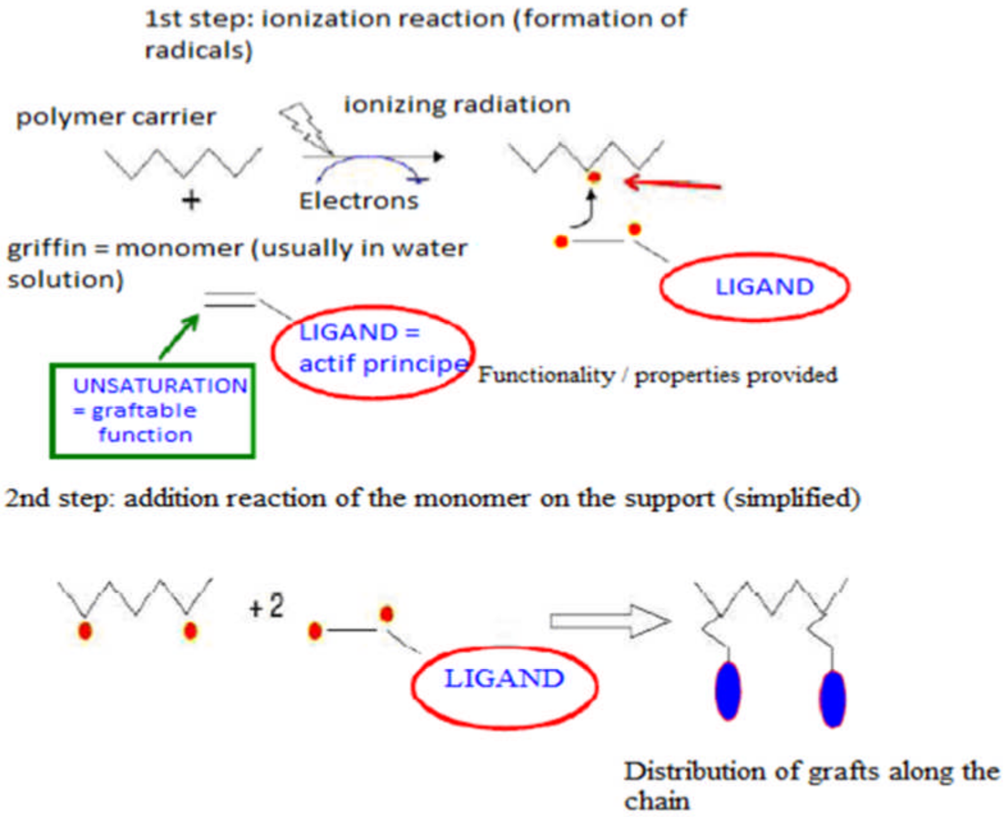


Figure I.8: Principle of two-step grafting**. [6]**

I.4.5.2.2 Crosslinking by silanes (S_iH_4)

The principle of crosslinking of polymers by silanes is that an unsaturated organo-silane having the general formula of RR'SiY2, where R is the hydrocarbonoxy radical, each Y represents the hydrolyzable organic radical and R' represents the radical R or the radical Y, which reacts with the free radicals generated in the polyolefins, such as vinyltrimethoxysilane and a quantity of peroxide are mixed with the polyolefins. Under the influence of the alkyl radicals formed by the peroxide, the vinyl silane is fixed on the polymer chain, in the case of isotactic polypropylene the silane is fixed on the tertiary carbon followed by the transformation and the manufacture of the finished product, and particularly the manufacture parts with metal insertion (technical car parts), then these parts are treated with hot water or steam, resulting in controlled cross-linking. This technique is also used for the manufacture of cross-linked polyethylene PE pipes **[6].** The general mechanism of crosslinking of polymer in presence of silane is shown in **Figure I.9.**

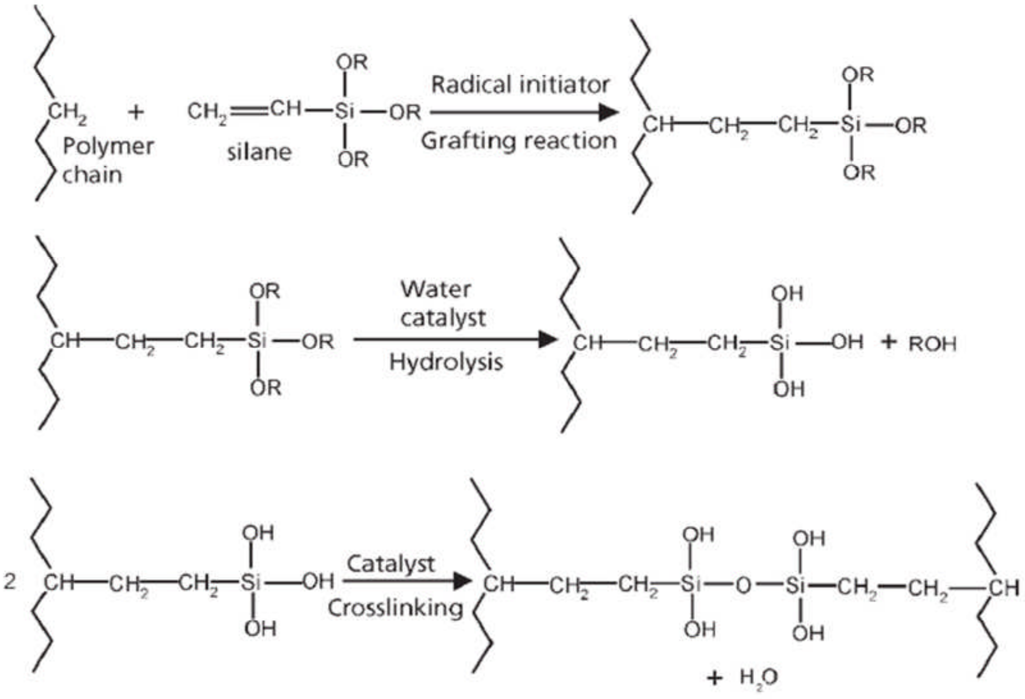


Figure I.9: Mechanism of crosslinking of polymer by silane **[6]**

I.4.5.2.3 Crosslinking by Acrylates

F.Romani et al. Have developed a new technique in recent years. They proposed another method for the chemical crosslinking of polypropylene using peroxide and furan or Bis-maleimide, the base agent promoting crosslinking. Crosslinking is partially observed at high peroxide concentrations using aromatic acyl derived peroxides. These initiators create, through the decomposition of aromatic radicals, which preferentially tear off the hydrogen atom from the methyl or methylene groups in the polypropylene chain, and do not lead to β scission through recombination. By adding an agent capable of giving a rapid addition to the macroradical, it is possible to prevent chain degradation, especially if the new macroradical is not able to extract the hydrogen from the tertiary carbon present in the macromolecular chains of the polypropylene **[6]**

I.4.6 Other modification of polypropylene

I.4.6.1 Ion implantation treatment

- **Ion implantation system**

Typically, an ion implantation system consists of an ion source, a mass separator, an ion acceleration column, a zone allowing focusing then scanning the beam and a vacuum implantation enclosure where an assembly maintains the targets and moves around **[6].**The ion source creates plasma containing a significant fraction of ions of the species to be implanted. The ions extracted from the source and pre-accelerated are filtered through an analysis slot. Mass separation is ensured by a magnetic field to select the desired ion species. The scanning of the beam making it possible to standardize the implantation on the surface is obtained by electrostatic way; the target can also be moved in front of the beam so as to perfect the uniformity of the implantation and to treat larger surfaces. Usually, the ion current is measured to determine the number of ions implanted per unit area; the target temperature must be controlled, because a large quantity of heat can be brought to it if a current is used raised. This heat can degrade the nature of the materials to be treated. The energies of implantation typically range from 10 to 100 keV, with sub-micron penetration depths.

I.4.6.2 Microwave plasma treatment

Microwave plasma (or cold plasma) treatment is able to activate the surface of the polymers and consequently to increase the wettability, the hydrophilic behavior and the adhesion in the extreme surface regions. The thickness of the treated layer varies from 0.1 to 10 nm. The treatment is carried out at low pressure with one or more gases which are introduced into an enclosure under vacuum (about 10*2 mbar).

This technique uses gaseous products in order to limit unwanted by-products **[6].**

The gas is electrically ionized, in the state of plasma. It contains gaseous species strongly excited, like molecules, ions, electrons. Unlike ion implantation, the plasma is evenly distributed within the enclosure. The major parameter for creating plasma is the electrical power (in watts). However, the power to be applied must be linked to the gas flow and to the excited gaseous species, so as to obtain a stable state of the plasma. Important Factors in Plasma Processing of a Polymer microwaves are:

- the flow of plasma towards the sample,

- the distance between the bottom of the ionization column and the sample,
- Processing time.

Since the value of the plasma flux and its distance from the sample are quantifiable, we can then set these two parameters and only vary the processing time the activation of the polymer surface results from a transfer of energy. The ionized species bombards the surface of the polymer, breaking the polymer chains and creating active sites. Following the degree of activation, the processing of polymers by microwave plasma can be classified into three categories: chemically neutral plasma, reactive plasma without polymerization and plasma for grafting wherein the substrate is first activated by the plasma and then immediately exposed to a vapor polymerizable in the absence of plasma gas **[6].**

I.4.6.3 Treatments by electron beam and by irradiation γ

For a later comparison with ionic treatments, we studied the electron beam and y-irradiation treatments. Electrons and photons, smaller and lighter than the ionized species, penetrate deeper into the polymer, at energies comparable incidents. It is thus possible to sterilize, at optimal doses, the devices medical devices by electron beam or by γ-irradiation **[3-5].**

The energy transmitted to the polymer, related to the unit of depth traveled in the material, is relatively low; it can then affect everyone volume. With a view to surface modification, treatments by electrons or by photons are only used in the case of the study:

- activation of the polymer surface by chain scission (low dose) or improving the cohesion between molecular chains by crosslinking (high dose),
- Grafting, which can be carried out by simultaneous irradiation, with an appropriate dose, polymer and the monomer liquid in which it is immersed **[3-5].**

I.4.7 Applications of polypropylene

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

Packaging Applications

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

a. **Flexible packaging**

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

b. **Rigid packaging**

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

Consumer goods

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

Automotive applications

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

Fibers and Fabrics

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

Medical Applications

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

I.5 Thermoplastic elastomers from Rubber/Plastics blends

Thermoplastic elastomers (TPEs) are a class of materials that combine the characteristics of rubber and plastics. They are a type of polymer blend made from a mixture of two or more polymers, typically one plastic and one elastomer. TPEs are unique in that they exhibit rubber-like elasticity and resilience, while also being processable like a plastic material.

The properties of TPEs can be adjusted by changing the ratio of plastic to elastomer, as well as the specific types of polymers used. TPEs are often used as a substitute for traditional rubber materials, as they offer improved processing, higher recyclability, and lower costs. They are also widely used in a variety of applications, such as automotive parts, medical devices, consumer products, and packaging materials.

The blend of rubber and plastic in TPEs allows for a wide range of physical and mechanical properties, including flexibility, durability, and resistance to impact and weathering. TPEs can be molded into complex shapes using a variety of processing methods, such as injection molding, extrusion, and blow molding. They are also known for their high resistance to chemicals and oils, making them ideal for use in harsh environments.

Overall, TPEs are a versatile and cost-effective material that combines the best properties of rubber and plastics. As new formulations and processing techniques are developed, TPEs are expected to play an increasingly important role in a wide range of industrial and consumer applications. **[7].**

I.5.1 The major advantages of TPEs

Thermoplastic elastomers (TPEs) offer a wide range of advantages over traditional rubber and plastic materials. Here are Some of the major Advantages of TPEs:

1. TPEs Do not require any compounding steps which are necessary for thermostat rubbers i.e. TPE pellets itself can be used for the fabrication of products.
2. The processing of TPE is much simpler than thermoset rubbers which require multi-steps for fabrication of products. This reduces the final cost of the product.
3. TPEs can be processed using thermoplastic fabrication methods such as blow moulding, heat welding and thermoforming, but are not practical for thermoset rubbers.
4. TPEs require shorter cycle times for the fabrication of a product compared to thermoset rubbers and this increase the production rate. The lower density of TPEs compared to thermoset rubbers leads to the production of a large number of articles from a given weight. Both these factors lead to cost reduction.
5. TPE scrap can be reused with negligible loss of properties. However thermoset rubbers scrap cannot be reprocessed.
6. TPEs are flexible and break at large elongation.

7. TPEs have good compression set and Superior vibration damping characteristics.
8. TPEs can be reinforced with fillers such as carbon black and silica.
9. TPEs have good resistant to impact, compressive and flexural loads.
10. TPEs have high fatigue failure resistance. **[8].**

I.5.2 Drawbacks of TPEs

Thermoplastic elastomers (TPEs) have many advantages over traditional rubber and plastic materials, such as flexibility, durability, and ease of processing. However, like any material, TPEs also have some disadvantages. Here are some of the disadvantages of TPEs:

1. Melting at elevated temperatures. This inherent property limits the use of parts from TPEs to service temperatures well below their melting point. A thermoset rubber would be probably suitable for a brief exposure to that temperature. Recent developments include an increasing number of TPE materials capable to be used at temperatures as high as 150 C or higher.
2. Limited number of low-hardness TPEs. Many TPEs are available at hardnesses about 80 Durometer A or higher. The number of materials softer than 50 Durometer A has greatly increased, and there are materials available that are gel-like.
3. Drying of most TPE materials prior to processing. This step is almost never used for conventional rubber materials but is quite common in fabrication of thermoplastics in general.
4. High Cost: Compared to traditional rubber and plastic materials, TPEs are generally more expensive. This can make them less cost-effective for certain applications, especially when large volumes of material are needed.
5. Poor Chemical Resistance: TPEs are not highly resistant to certain chemicals, such as solvents and oils. Exposure to these chemicals can cause the material to break down and lose its mechanical properties.
6. Limited Recycling Options: TPEs are not easily recyclable, and their recycling options are limited compared to traditional rubber and plastic materials. This can make them less environmentally friendly than other materials. **[9].**

I.5.3 Classification of TPEs

TPEs can be classified into several different categories:

1. Styrenic block copolymers (SBCs): These TPEs are composed of polystyrene blocks and rubber blocks, typically polybutadiene or polyisoprene. SBCs can be further

classified into several subcategories, including styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), and styrene-ethylene-butylene-styrene (SEBS).

2. Thermoplastic polyurethanes (TPUs): These TPEs are composed of a hard segment, typically a diisocyanate and a chain extender, and a soft segment, typically a polyol. TPUs can have a wide range of properties, including high elasticity, abrasion resistance, and chemical resistance.

3. Thermoplastic olefins (TPOs): These TPEs are composed of a mixture of a polyolefin, typically polypropylene or polyethylene, and an elastomer, typically an EPDM rubber. TPOs are often used in automotive applications due to their good weatherability and impact resistance.

4. Thermoplastic copolyesters (TPEEs): These TPEs are composed of a polyester segment, typically polyethylene terephthalate (PET), and an elastomer segment, typically a polyether or a polycarbonate. TPEEs are often used in applications where high strength and stiffness are required.

5. Other TPEs: There are several other types of TPEs that do not fit into the above categories, including thermoplastic polyolefin elastomers (TPOEs), thermoplastic vulcanizates (TPVs), and others. These TPEs can be composed of a wide range of polymers and elastomers, depending on the desired properties and application requirements. **[10].**

I.5.4 Factors determining the properties of TPEs

The properties of TPEs, or thermoplastic elastomers, are influenced by several factors, including:

- **Chemical composition:** The type and amount of polymer and elastomer used in TPEs can significantly impact their properties. For example, TPEs made with high amounts of polypropylene tend to be stiffer and have a higher melting point than those made with high amounts of ethylene. Additionally, the type of elastomer used can affect the TPE's ability to withstand repeated flexing or compression. For instance, TPEs made with styrene-based elastomers are generally stiffer and more rigid than those made with polyurethane or polyolefin elastomers.

- **Processing conditions**: The processing conditions used to produce TPEs can affect their final properties. For example, higher temperatures during processing can lead to a more homogeneous blend of polymers and elastomers, resulting in a TPE with more uniform properties. On the other hand, higher shear rates can cause more degradation of the polymer and elastomer, which can lead to a reduction in properties like tensile strength and elongation at break.

- **Additives**: Additives can be used to modify the properties of TPEs. For example, the addition of plasticizers can improve the TPE's flexibility and softness, while stabilizers can increase its resistance to UV degradation and other environmental factors. Fillers like carbon black or silica can be added to improve the TPE's mechanical properties, such as its strength and wear resistance.
- **Molecular structure**: The molecular weight and architecture of the polymers and elastomers used in TPEs can affect their properties. Higher molecular weight polymers and elastomers can lead to TPEs with higher tensile strength and toughness, while those with more branched or crosslinked structures can improve the TPE's resistance to deformation and thermal stability.
- **Blending technique**: TPEs are often produced by blending different polymers and elastomers together, and the blending technique can affect the resulting TPE's properties. For example, blending polymers with different solubility parameters can lead to a more phase-separated TPE, with different domains of polymers and elastomers throughout the material. This can impact the TPE's mechanical properties, such as its elongation at break or tear strength.
- **Environmental factors**: TPEs can be affected by environmental factors like temperature, humidity, and exposure to chemicals or UV radiation. For example, exposure to UV radiation can cause TPEs to become brittle or discolored over time, while exposure to chemicals like solvents or acids can cause them to degrade or swell. **[11].**

I.6 Thermoplastic vulcanizates

Thermoplastic vulcanizates (TPVs) are prepared by a dynamic vulcanization technique by adding curatives during the mixing operation. The TPVs consist of the dispersion of vulcanized rubber domains in the thermoplastic matrix, which differs from the simple blends. The dynamic vulcanization occurs through two stages: first, blending without crosslinking or simple blending, and second, a superimposed crosslinking and mixing. The viscosity plays a significant role on the formation of TPV morphology. When the degree of vulcanization is high, the rubber particles may be broken into micron size of elastomeric particles. The dynamic vulcanization of the rubber phase in the plastic matrix leads to the formation of materials with improved properties of high elasticity, while the thermoplastic phase provides the melt processing characteristics. The varieties of TPVs have already found commercial applications, especially in the automotive sector **[12-14].**

In the first blending step, the morphology of both phases changes to a co-continuous structure (**Figure I.10** (a)). The continuous mixing leads to formation of smaller grains of the co-continuous structure under the action of shear and elongational stresses on a highly viscous co-continuous structure (**Figure I.10** (b)). After addition of the curatives, the viscosity of the rubber phase quickly increases and the co-continuous structure is deformed by a shearing process (**Figure I.10** (c)). The break-up mechanism of the highly deformed co-continuous structure happens after the blend reaches a critical stress from increased viscosity, which results in the dispersion of the crosslinked rubber phase in the thermoplastic matrix. At high amount of crosslinks in the rubber, the rubber phase will break up into a finely dispersed particles morphology (**Figure I.10** (d) and (e)) **[12, 14-15].** This is the moment where the co-continuous morphology is transformed into a dispersed matrix phase, which depends on blend composition, viscosity and elasticity ratio, processing conditions and crosslinking conditions. Therefore, TPV morphology typically consists of the crosslinked rubber particles finely dispersed in the thermoplastic matrix. However, at high content of the rubber phase or rubber-rich TPV, the crosslinking is insufficient to enforce phase inversion and it is commonly difficult to separate the rubber particles in the rubber-rich TPV.

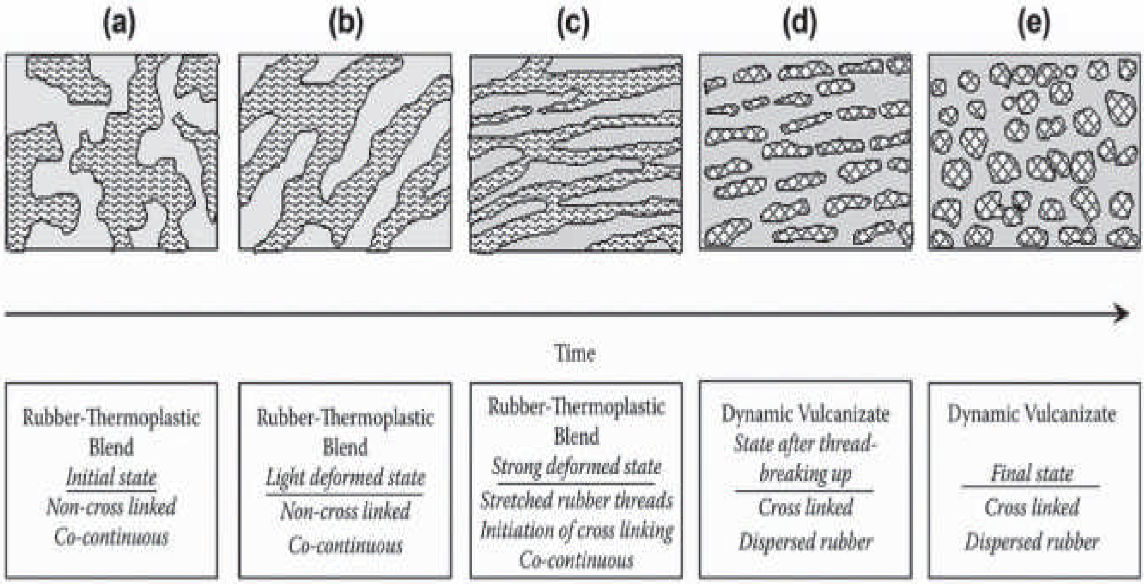


Figure I.10 Schematic diagram of morphology transformation during the dynamic vulcanization of polymer blends **[12]**

The vulcanization system is one of the most important factor in determining the physical properties of the dynamic vulcanizates. TPVs have been extensively investigated by using various types of the vulcanization system such as a phenolic resin **[12, 16-19],** sulfur **[20, 21],** a peroxide **[22, 23],** and mixed curatives (sulfur and peroxide) **[18, 24].** Recently, the phenolic cured system has received more attention in TPVs. This is because the fine dispersion of rubber particles in the matrix is obtained. As a consequence, improvement in mechanical properties of the TPV was achieved **[18].** The sulfur cured TPV provided superior mechanical properties in terms of tensile strength and elongation at break as compared with peroxide cure but it always gives an unpleasant smell during processing **[24].** TPV based on the peroxide cured system showed good elastic behavior in particular the compression set, heat resistance and no discoloration of the final products. However, the peroxide cured material shows a blooming effect and a decomposition of the peroxide into smelly by-products along with a β-chain scission reaction of the PP **[18, 22].** The use of multifunctional peroxide may overcome the drawbacks and provide PP-based TPV with appropriate mechanical properties **[25, 26].**

I.7 Theoretical aspects of compatibilization

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 **[27, 28].**

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, and also serve as repulsive “springs” when two droplets are in proximity **[29].**

I.7.1 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 lower 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 **[30].**

I.7.2 Non-reactive compatibilization (Physical compatibilization)

Non –reactive compatibilization commonly known as physical compatibilization involves the compatibilization of immiscible blends by the addition of a third component as block and graft copolymers, which do not react with the component polymers, or homopolymers. In the compatibilization of an immiscible blend (A/B) by a symmetric copolymer A'-B' the mechanism of the action of compatibilizer can be represented in **Figure I.11.** If the block A' mixes only with A and the block B' with B, the copolymer can located at the interface as shown in the **Figure I.11.**

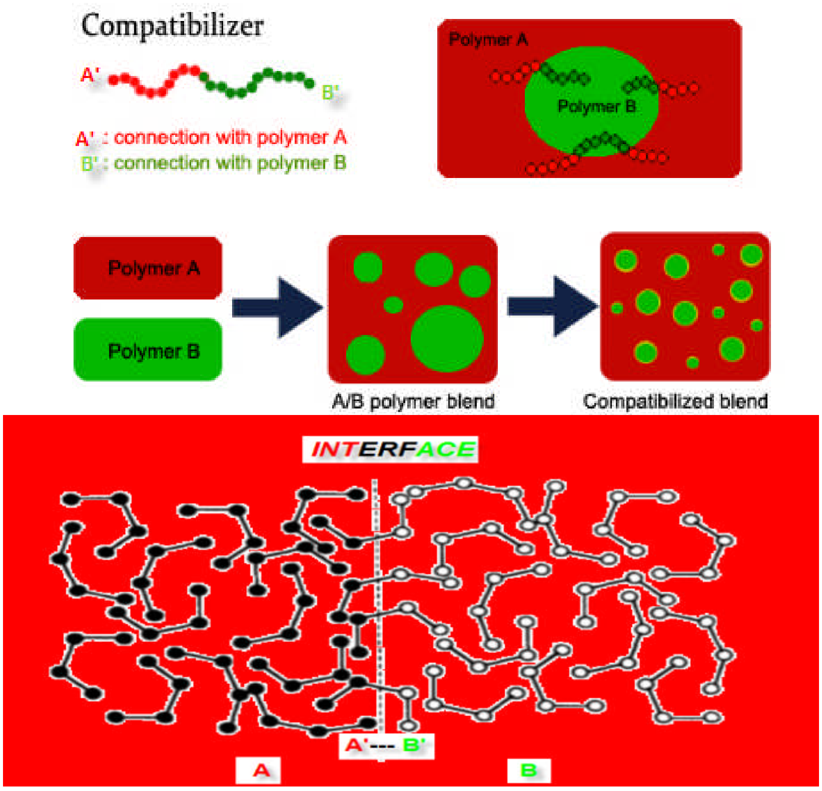


Figure I.11 Effect of compatibilizer A'-B' in the interface between the phases of two homopolymers A and B.

I.7.3 Reactive compatibilization (Chemical compatibilization)

Reactive processing involves various chemical reactions, including bulk polymerisation, controlled degradation, coupling, grafting, functionalization, and reactive compatibilisation. The latter involves the formation of copolymers through covalent or ionic bonding during melt blending, where one phase contains inherent reactive groups while the other does not. These reactive groups can be introduced into the second phase by adding a functionalized polymer, resulting in copolymer compatibilisers that enhance the interfacial adhesion between the phases, reducing the size of the dispersed phase and improving the physical properties of the blends. Compared to pre-made block or graft copolymers, micelle formation is minimal in reactive compatibilisation, making it a more viable option for extrusion processes where mixing equilibrium may not be fully attained. Addition of a reactive third polymer with appropriate functionality can also enable reactive compatibilisation.

As these reactions are typically rapid, they can be carried out within the time frame of an industrial extruder, making reactive blending a feasible option for industries. Reactive compatibilization produces a robust interface that exhibits impressive stability under high levels of stress and strain. In recent years, in-situ compatibilization between two polymers has garnered significant attention due to its economic advantages over using a pre-formed compatibilizer. The primary research focus has been on identifying the suitable functionalized copolymers that can react during the mixing process.

To achieve an effective reactive compatibilization process, several conditions must be met:

- ✧ One polymer must be highly dispersed within the other.
- ✧ There must be complementary groups present that can form a stable chemical bond.
- ✧ The reactive groups involved must be highly reactive to facilitate interaction through the polymer melt.
- ✧ The chemical bond that forms during the blending process must also be stable under subsequent processing conditions.
- ✧ The reaction time must be brief, i.e., shorter than the residence time in the extruder or mixer. **[30].**

I.7.3.1 Advantage of reactive compatibilization

1- In reactive compatibilisation chemical reactions are involved in the blending process. This makes reactive compatibilisation very attractive and cost effective.

2- It offers the possibility of generating compatibilisers during melt blending directly at the interfaces between the base polymer components without separate synthetic and purification steps.

3- The formation of the copolymer at the polymer-polymer interface, where it is needed most, directly during the melt blending, leads to the significant reduction in the particle size and significant reinforcement of the interfacial Wughness.

4- Sometimes the desired compatibilisers cannot be synthesized separately by existing synthetic procedures. Reactive compatibilisation then becomes the method of choice. The functionalization of existing polymers in the melt can now be done in a polymer processing machine.

5- The main advantage of the reactive blending technique to some commercial organizations is that the process can be conducted in different ways with different property outcomes. Thus, the product cannot be de-engineered by analysis, which provides an element of secrecy to the manufacture. **[30].**

I.7.3.2 Comparison of Reactive Versus Physical Blending

Reactive groups can be introduced by free radical copolymerization or by melt blending of reactive groups on to chemically inert polymer chains.

Reactive polymers generate block or graft copolymers only at the site where they are needed i.e.. at the interface of an immiscible polymer blend.

Although micelles can be formed by graft and block copolymers when added to or created in a blend, the likelihood of surpassing the critical micelle concentration is actually greater in the case of pre-existing structures. Additionally, the melt viscosity of a reactive linear polymer is lower than that of a pre-made block or graft copolymer, particularly when the molecular weights of the reactive blocks and the blocks in the pre-made copolymer are comparable.

Reactive compatibilization is advantageous in reactive blending processes where time is limited, as the low molecular weight of the precursor allows for rapid diffusion towards the interface.

It is important to consider that in reactive blending, the functionalities must possess a suitable reactivity to react at the melt phase boundary within the brief blending period. Furthermore, any covalent bonds formed must be durable enough to withstand subsequent processing conditions. **[30].**

I.8 Literature Review

In recent years, elastomeric rubber-plastic mixture has become technologically important for use as thermoplastic elastomer (TPE). The objective of the mixture of plastic and rubber is the improvement of physical, thermal and mechanical properties as well as the modification of processing characteristics and cost reduction of the final product.

Polypropylene (PP) is one of the commonly employed polyolefin because of its low price, stabilized properties, and simple processability. Acrylonitrile butadiene rubber (NBR) is well known unsaturated copolymers for about five decays. It has been used in many industrial required purposes as hoses, O-ring seals, insulation base product and other many packaging materials.

The mixture of polypropylene (PP) / acrylonitrile butadiene rubber (NBR) combines the oil resistance of NBR as well as excellent chemical and moisture resistance, good ductility and stiffness, low density, and easy processing characteristics of PP. Actually, PP and NBR are highly incompatible and usually exhibit phase separated morphology because of poor physical, mechanical and chemical interactions across the phase boundaries. Hence, these properties can be further improved with suitable compatibilization techniques.

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

For example**, S.George et al [31],** have studied the compatibilization of isotactic polypropylene (iPP) and nitrile rubber (NBR) thermoplastic elastomer (TPE) blends using maleic anhydride –grafted polypropylene (PP-g-MA) and phenolic-modified polypropylene (Ph-PP) as compatibilizers. Morphology and mechanical properties of TPE blends have been investigated with special reference to the effects of the blend ratio. The effects of concentrations of PP-g-MA as well as Ph-PP on the morphology and mechanical properties of the TPE blends were also investigated. They have found that the morphological observations of blends showed a two-phase system, in which the rubber phase was dispersed as domains in the continuous PP matrix at lower proportions of NBR (≤50%). The 30/70 PP/NBR blend was found to exist as a co-continuous system. It was found also that the compatibilizer concentrations affect much in the morphological and mechanical properties. In other words, the domain size of the dispersed NBR particles decreased with the addition of a few percent of the compatibilizer followed by a leveling off at higher concentrations. The leveling off was an indication of interfacial saturation. The mechanical properties of the blends were improved also by the addition of the compatibilizer followed by a leveling off at higher concentrations.

In another publication, Tearing behavior of blends of isotactic polypropylene (iPP) and nitrile rubber (NBR) has been investigated by **S.George et al [32],** with special reference to the effect of blend ratio and addition of compatibilizing agents. They have found that the tear strength of the PP/NBR blends decreases with increase in NBR concentration. The tear strength of the blends depends on the morphology of the blends. The tear strength-composition curve shows a negative deviation from the additivity line. Various composite models have been used to fit the experimental tear strength data. The tear strength of blends could be predicted by Coran’s equation. The phenolic modified polypropylene (Ph-PP) is found to act as a compatibilizer in PP/NBR blends. With the increase in Ph-PP concentration, the tear strength increases up to 10 wt% Ph-PP and after that it levels off. The increase in tear strength with Ph-PP concentration is associated with the decrease in the domain size of the NBR phase and the increase in interfacial adhesion.

Free radical melt grafting of glycidyl methacrylate (GMA) onto polypropylene (PP) was studied by **Li-Feng Chen et al [33]**. The extent of GMA grafting and the molecular weight of the functionalized PP copolymers were controlled by carefully manipulating various reactions factors, such as monomer concentration, initiator concentration, reaction temperature, and molecular weight of the starting PP homopolymer. The use of a second monomer, styrene, in the grafting process helped to increase GMA grafting further and reduce chain scission. From their results, the GMA modified PP copolymer was found to be able to reactively compatibilize PP / acrylonitrile-co-butadiene-co-acrylic acid rubber (NBR) blends. Up to an eight-fold increase in the impact energy of the PP/NBR blend was obtained. The compatibilizing capacities of the reactive copolymers, in terms of impact energy improvement of the PP/NBR blend, were found not to be exclusively dependent on the total concentration of reactive functionalities in the matrix of the blend. The characteristics of the reactive copolymers, i.e., the extent of functionalization and the molecular weight, were found to have significant influences on the compatibilizing capacity. A large amount of moderately functionalized copolymer offers better compatibilization performance than a small amount of highly functionalized copolymer. A significant drop in impact energy was observed with declining molecular weight of the copolymer.

In another study, the effect of blend ratio and compatibilization on dynamic mechanical properties of PP/NBR blends was investigated at different temperatures by **S.George and coworkers [34],** the effect of the blend composition and compatibilization on the dynamic mechanical properties was investigated in the temperature range -50 to 150°C. These investigations indicate that the PP/NBR blends are incompatible, as shown by the presence of two relaxation peaks corresponding to the Tg’s of PP and NBR. As the concentration of rubber increases, the storage modulus of the system decreases, while the loss modulus and tan δ increase. The increase in loss modulus is more pronounced after the 50 wt % NBR phase. The change in viscoelastic properties with blend composition can be correlated with the blend morphology. Various composite models have been used to fit the experimental viscoelastic data. The Takayanagi model was found to fit the experimental values for a 20% parallel coupling. The addition of phenolic-modified polypropylene (Ph-g-PP) and maleic anhydride-modified polypropylene (MA-g-PP) are found to increase the storage modulus at a lower temperature, which indicate an increase in interfacial adhesion on the addition of these compatibilizers. At a higher concentration of these compatibilizers the storage modulus decreases due to interfacial saturation. As the concentration of the compatibilizers increased, the domain size of the dispersed NBR particles decreased initially, followed by a leveling off or increase at a higher concentration, indicating the presence of interfacial saturation concentration. Among the vulcanized systems, the DiCUP system shows the highest modulus, and sulfur system the lowest. The mixed system showed an intermediate behavior.

In another paper, the rheological behaviour of polypropylene (PP)/acrylonitrile–butadiene rubber (NBR) blends has been investigated with special reference to the effect of blend ratio, compatibilization and dynamic vulcanization by **S.George and coworkers [35].** The morphology of the extrudates and the size and distribution of domains were examined. The blends showed pseudoplastic behaviour which is indicated by a decrease in viscosity with shear rate. The viscosity of these blends increased with increasing NBR concentration and showed a sharp change after 50 wt% NBR. The variation in viscosity was correlated with the phase change of NBR from a dispersed phase to a continuous phase. The blends showed negative deviation, which indicated a lack of interaction between the polar nitrile rubber and the non-polar polypropylene. Various theoretical models have been used to predict the experimental viscosity values. The viscosity values fit well with those calculated using an altered free volume model. The compatibilization of these blends with phenolic-modified polypropylene was found to increase the viscosity of the system, indicating an increase in interfacial interaction. The variation in viscosity was correlated with the morphology. As the compatibilizer concentration increases the domain size decreases and shows a levelling-off at high concentration. The dynamic vulcanization of PP/NBR blends leads to a fine and uniform distribution of NBR particles, the size of the dispersed NBR particles varying in the order DCP, mixed, sulfur-cured system.

Among the dynamic vulcanized blends, the sulfur-cured system has the highest viscosity and the DCP-cured system has the lowest viscosity. In peroxide and mixed cured systems PP was degraded in the presence of DCP. The die swell values of the blends are decreased on dynamic vulcanization. The temperature dependence of viscosity was studied by use of the Arrhenius equation. The compatibilized system showed higher values of activation energy compared with uncompatibilized one. A shear rate– temperature superposition master curve has also been developed for polypropylene and 70/30 PP/NBR blends. The melt-flow index of PP/NBR blends decreased with increasing rubber concentration and correlated the MFI values obtained from capillary rheometer data, so that a master curve was obtained for different blend compositions. The effect of annealing on the morphology of uncompatibilized and compatibilized blends has been investigated. The domain size of NBR particles increased in the uncompatibilized system upon annealing the samples for 1 h. interestingly, the morphology of the compatibilized system was really stable.

S. George et al [36], have reported the thermal stability and crystallization behaviour of isotactic polypropylene (iPP)/nitrile rubber (NBR). The effects of blend ratio, compatibilization and dynamic vulcanization on thermal stability were investigated. The thermal degradation of PP/nitrile rubber blends was investigated using the thermogravimetric method. It was found that the incorporation of nitrile rubber into PP improved the thermal properties of PP. The initial degradation temperature of PP was increased upon blending with nitrile rubber. Among the three blend compositions, the P_{50} blend showed the lowest degradation temperature. The thermal behaviour of various blend compositions was correlated with blend morphology.

The weight loss corresponding to different temperatures was also decreased upon blending. The effect of compatibilisation of PP/NBR blend using phenolic modified PP and maleic anhydride modified PP on thermal degradation was also investigated. The compatibilisation increased the degradation temperature. The dynamic vulcanisation of the blends using sulphur, peroxide and mixed system consisting of sulphur and peroxide improved the thermal stability. Among the three vulcanised systems, the mixed vulcanised system showed the highest degradation temperature and sulphur-cured system showed the lowest value. The thermal behaviour of three types of dynamic vulcanised blends was correlated with the type of crosslinks formed. The melting behaviour of binary PP/NBR blends was also investigated using DSC. The melting temperature and heat of fusion values were decreased on the addition of NBR. The crystallinity of PP/NBR blends also decreased with increase in nitrile rubber concentration. The crystalline structure of PP/NBR blends was also investigated. The pure PP and the blends showed a-monoclinic structure as shown by the presence of four reflections corresponding to the four planes. The compatibilisation of the blends did not affect thea-monoclinic crystalline structure of PP. The incorporation of nitrile rubber into PP was found to increase the interplanar distance, which indicated the presence of rubber phase in intra spherulitic regions.

Compatibilization of Polypropylene / Nitrile Rubber (PP/NBR) blend using electron beam irradiation in presence of polyfunctional monomers was investigated by **H.A.Youssef et al [37].** The mechanical properties and scanning electron microscope (SEM) measurements were performed for different ratios of PP/NBR blends 20/80, 30/70, 40/60, 50/50, 60/40, 70/30 and 80/20. The results obtained indicate that increasing PP% was accompanied by sharp increase in the tensile strength at 40% PP concentration. SEM micrograph showed that for 40/60 ratio both NBR and PP form co-continuos phases. The mechanical properties, TGA, DSC and FTIR measurements for the loaded blends with polyfunctional monomers demonstrate their effectiveness as compatibilizing agents even at low concentration (3%) and irradiation dose (20 kGy). The compatibility of the blends was reflected by the improvement of the tensile strength and thermal stability.

In another study of **J. Pan and coworkers [38]**, four kinds of compatibilizers—chlorinated polyethylene (normal CPE), highly chlorinated CPE, maleic anhydride grafted with polypropylene (PP-g-MA), and chlorinated polypropylene (CPP) were used to study the influence of compatibilizing agents on the properties of nitrile-butadiene rubber and polypropylene (NBR/PP) thermoplastic elastomer blends. The results show that the most proper amount of normal CPE, highly chlorinated CPE, PP-g-MA, and CPP are 9, 8, 7, and 6 wt%, respectively, in the NBR/PP blends. The CPP was the best compatibilizer for NBR/PP blends among the four compatibilizers. NBR/PP blends obtained excellent properties of thermoplastic materials and can be molded with the general processing technologies for thermoplastics, such as injection, and extrusion.

In another article, **X.Zhang and coworkers [39]** have studied the effects of compatibilization of Nitrile Rubber/Polypropylene thermoplastic vulcanizate (TPV) blends using Glycidylmethacrylate(GMA) grafted PP/amino-compound as a compatibilizer in the mechanical properties. The preparation of uncompatibilized as well as compatibilized NBR/PP thermoplastic elastomer was performed at temperature of 200°C and a rotor speed of 80 rpm in a Haake Rheocord 90 batch internal mixer. The effects of the curing systems, compatibilizers, PP type, on the mechanical properties of NBR/PP TPE samples were also investigated. Experimental results showed that the addition of amino-compound in the compatibilizer can significantly increase the mechanical properties of the NBR/PP thermoplastic elastomer. Compared with other amino-compounds, diethylenetriamine (DETA) has the best effect. PP with higher molecular weight is more suitable for preparing NBR/PP thermoplastic elastomer with high tensile strength and high elongation at break. These effects of compatibilizers could be attributed to improve and enhance the interfacial adhesion and reduce the interfacial tension between the two polymer phases (i.e: NBR, and PP).

In another study, **B.G. Soares et al [40]** have reported the compatibilization of the Thermoplastic vulcanizates based on PP/NBR (50/50 %wt) which have been prepared by dynamic vulcanization, using reactive phenolic resin as the curing system with $SnCl_2$ as a catalyst and maleic anhydride-functionalized PP (PP-g-MA) as well as carboxylated NBR (XNBR) as the compatibilizing agent system. Triethylenetetramine (TETA) was also employed to promote the reaction between the functionalized polymers. The effect of blending procedure and vulcanization time on the morphological and mechanical properties has been evaluated for uncompatibilized and compatibilized TPV's. The evolution of the morphology before vulcanization was also investigated. From their results, Compatibilized and vulcanized samples showed an improvement on the elongation at break as well as a morphology property by fine vulcanize rubber particles which dispersed inside in the PP matrix. This phenomenon can be attributed to phase inversion. The best mechanical and morphological performances have been achieved when TETA was previously reacted with PP-g-MA before the addition of rubber components (NBR/XNBR).

In another publication, **B.G. Soares and co-workers [41]** have investigated the effect of Peroxide/Bis-Maleimide Curing System and Different Compatibilizing Systems on the mechanical properties of PP/NBR TPV samples. The efficiency of dicumyl peroxide (DCP) in combination with N,N'-m-phenylene-bismaleimide (BMI) as a crosslinking system for the polypropylene (PP)/nitrile rubber (NBR) (30 : 70 wt %) thermoplastic elastomers was investigated in the presence of two compatibilizing agents namely: maleic anhydride-grafted-PP (PP-g-MA)/amino compound and glycidyl methacrylate-grafted-PP (PP-g-GMA) with or without amino compound. They were employed in a proportion of 5 wt % together with different amounts of carboxylated NBR (XNBR). The mechanical properties of the compatibilized blends as well as uncompatibilized ones were evaluated by means of tensile test and compression set. Excellent mechanical properties were achieved without the addition of compatibilizer, suggesting that BMI should act as compatibilizing agent. The other functionalized systems exerted an additional improvement on tensile properties and reprocessing ability. The PP-g-MA/TETA/XNBR, PP-g-GMA/TETA/ XNBR, and PP-g-GMA/XNBR are efficient compatibilizing systems, since they promote an improved tensile properties and compression set when compared with noncompatibilized blend.

H. Ismail et al [42], have studied the compatibilizing effect of epoxy resin (EP) on polypropylene (PP)/recycled acrylonitrile-butadiene rubber (NBRr) blends. This new method was used to prepare thermoplastic elastomers based on polypropylene (PP)/recycled acrylonitrile-butadiene rubber (NBRr) with improved mechanical properties. An epoxy resin (EP) was used as a compatibilizing agent. The effect of EP on mechanical properties, swelling percentage, and morphological characteristics of the blends was investigated with different blend compositions. The results showed that the incorporation of EP has improved the tensile strength, Young's modulus, and elongation at break of PP/ NBRr-EP blends compared with PP/NBRr blends. The enhancement of tensile properties of PP/NBRr-EP blends is due to the better adhesion between the two phases with the incorporation of EP. This is quite evident by scanning electron microscopy of tensile fractured surfaces. PP/NBRr-EP blend exhibits lower stabilization torque and swelling percentage than PP/NBRr blends. The lower stabilization torque is an indication of better processing characteristics.

A. M. Motawie and coworkers [43], have studied the compatibility between Polypropylene and Acrylonitrile Butadiene Rubber TPE Blends. Blends of polypropylene (PP) and acrylonitrile-butadiene rubber (NBR) were prepared with different weight compositions with a plasticorder at 180°C at a rotor speed of 60 rpm for 8 min. The physicomechanical properties and mass swell of the prepared blends were investigated with special reference to the effects of the blend ratio. The prepared epoxidized linseed oil (EL) (i.e., E0.5L, E1L, E1.5L, and E2L using 0.5, 1, 1.5, and 2 mol H_2O_2/mole of unsaturation in linseed oil) and maleic acid anhydride (MA) were melt mixed in various contents (i.e., 1, 5, 10, and 15 wt %) with a PP/ NBR blend with a weight ratio of 70/30 and used as compatibilizers. The effects of the compatibilizer contents on the physicomechanical properties and mass swell of the binary blend were investigated. They have found that with an increase in the compatibilizer content up to 10 wt %, the blend showed an improvement in the physicomechanical properties and reduced mass swell in comparison with the uncompatibilized one. The addition of a compatibilizer beyond 10 wt % did not improve the blend properties any further. The efficiency of the compatibilizers (10 wt%) was also evaluated by studies of phase morphology.

Dilini Galpaya et al [44] investigated the effects of PP-g-MA on the physical properties and morphology of polypropylene (PP)/recycled acrylonitrile-butadiene rubber (NBRr) blends. The blends were prepared by melt mixing using a Haake Rheomix Polydrive R 600/610 mixer at 180°C. The processing torque was used to investigate the mixing process. The better mixing of compatibilized blends (PP/NBRr-MA) was evidenced by the higher stabilization torque. Compared to uncompatibilized PP/NBRr blends, tensile properties and oil resistance of compatibilized PP/NBRr were improved. SEM micrographs of tensile fractured surfaces showed better dispersion and better interfacial adhesion between the phases of compatibilized blends compared to uncompatibilized counterparts.

The Effects of Recycled Acrylonitrile Butadiene Rubber Content and Maleic Anhydride Modified Polypropylene (PP-g-MAH) as a compatibilizer on the Mixing, Tensile Properties, Swelling Percentage as well as Morphology of Polypropylene/Recycled Acrylonitrile Butadiene Rubber/Rice Husk Powder (PP/NBRr/RHP) Composites were examined by **H. Ismail et al [45]**. The effect of recycled acrylonitrile butadiene rubber (NBRr) content and PP-g-MAH as a compatibilizer on the properties of PP/NBRr/RHP composites were examined using a Haake Rheomix at 180°C, 60 rpm for 9 min. Results showed that higher stabilization torque, Young's modulus and tensile strength were obtained for PP-g-MAH compatibilized composite as compared to uncompatibilized composites. However, for elongation at break (Eb) and swelling percentage of compatibilized composites exhibited lower values than uncompatibilized composites. The increase of NBRr content in both compatibilized and uncompatibilized composites resulted in higher stabilization torques, swelling percentage and elongation at break but lower tensile strength and Young modulus. Tensile fractured surfaces observed by scanning electron microscopy showed good adhesion between NBRr and PP matrix and better dispersion of RHP for the compatibilized composites.

Ming Tian et al [46] have reported the effect of the compatibility on the morphology and properties of acrylonitrile-butadiene rubber/polypropylene Thermoplastic Vulcanizates (TPVs). The morphologies of three types of acrylonitrile-butadiene rubber (NBR)/polypropylene (PP) thermoplastic vulcanizates (TPVs) (with an NBR/ PP blend ratio of 70/30) were compared. The TPVs were (1) an ultrafine fully vulcanized acrylonitrile-butadiene rubber (UFNBR)/PP TPV made by the mechanical blending of UFNBR with PP, (2) a dynamically vulcanized NBR/PP TPV without the compatibilization of maleic anhydride grafted polypropylene (MP) and amine-terminated butadiene–acrylonitrile copolymer (ATBN), and (3) a dynamically vulcanized NBR/PP TPVs with the compatibilization of MP and ATBN. The influence of the compatibility therein on the size of the dispersed vulcanized NBR particles and the crystallization behavior of the PP in the TPVs and the resultant properties are also discussed. As indicated by Fourier transform infrared spectroscopy, scanning electron microscopy, differential scanning calorimetry, polarizing microscopy, dynamic mechanical thermal analysis, and rheological and mechanical testing, the compatibility was significantly improved by the reactive compatibilization of MP and ATBN, which led to a uniform and fine morphology. The compatibilization increased the crystallization rate and reduced the size of the spherulites of PP. On the other hand, it was found that the dispersed vulcanized NBR particles lowered the degree of crystallinity. The better the compatibility of the blend was, the lower the degree of crystallinity and the storage modulus were, but the higher the loss factor and the processing viscosity were. All TPVs showed almost the same oil resistance, but the TPV prepared with reactive compatibilization had the best mechanical properties.

G.M. Mamoor and co-workers [47] have studied the Effects of Recycled Polypropylene and compatibilizing agent on the Mechanical and Rheological Properties of Polypropylene-NBR Thermoplastic Vulcanisates. Virgin polypropylene (PP), recycled polypropylene (RPP) and acrylonitrile butadiene rubber (NBR) were mixed together to prepare ternary blends (PP/ RPP/NBR) of thermoplastic vulcanisates (TPVs). The blends comprised 30 parts per hundred (phr) NBR and 70 phr PP and RPP. Sulphur was used to dynamically crosslink the NBR during the blending process. Maleic anhydride grafted polypropylene (MA-g-PP) was used as compatibiliser to enhance the interaction of the polypropylene and the rubber. The loading of RPP as well as PP-g-MA in the PP/NBR TPE system at the previous properties were studied. They have found that the hardness and the tensile strength of the TPVs increased upon increasing the RPP loading. The RPP exhibited an adverse effect on elongation at-break of the vulcanisates, with the pseudo-plastic flow behaviour and the viscosity of the vulcanisates increasing with the increased loading of RPP.

In another study, **Chuanhui Xu et al [48]** have demonstrated a new approach to compatibilization of polypropylene (PP) and acrylonitrile butadiene rubber (NBR) using maleic anhydride grafted polypropylene (MA-g-PP) as a compatibilizer in the presence of zinc dimethacrylate (ZDMA). PP/NBR/ZDMA/MA-g-PP blends have been successfully prepared through dynamic vulcanization, using DCP as a curing agent. The mechanical, morphological, Dynamic Mechanical and Thermal properties were also investigated by means of tensile test, Scanning Electron Microscopy, Dynamic Mechanical Thermal analysis, and Differential Scanning Calorimetry. It was observed that ZDMA increased the interfacial bonding between NBR and PP matrix. The incorporation of MA-g-PP further increased the mechanical properties of the resultant blends. As a result, and as demonstrated by SEM, DMA, and DSC studies, the integration of MA-g-PP results in that more ZDMA diffused from NBR to the interface between PP and NBR. Also, the possible creation developed from the polymerization of ZDMA combined with MA-g-PP increased the interface adhesion and compatibility between PP and NBR phases, which contributed to the considerable improvement in mechanical properties of the resultant blends.

In another publication**, Chuanhui Xu et al [49],** have studied the compatibilization between polypropylene (PP) and nitrile butadiene rubber (NBR) by using zinc dimethacrylate (ZDMA) as a reactive compatibilizer in the presence of peroxides. The PP/NBR/ZDMA ternary blends were successfully prepared via peroxide dynamic vulcanization. The mechanical behavior, Morphological examination, as well as thermal properties were also investigated. They have found that the mixing torque and complex viscosity of the blends with ZDMA are significantly increased. Morphology studies showed that the addition of ZDMA reduced the size of the crosslinked NBR phase. According to the transmission electron microscopy (TEM) combined with scanning electron microscopy (SEM) verified that the possible reactions between ZDMA, NBR, and PP increased the interfacial thickness and improved the compatibility between NBR and PP phases. The addition of ZDMA might promote the nucleation process of PP and increase PP crystallinity. Thermal gravimetric analysis (TGA) showed that the maximum degradation temperature was increased by ZDMA.

In another paper, **A. E. Zaikin and G. B. Bobrov [50]** have investigated the Compatibilization of Polypropylene and Butadiene–Acrylonitrile Rubber Using an Organic Peroxide and an Oligoether Acrylate. The relationships and causes of changes in the deformation and strength properties of PP/NBR blends with variation of the content of an organic peroxide, 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane, and an oligoether acrylate, triethylene glycol dimethacrylate were also reported. The observed changes in the deformation and strength properties of the blend were accounted for on the basis of the experimental data on the density of the vulcanization network of the butadiene–acrylonitrile rubber, on the morphological structure of the blend, on the adhesion between the two polymers, and on the degree of crystallinity and molecular mass of polypropylene. It was also found that the Introduction of peroxide and oligoether acrylate into a blend of polypropylene and butadiene–acrylonitrile rubber leads to a significant increase in the strength and elongation at break of the material. This increase is caused by enhancement of the adhesion between the polymeric components, strengthening of the butadiene–acrylonitrile rubber phase due to vulcanization, and formation of the morphological structure characteristic of thermoplastic elastomers, a thermoplastic matrix in which fine particles of the vulcanized elastomer are distributed. In addition, incorporation of oligoether acrylate jointly with peroxide into the blend of polypropylene and butadiene–acrylonitrile rubber reduces the destructive action of peroxy radicals on polypropylene, which leads to strengthening of the polypropylene matrix and of the blend as a whole.

The compatibilizing effects of polypropylene –grafted- maleic anhydride (PP-g-MA) on the mechanical and morphological properties of polypropylene (PP)/ acrylonitrile butadiene rubber (NBR)/palm kernel shell (PKS) composites were investigated by **Ragunathan Santiago et al [51].** The composites were melt mixed using heated two roll mills at 180°C and a speed of 15 rpm with six different loadings (100/0/10, 80/20/10, 70/30/10, 60/40/10, 50/50/10, 40/60/10 phr) with fixed 5 phr of PP-g-MA. The mechanical behavior and Morphological examination were also investigated. Tensile strength and Young’s modulus decreased but elongation at break increased with increasing NBR loading of both PP/NBR/PKS and PP/NBR/PKS compatibilized composites. The results showed that PP-g-MA compatibilized composites exhibited enhanced tensile strength and Young's modulus compared to those of uncompatibilized ones. Tensile fractured surfaces observed by scanning electron microscopy (SEM) indicates improved adhesion of palm kernel shell with polypropylene/acrylonitrile butadiene rubber matrix in the presence of polypropylene – grafted- maleic anhydride.

In another study, **Anna Paula Azevedo et al [52]** have studied the effect of rotor speed during polymer mixing and the dynamic vulcanization process of polypropylene and nitrile rubber NBR/PP blends. Bis-maleimide was used and employed as multipurpose agent (crosslinking coagent for peroxide and compatibilizer). Morphology, mechanical properties, compression set and oil resistance tests were evaluated for compositions containing 50 and 70 Phr of elastomer. The compatibilization of TPV was realized by infrared spectroscopy which showed a compatibilizer effect and better dispersion, achieving the inversion phase, only studying the effect of processing conditions (rotor speed, addition sequence, additives), without any extra interfacial agent. There is an observed trend towards improved performance when reducing the speed during dynamic vulcanization and/or torque stabilization, particularly for blends containing 50 Phr of rubber. According to the results shown in their work, TPVs based on PP/NBR with morphology and reasonable properties were successfully achieved without the use of plasticizer or another compatibilizer agent, only studying the effect of processing conditions as the rotor speed. Further, the multipurpose action of BMI coagent was shown. The torque rheometer results shows that reducing rotor speed on dynamic vulcanization and increase it on mixing torque stabilization provides the best values of elastic torque, better dispersion of vulcanizes domains on PP matrix and major stability to TPV, besides decreasing the energy expenditure of the process. The speed and lower rubber content affected the crosslinking density of PP/NBR blends improving the tensile properties. The compression set shows that profile provides greater crosslinking density to elastomeric phase in PP/NBR 50/50 blends. On the other hand, the profile was really better for crosslinking efficiency and was confirmed by oil resistance. Finally, decrease rotor speed of internal mixer during dynamic vulcanization or/and return to initial speed at mixing torque stabilization stage exerted a strong influence on the final properties. It allows development a material that can join the elasticity of rubber and the thermoplastic easy process, enabling the development of a TPV through a more economical process, using known materials and favoring reprocessing conditions.

In another work, **Fei Lv et al [53]** have prepared PP/EPDM/butadiene acrylonitrile rubber (NBR) ternary TPVs with good oil resistance by core-shell dynamic vulcanization. Based on the theoretical analysis of the spreading coefficient and the examination of transmission electron microscopy results, it was observed that the rubber phases displayed a distinct core-shell structure. Specifically, the cross-linked NBR-core was enveloped by the EPDM-shell. This core-shell arrangement played a crucial role in enhancing the interfacial compatibility between the PP and NBR phases. By preventing direct contact between them, facilitated by the presence of the EPDM-shell, the mechanical properties of the thermoplastic vulcanizate (TPV) were effectively improved. In addition, the oil resistance of PP/EPDM TPV also improved with the introduction of NBR.

In another article, **Amir Bakhtiari et al [54]** have applied the response surface methodology (RSM) to simultaneously optimize the tensile and impact strength of polypropylene (PP)/nitrile butadiene rubber (NBR)/halloysite nanotubes (HNTs)/maleic anhydride (MA)-grafted PP nanocomposites. The experimental design incorporated Box-Behnken's design principles and involved the utilization of three different levels for the material parameters. These parameters included NBR (at 10, 20, and 30 wt%), HNTs (at 1, 3, and 5 wt%), and PP-g-MA (at 3, 9, and 15 wt%) as compatibilizers. In order to investigate the morphology of nanocomposite samples, a scanning electron microscope was used. As a result, All material parameters had significant effects on the responses, and their two-way interactions also affected the responses. Also, an increase in HNT content reduced rubber particles size. In addition, PP-g-MA refined the dispersion of HNTs and also caused their better adhesion with the matrix. It also resulted in the reduction of interfacial tension between NBR and PP.

The melting and crystallization behaviors of isotactic polypropylene (iPP)/acrylonitrile-butadiene rubber (NBR) blends were investigated by **A.Joseph et al [55]** using differential scanning calorimetry. The samples were scanned at a heating rate of 20°C/min in a nitrogen atmosphere. The effects of blend ratio, compatibilizers (PP-g-MA, and Ph-PP), and fillers (high-abrasion furnace black (HAF-N 330) and silane-treated silica (TSi)) addition on the melting and crystallization characteristics of the blends were analyzed. Analysis showed that blend ratio had a predominant effect on the values of onset of crystallization and crystallization temperature, although the heat of fusion (ΔH_f), the onset of melting, and melting temperature were unaffected. The presence of compatibilizer in the blend had an appreciable influence on the crystallization behavior. ΔH_f, the heat of crystallization, and percentage crystallinity of the compatibilized blends were higher than those of the uncompatibilized blends. Fillers had little impact on the melting behavior of the blends. The morphology of the blends was analyzed with scanning electron microscopy. Hot-stage polarizing optical microscopy was used to study the spherulitic morphology of PP on the addition of NBR. The addition of a few percentages of NBR significantly reduced the average spherulite size of PP in the blend followed by a marginal decrease. The blend ratio had a pronounced impact on the growth rate of PP spherulite.

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Chapter

II

Materials and Experimental Procedures

II.1 Introduction

The materials and experimental methods used for the present investigation are discussed in this chapter. A brief account of the material characteristics, the compatibilizers preparation and characterization of the blends is given. Different instrumentation techniques used for the characterization of the samples are explained. The different methods include spectroscopic structural analysis; melt rheological behavior, mechanical property measurements, dynamic mechanical analysis, scanning electron microscopic analysis, atomic force microscopy, differential scanning calorimetry, and thermogravimetric analysis are also given.
The section covering blend preparation is divided into two parts:

I-First part: Preparation of compatibilizing agents from 50/50 ENR/PP-g-MA blends;

II-Second part: Preparation of the CA-containing 50/50 NBR/PP systems.

It should be remembered that the main objective of this work is to:

1- Study the effect of the incorporation of two types of compatibilizing agents (i.e: ENR_{25}/PP-g-MA, and ENR_{50}/PP-g-MA) at different concentrations: 5, 10, and 15 Phr on the rheological, mechanical, dynamic mechanical, morphological, and thermal properties of the 50/50 NBR/PP blend.

2- Study the effect of the epoxidation level: two levels of epoxidation in ENR (i.e: ENR_{25} and ENR_{50} with 25 and 50 mole % epoxide, respectively) were used to prepare the CAs-containing NBR/PP blends.

II.2 Materials used

The characteristics of the materials used in this study are listed below:

II.2.1 Polymers

- **Nitrile Rubber (NBR)**

The NBR was of a commercial grade (NBR-3305) and was supplied by Synthetics and Chemicals, Bareli, UP, India. Acrylonitrile–butadiene rubber having an acrylonitrile content of 34% with a density of $1g/cm^3$ and a Mooney viscosity $M_L(1+4)100$ of 50.

- **Epoxidized natural rubber (ENR)**

The ENR grades contained either 25 or 50 mol % epoxidation (denoted furtheron ENR_{25} and ENR_{50}, respectively) were obtained from Kumpulan Guthrie Sdn.Bhd., Seremban, Malaysia. The Mooney viscosities measured at M_L (1+4) 100 °C were 110 (ENR_{25}) and 140 (ENR_{50}). Their glass transition temperatures were -47 °C, -24°C, and a density of 0.97gr/cm^3, and 1.2gr/cm^3, respectively.

- ★ **Polypropylene (PP)**

The Polypropylene PPH 3060 was of commercial grade and was supplied by Songhan Plastic Technology (China). PP 3060 was a commercial extrusion grade (PP Homopolymer 3060) from Fengxian District, Shanghai City-China , having a density of 0.90 g/cm^3 and a melt flow index (MFI) (230°C/ 2.16 Kg) of 1.7 g/10 min.

- ★ **Poly(propylene-g-maleic anhydride) (PP-g-MA)**

Poly (propylene-g-maleic anhydride) Polybond **3200** homopolymer with a MFI of 9g/10 min (ASTM D-1238) at 190°C and 1.2 wt% maleic anhydride content was purchased from CHEMTURA, USA.

A full description of the polymers used is given in **Table II.1**

Table II.1 Description of the polymers used in this study.

Materials	Commercial designation	Supplier	Properties
NBR	NBR-3305	Synthetics and Chemicals, Bareli, UP, India.	Mooney viscosity M_L (1+4) = 50 at 100 °C d=1.00 g/cm^3
ENR_{25}	Epoxyprene $_{25}$	Kumpulan Guthrie Sdn.Bhd., Seremban, Malaysia.	Mooney viscosity M_L (1+4) = 110 at 100 °C d=0.97 g/cm^3
ENR_{50}	Epoxyprene $_{50}$	Kumpulan Guthrie Sdn.Bhd., Seremban, Malaysia.	Mooney viscosity M_L (1+4) = 140 at 100 °C d=1.2 g/cm^3
PP	PP Homopolymer 3060	Songhan Plastic Technology (China).	MFI= 1.7 g/10 min,d= 0.90 g/cm^3
PP-g-MA	Maleic Anhydrid-grafted Polypropylene Polybond **3200**	Sig Chemtura, USA	MFI=9 g/10 min,d= 0,91 g/cm^3

II.2.2 Compatibilizers

The compatibilizers that will be referred to as CA_{25} and CA_{50} were a 50/50 blend of ENR_{25}/PP-g-MA and ENR_{50}/PP-g-MA respectively. The CAs were prepared using a Brabender Plastograph^{EC} internal mixer preheated at 180°C, using a cam-type mixer with a rotor speed of 60 rpm.

II.2.3 Chemicals

The solvents used; namely: toluene, deuterated toluene-d8, xylene, tetrahydrofuran (THF) deuteratedchloroform-d8 ($CDCl_3$), and cyclohexane were of a laboratory reagent grade material and were purchased from Sigma-Aldrich (Germany).

II.3 Experimental procedures

II.3.1 Compatibilizing agents and blends preparation

Melt mixing of CAs as well as TPE blends were carried out in a Brabender Plastograph internal mixer (model EC) with a mixing chamber of 80 cm^3 (**Figure II.1**). The mixer was heated at 180°C, and mixing was carried out using a cam-type mixer with a rotor speed of 60 rpm.

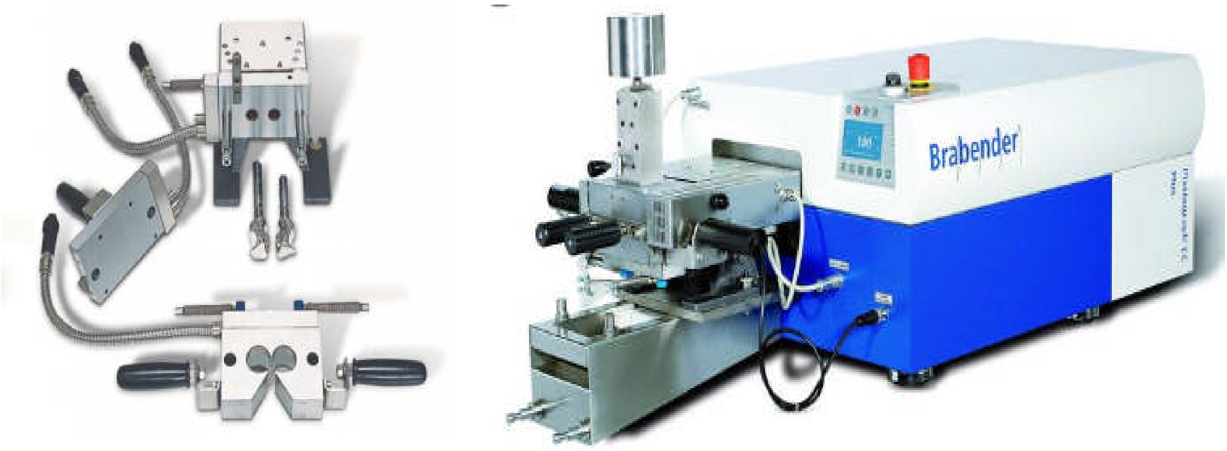


Figure II.1 Brabender Plastograph^{EC} internal mixer.

II.3.1.1 Preparation of the ENR/PP-g-MA compatibilizers (CAs)

PP-g-MA was first incorporated into the mixing chamber of a Brabender Plastograph and preheated for 5 minutes without rotation at 180°C. The polymer was then melt mixed for 3 minutes at a rotor speed of 60 rpm. ENR was then added and mixing was continued for 4 minutes. The final product was cut into small pieces.

II.3.1.2 Preparation of TPE based on NBR/PP blends

In this study, all the NBR/PP blends contained 50/50 rubber to plastic ratio. In a typical procedure, the control 50/50 NBR/PP blend was prepared by first introducing PP in the mixing chamber and preheated for 5 minutes without rotation, and it was let to melt mixed for 2 minutes at a rotor speed of 60 rpm. Then NBR was added and the two polymers were allowed to blend for 10 minutes. At the end of the mixing process, the molten mixtures were removed from the plastograph chamber, and cooled down in open air to room temperature.

The blends containing the compatibilizing agents CA_{25} and CA_{50} were prepared in the internal mixer chamber at a three-step process. First, neat PP was introduced and sheared for 2 minutes. The compatibilizing agents were added and mixed for 4 minutes. Finally, the neat NBR was added and mixed with PP/Compatibilizer for 4 minutes. The compositions and designations of the different studied TPEs are presented in **Table II.2**.

Table II.2 Compositions and designations of the different TPE blends in parts per hundred parts of rubber (phr).

Materials	**Compositions, content (phr)**								
Designations	**CA_{25}**	**CA_{50}**	**B0**	**B1**	**B2**	**B3**	**B4**	**B5**	**B6**
NBR	-	-	50	50	50	50	50	50	50
PP	-	-	50	50	50	50	50	50	50
ENR_{25}/PP-g-MA	50/50	-	-	5	10	15	-	-	-
ENR_{50}/PP-g-MA	-	50/50	-	-	-	-	5	10	15

II.4 Moulding of samples

The samples for testing were stamped out from 1 mm thick sheets prepared by compression molding at 180°C and using an electrically heated hydraulic press (Gumix- hydraulic press Model Guix-TP 300/450/1). Teflon sheets were used to allow an easy release of mouldings. The following procedure was used:

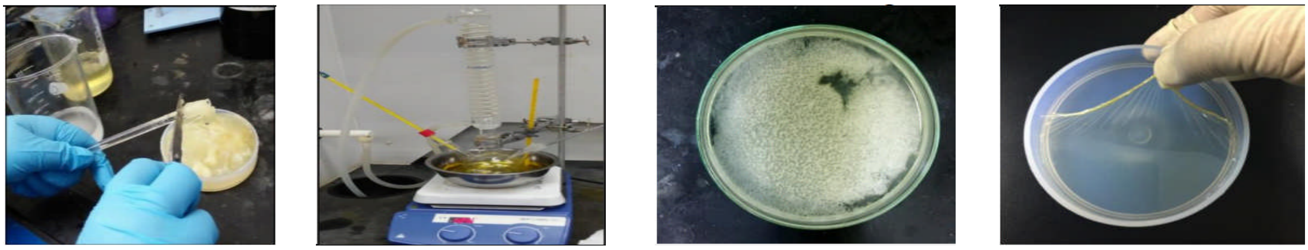
First the sheeted blend was put into the cavity of a square mold and pressed under 50 bars for 5 minutes before lowering the pressure back. Second, without taking out the platens the pressure was raised to 150 bars and the material was pressed for 2 minutes. After releasing the pressure again, a final pressure of 200 bars was applied for 8 minutes. Finally, the cooling took place inside the hydraulic press under cold water circulation.

II.5 Characterization techniques

II.5.1 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra were obtained using a Perkin-Elmer spectrum one series equipment and the attenuated total reflection (ATR) technique was adopted. The selected spectrum resolution and the scanning range were 4 cm^{-1} and 650-2000 cm^{-1}, respectively.

FTIR samples of PP-g-MA, CA_{25}, and CA_{50} were obtained by pressing in an electric press heated at 180°C under a pressure of 150 $kg.cm^{-2}$. But for ENR_{25} and ENR_{50}, it was not possible to obtain thin films by pressing because the material, at such a high temperature, sticks to the Teflon film used to cover the plates. As a result, the specimen were prepared using the casting method (**Figure II.2**), which consisted of dissolving small chunks (approximately 80 mg) as shown in **Figure II.2.1** in toluene at 80°C for ENR_{25} and in tetrahydrofuran (THF) at 40°C for ENR_{50} under continuous stirring for 12 h (**Figure II.2.2**). The resulting solutions were then poured on glass plates (**Figure II.2.3**), and after drying at room temperature, thin films were peeled off (**Figure II.2.4**).



(1) (2) (3) (4)

Figure II.2 Chemical method for the preparation of thin films of ENRs.

II.5.2 Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR)

The ^{1}H-NMR experiments were performed on a Bruker 400 MHz instrument operating at 400 MHz. The spectra were acquired and processed using the Mestre-Nova software. Deuterated Chloroform and Toluene-d8 were used as solvents as well as internal references $\delta\ [^1H]_{CHCl3}$= 7.26 ppm and $\delta\ [^1H]_{Toluene\text{-}d8}$= 2.08 ppm. Before analysis, a sample of PP-g-MA (about 30 mg) was dissolved in Toluene-d8 (0.7 mL) at 25°C in a 10 mm Wilmad NMR tube (Sigma-Aldrich). However, ENR_{25}, and ENR_{50} were dissolved in Deuterated chloroform $CDCl_3$.In this part also, great efforts have been made to dissolve the compatibilizing agents in many solvents, namely: toluene, deuterated toluene-d8, hot xylene, tetrahydrofuran, and deuterated chloroform-d8.Once the sample was completely dissolved, the tube was inserted in the spectrometer; the homogeneity of the magnetic field (shims) was carefully adjusted before acquisition. **[1]**

II.5.3 Rheological Measurements

II.5.3.1 Brabender Plastograms

The study of the rheological behavior of CAs as well as the TPE blends was performed using the rheograms giving the variations of the torque as a function of mixing time, recorded during the blends melt mixing within the internal mixer.

II.5.4 Stress-Strain behaviour (Tensile Test)

The tensile test was performed on INSTRON-3366 testing machine using dumbbell specimens of Type 4 following the UNE-ISO 37 test method at a cross-head speed of 200 mm/min. and the machine recorded the load-extension curve. The tensile strength was calculated as the maximum load divided by the cross-sectional area of the specimen. Average values from seven measurements were calculated for each formulation.

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Chapter

III

Spectroscopic Structural Analysis, Melt Rheological and Mechanical Properties

III.1 Introduction

Upon blending ENR with PP-g-MA, these two polymers react with each other through their functional groups. Therefore, and in order to check this possibility, Fourier-Transform Infrared Spectroscopy (FTIR) was carried out. In addition to FTIR spectroscopy, there is another technique namely Nuclear Magnetic Resonance (NMR) which was also used for structure analysis.

III.2 Fourier transform infrared spectroscopy of the CAs

Figure III.1 (**a, b, c**) shows the FTIR spectra of PP-g-MA, ENR, and ENR/PP-g-MA blend respectively. The spectrum of PP-g-MA exhibits three characteristic bands at **1854**, **1785**, and **1710 cm**$^{-1}$. The first two bands are due to the symmetric and asymmetric C=O stretching vibrations of maleic anhydride while the last one is attributed to the vibration of the C=O group of an acid function. These bands are justified by the opening of the maleic anhydride ring because of its susceptibility to undergo hydrolysis **[1]**. On the other hand, the spectrum of ENR (**Figure III. 1 b**) presents three main bands at **1250**, **875**, and **840 cm**$^{-1}$. The first two bands correspond to the stretching of the epoxide group. The band which appeared at **840 cm**$^{-1}$ corresponds to the C=C groups of the polyisoprene (NR) chain.

The spectrum of ENR/PP-g-MA indicates that all the bands assigned to anhydride groups have disappeared because of their reaction with the epoxide groups of ENR. However, the epoxy characteristic groups bands at **1250**, **875**, and **840 cm**$^{-1}$ are still present. This suggests that not all the epoxy functional groups have reacted. Moreover, a new absorption band appears at **1735 cm**$^{-1}$. This band is due to the stretching vibration of the carbonyl groups (C=O) and is attributed to the formation of an ester function. These findings demonstrate that a chemical reaction occurred between PP-g-MA and ENR.They are in accordance with the chemical reaction mechanism proposed by C. Nakason et al. **(Scheme III.1) [1]**. According to this mechanism, the maleic anhydride group in PP-g-MA undergoes ring opening under the presence of moisture (H_2O) to produce succinic acid which further reacts with the epoxy groups of ENR to form epoxidized natural rubber-grafted polypropylene characterized by an ester and acid-based crosslink. The FTIR analysis allowed therefore confirming that mixing PP-g-MA with ENR resulted in a blend which has a structure that would compatibilize the NR/PP thermoplastic elastomer.

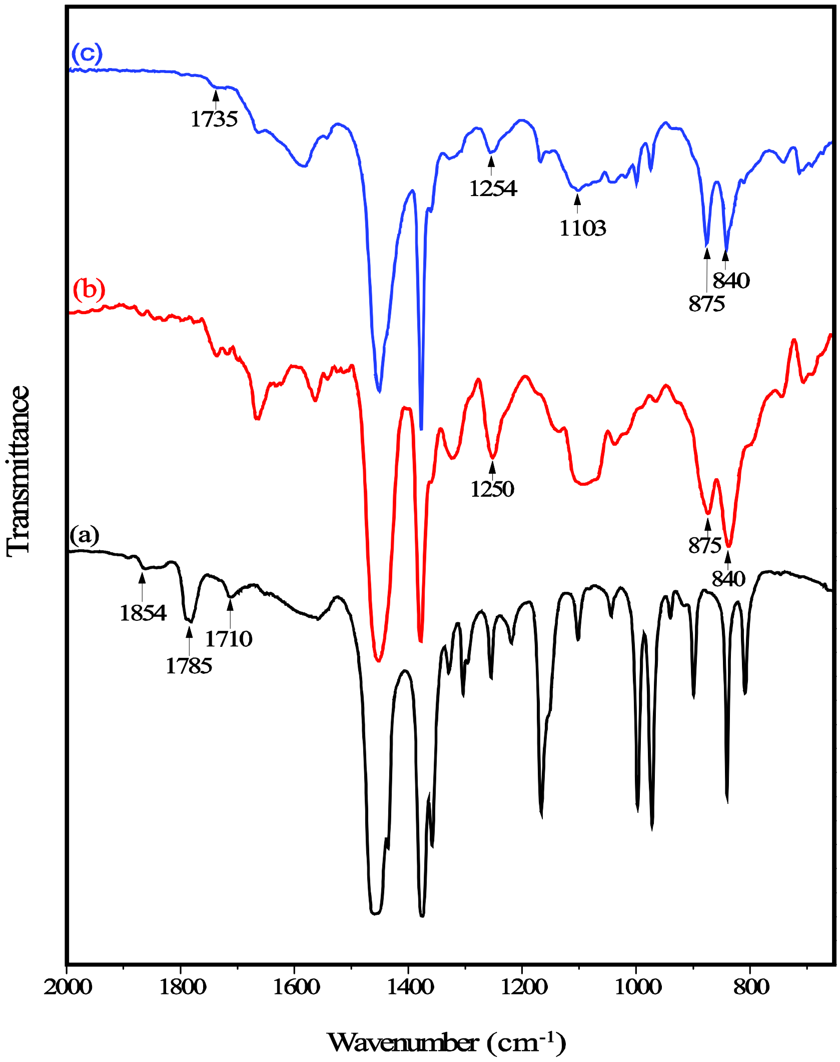
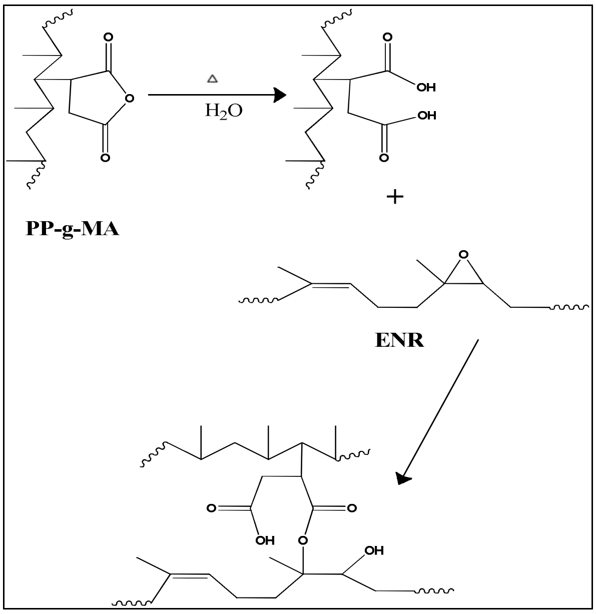


Figure III.1 FT-IR spectra of (a) PP-g-MA, (b) ENR_{25} and (c) ENR_{25}/PP-g-MA.



Scheme III.1 Possible mechanism of the chemical reaction between PP-g-MA and ENR molecules **[1]**.

III.3 Nuclear magnetic resonance spectroscopy of the raw materials

III.3.1 Characterization of the ENR structure

The ^{1}H-NMR technique was used to analyze the molecular structure and to determine the exact level of epoxide content in the ENRs. Deuterated chloroform ($CDCl_3$) was used to dissolve the ENR samples. The ^{1}H-NMR spectra of the ENRs are shown in **Figure III.2** and **Figure III.3** respectively. The integral values under these peaks at 2.7 and 5.1 ppm are taken to calculate the epoxide content in ENR according to Equation 2 **[2].**

$$Epoxide\ content\ (mol\%) = \frac{I_{2.7}}{I_{2.7}+I_{5.1}} \text{ x } 100 \ldots\ldots\ldots\ldots \textbf{(1)}$$

Where $I_{2.7}$and $I_{5.1}$ are the integrals of the absorption peaks at the chemical shifts of 2.7and 5.1 ppm, respectively. In this experiment, the integrals at chemical shifts of 2.7 and 5.1 ppm were 0.44 and 1.00 for ENR_{25}; 1.26 and 1.00 for ENR_{50}, respectively.

Table III.1 presents the exact level of epoxide content that was determined by ^{1}H-NMR technique.

Table III.1 Exact level of epoxide content determined by ^{1}H-NMR technique.

Epoxidized Natural Rubber	Epoxide content (mol %)
ENR_{25}	30.55 mol% epoxide groups
ENR_{50}	55.75 mol% epoxide groups

The ^{1}H-NMR spectrum of ENR_{25} (**Figure III**.**2**) shows the presence of signals at 5.1 and 2.7 ppm, assigned to the olefinic proton of cis-1,4-polyisoprenic structure and the methyne proton adjacent to the epoxide ring, respectively. The signal of methyl group adjacent to the epoxide unit was observed at 1.3 ppm. The residual unreacted unsaturation exhibited the signals of methyl and methylene protons next to the carbon– carbon double bond at 1.7 and 2.1 ppm, respectively. These results are in agreement with those of a recent work by Yokshan **[3]** and Hamzah et al **[4]**. The peak positions obtained from the ^{1}H-NMR spectrum of ENR are represented in **Table III.2**.

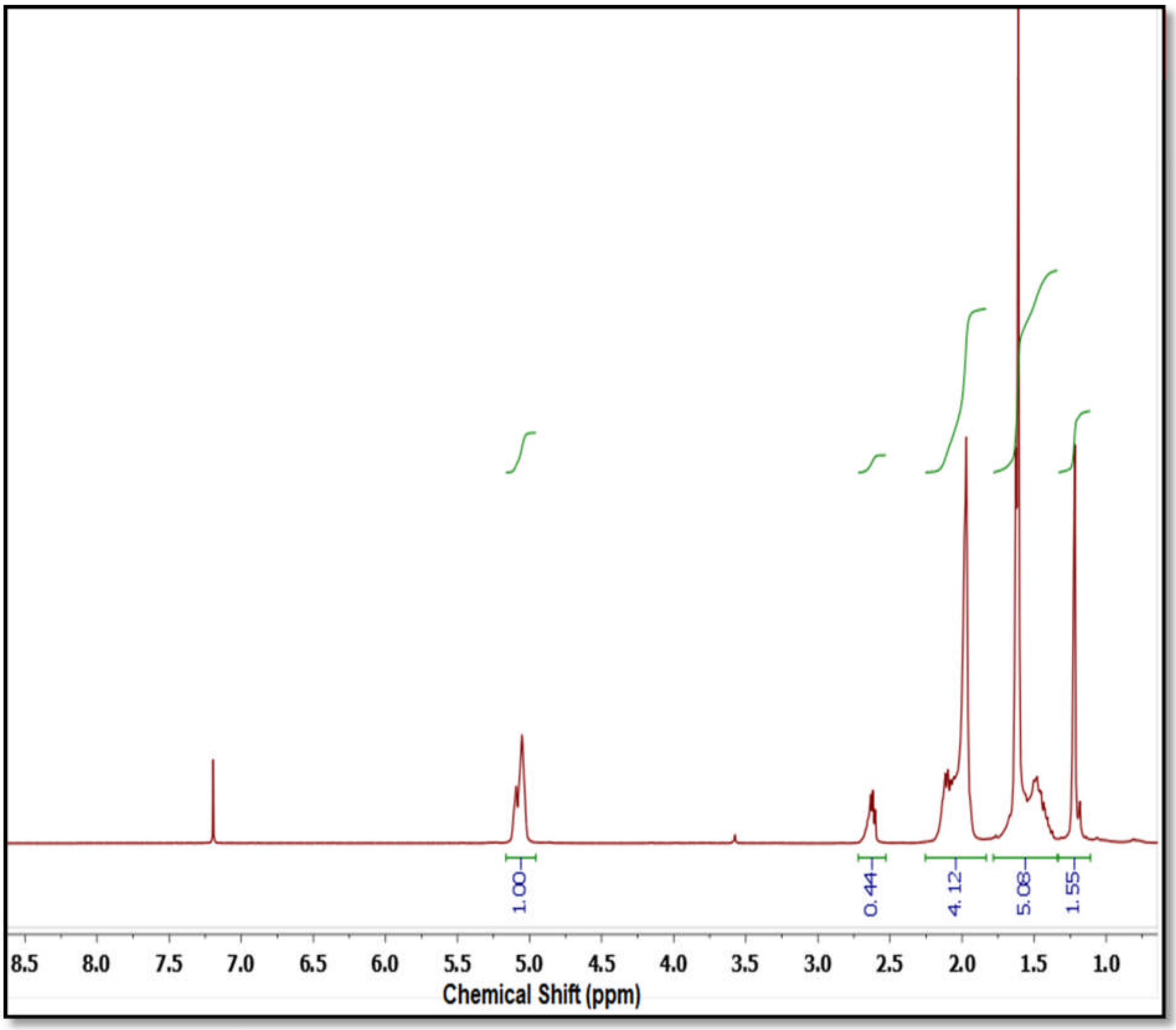


Figure III.2 ^{1}H-NMR spectrum of 25 mole% Epoxidized Natural Rubber in $CDCl_3$.

Table III.2 Peak assignments in the ^{1}H-NMR spectrum of ENR_{25}.

Peak position (ppm)	**Characteristic group**
1.3	Methyl of epoxy group
1.7	Methyl
2.1	Methylene
2.7	Methyne of epoxy group
5.1	Unsaturated methyne/olefinic hydrogen

The ^{1}H-NMR spectrum of the ENR_{50} which is presented in **Figure III.3**, shows the characteristic signals of methyl, methylene, and unsaturated methyne protons of cis-1,4-isoprene units appeared at 1.7, 2.1 and 5.1 ppm, respectively. It also shows two additional signals that appeared at 1.3 and 2.7 ppm which represent the methyl and methyne protons of the epoxy group, respectively.

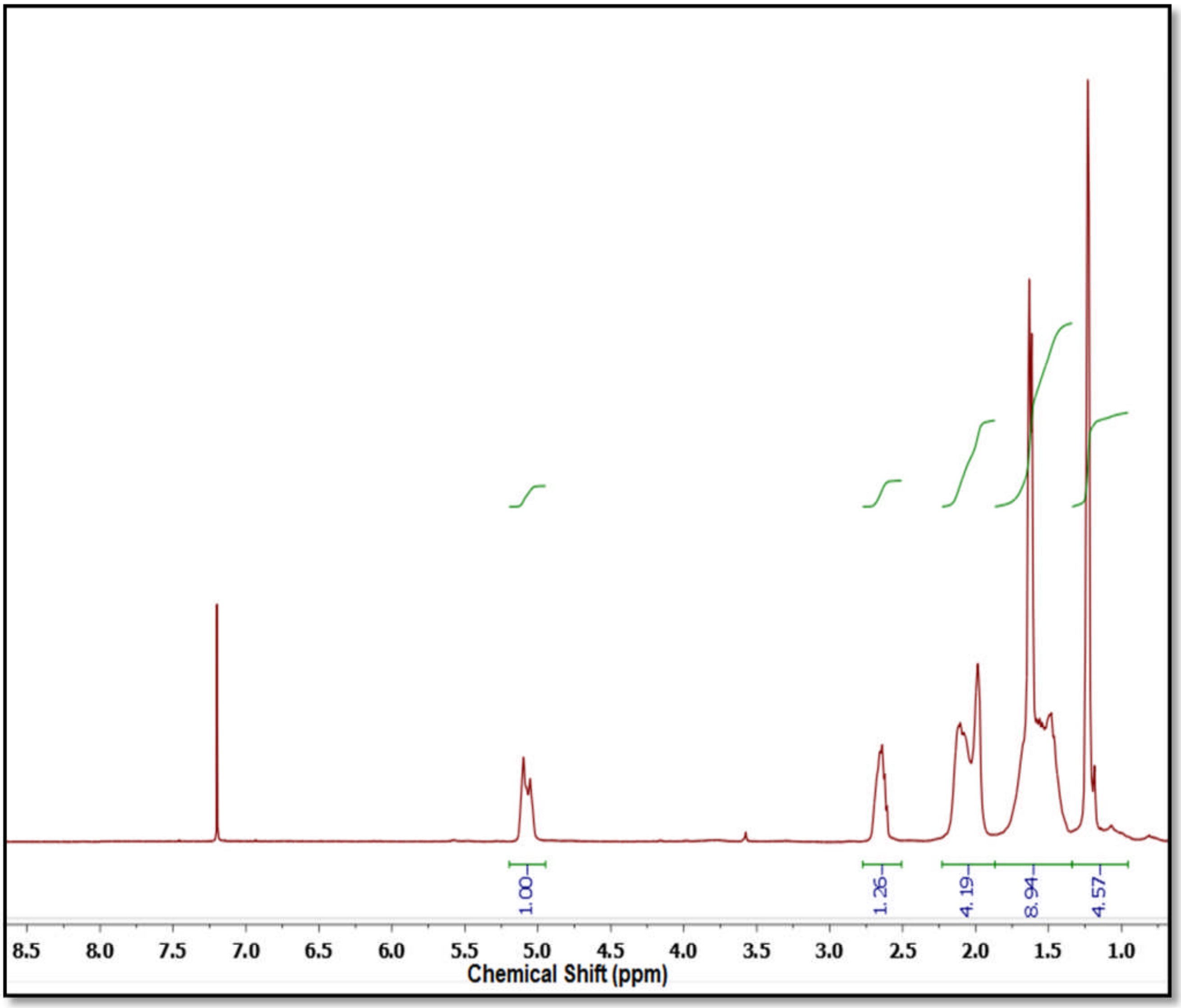


Figure III.3 ^{1}H-NMR spectrum of 50 mole% Epoxidized Natural Rubber in $CDCl_3$.

III.3.2 NMR analysis of maleic anhydride grafted polypropylene

Figure III.4 presents the ^{1}H-NMR spectrum of PP-g-MA. It shows a signal at about 7.00 ppm which is the characteristic of Toluene-d8.The succinyl functional groups of maleic anhydride are generally found in the region of 2-3 ppm. However, this peak appears in the spectrum in the region of (δ: 2.1-2.5 ppm) as a very tiny peak. In fact, it appears as a small shoulder (shown in the enlarged view) which confirms the grafting of MA on PP, but it is too small to be quantified in terms of MA grafting content. This confirms the low grafting content of 0.6 wt % reported by the PP-g-MA supplier **[5]**.

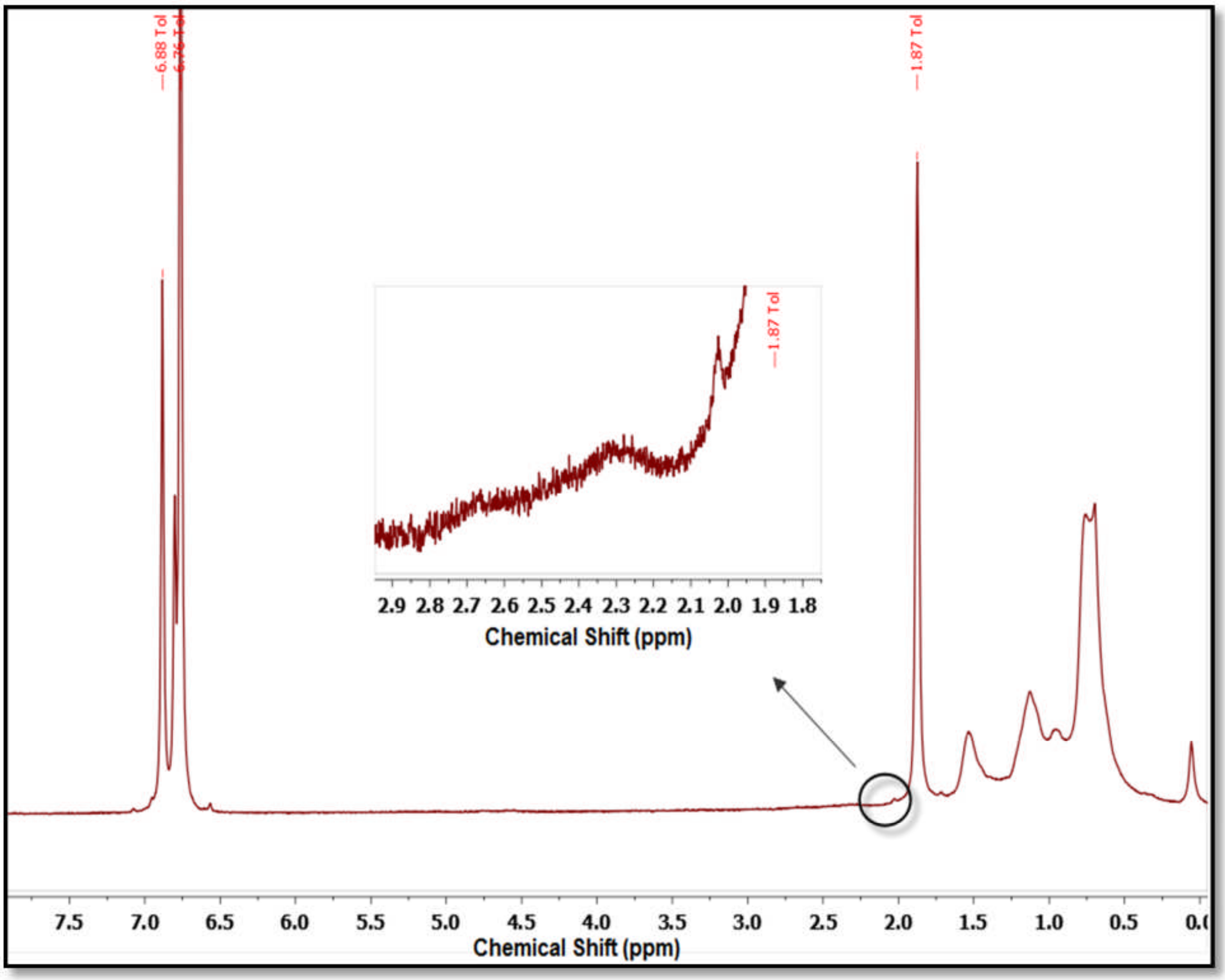


Figure III.4 ^{1}H-NMR spectra of maleic anhydride –grafted- Polypropylene in Deuterated Toluene-d8.

III.3.3 Characterization of the CAs structure

An attempt was made in order to characterize the CA structure by means of the ^{1}H-NMR analysis. However, upon the sample preparation, no solvent could dissolve this material. In fact all the solvents including deuterated toluene-d8, deuterated chloroform-d8 ($CDCl_3$),that have been used failed to produce a single phase solution. Dissolving the CA in hot xylene (80°C) even for 48 hours produced only a swollen gel. This could confirm the fact that blending of ENR with PP-g-MA lead to a crosslinked structure.

III.4 Rheological characterization

Rheology has always been considered a strong characterization tool due to the existing highly reciprocal relationship between rheology and morphology. Generally several factors such as the intrinsic rheological properties of the constituent polymers, the interfacial properties, and eventually the presence of several additives such as compatibilizers drastically affect the rheological response of the polymeric materials.

In this chapter, the results of the rheological characterization by means of the Brabender internal mixer will be discussed.

III.4.1 Study of the brabender plastograms

The progress of mixing can be appropriately followed by monitoring torque with mixing time. The variation of torque with mixing time for the thermoplastic elastomer blends of 50/50 NBR/PP are shown in the following plastograms.

III.4.1.1 Histograms of NBR/PP TPE blend

Figure III.5 presents the bargraphs of the final maximum torque for neat NBR, neat PP and their 50/50 blend. The data points shown were selected from the actual Brabender plastograms. Each bargraphs was obtained separately for the different blends studied. It is shown that NBR exhibited higher values of maximum torque than those of PP and that the bargraphs of the 50/50 NBR/PP blends had intermediate values. This could be attributed to the fact that NBR has a very high molecular weight and therefore requires mastication, compared to PP.

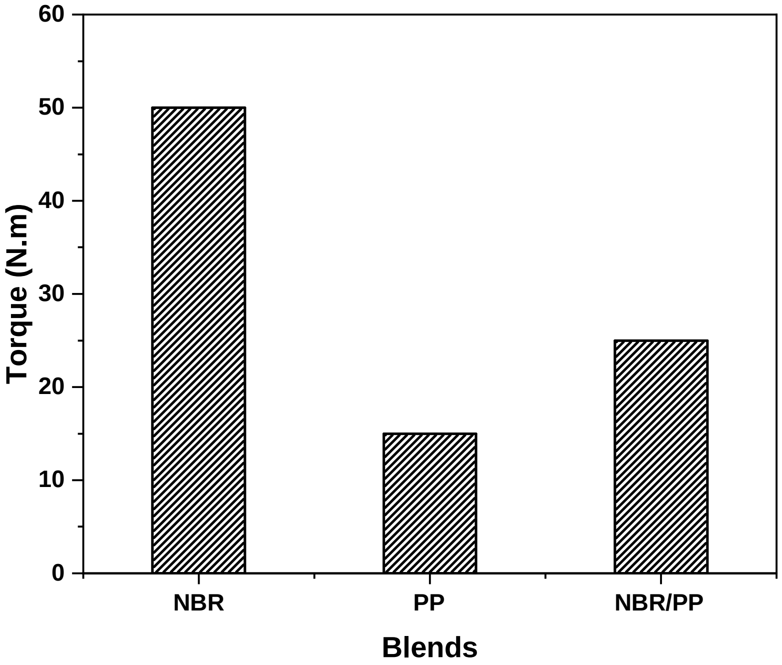


Figure III.5 Maximum torque values of neat NBR, neat PP, and NBR/PP blend.

III.4.1.2 Plastograms of the compatibilizing agents (CA_{25}, and CA_{50})

Figure III.6 presents the plastograms for the two polymers used to prepare the compatibilizing agents CA_{25} and CA_{50}; i.e. the 50/50 blend of ENR with PP-g-MA, along with the plots of the temperature evolution that accompanies the variation of the torque with mixing time. These curves show also a similar general form as that noted for neat components (neat NBR, and neat PP). That is an initial increase of the torque which corresponds to the time when PP-g-MA was first introduced in the mixing chamber, then as this polymer was sheared the torque decreased before levelling off. When ENR was added the plastograms exhibited a rapid increase followed by a slight reduction of the mixing torque. There is a second increase of the moment that follows and lasts for almost 1 min. The torque then further levels off indicating a final state of homogenization of the resulting blend. The increase of the torque that precedes the final plateau is attributed to the crosslinking reaction which took place between ENR and PP-g-MA. This means that the formation of crosslinks restricted the mobility of the polypropylene chains and those of epoxidized natural rubber and therefore increased the viscosity of the resulting CA_{25} and CA_{50} leading to a rise in the torque, which was accompanied by a rise of the temperature from 154 °C to 180 °C, and confirming hence the reaction mechanism proposed by C. Nackason and coworkers **[1]**.

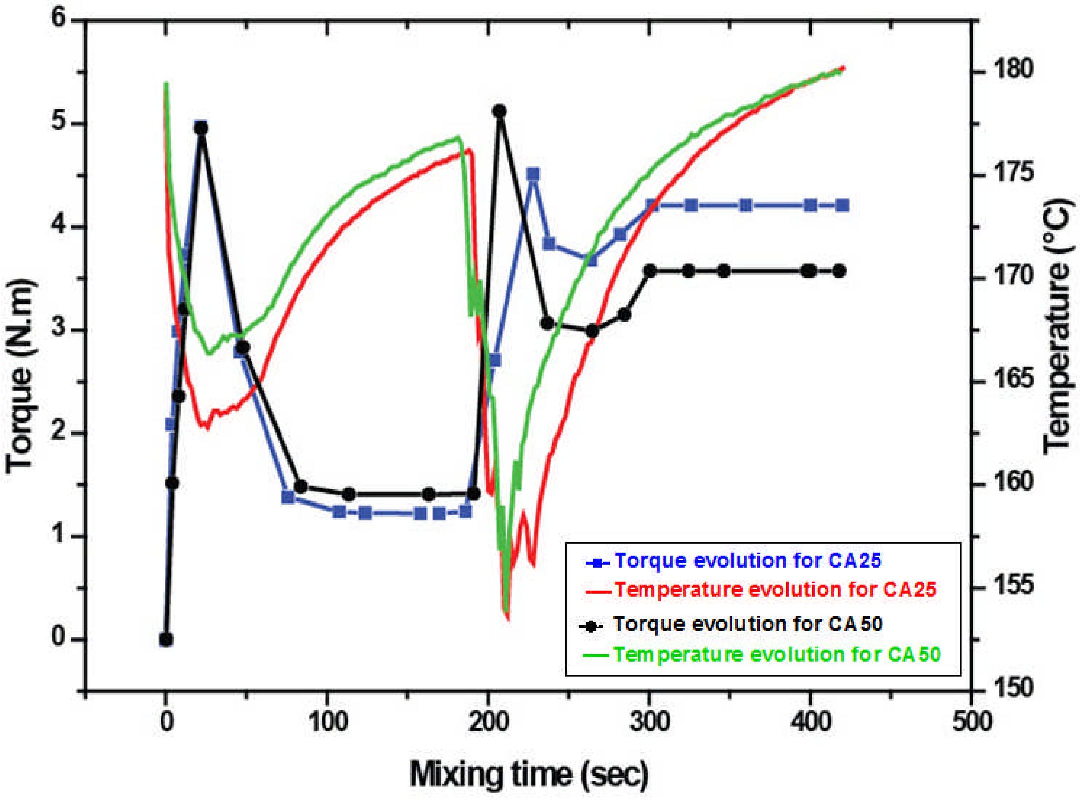


Figure III.6 Plastograms and evolution of temperature with mixing time for CA_{25}:ENR_{25}/PP-g-MA, and CA_{50}:ENR_{50}/PP-g-MA.

III.4.1.3 Histograms of CA_{25} and CA_{50}-containing NBR/PP TPE blends

Figure III.7 and Figure III.8 present the effects of the addition of CA_{25} and CA_{50} at concentrations of 5, 10, and 15 phr on the plastograms of the NBR/PP/CA_{25} and NBR/PP/CA_{50} respectively.

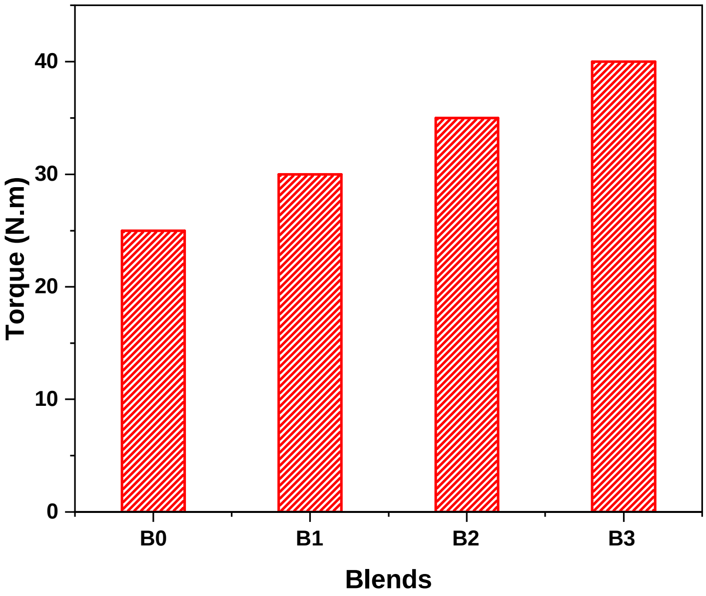


Figure III.7 Maximum torque values of B0: NBR/PP, B1: NBR/PP/CA_{25} (5 phr), B2: NBR/PP/CA_{25} (10 phr), B3: NBR/PP/CA_{25} (15 phr).

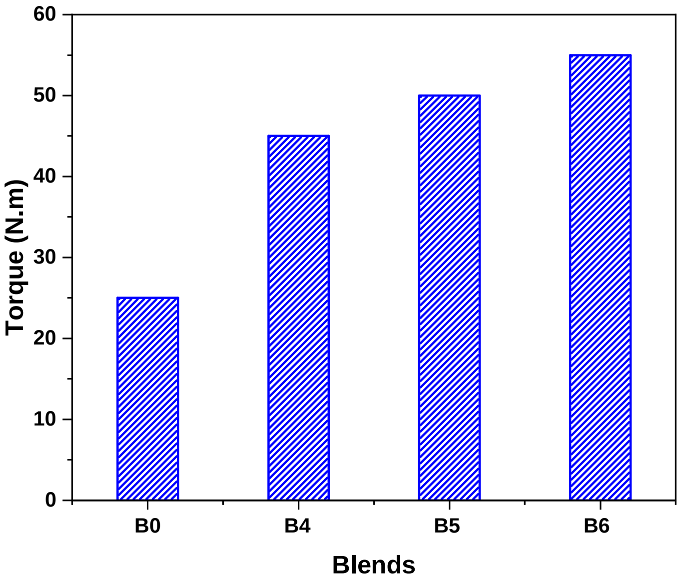


Figure III.8 Maximum torque values of B0: NBR/PP, B4: NBR/PP/CA_{50} (5 phr), B5: NBR/PP/CA_{50} (10 phr), B6: NBR/PP/CA_{50}(15 phr).

We can observe that the torque values increases when CA was added at different contents. This reflects to the interaction of CA_{25} and CA_{50} with PP and NBR phases. This increase could be explained by the fact that this interaction is inherent to only physical interactions that developed, on one hand between PP chains and those of the PP-g-MA present in the compatibilizing agent, and on the other hand a chemical interaction that developed, between NBR chains and those of ENR.

III.5 Tensile properties

The addition of ENR/PP-g-MA as a compatibilizer for NBR/PP blend is expected to affect the mechanical properties of the resulting TPE blends. In this part, the effects of varying the concentration of the CA used on the mechanical properties will be discussed for NBR/PP TPE blends.

Figure III.9 which presents the mechanical properties in terms of tensile strength, Young's modulus, and elongation at break,

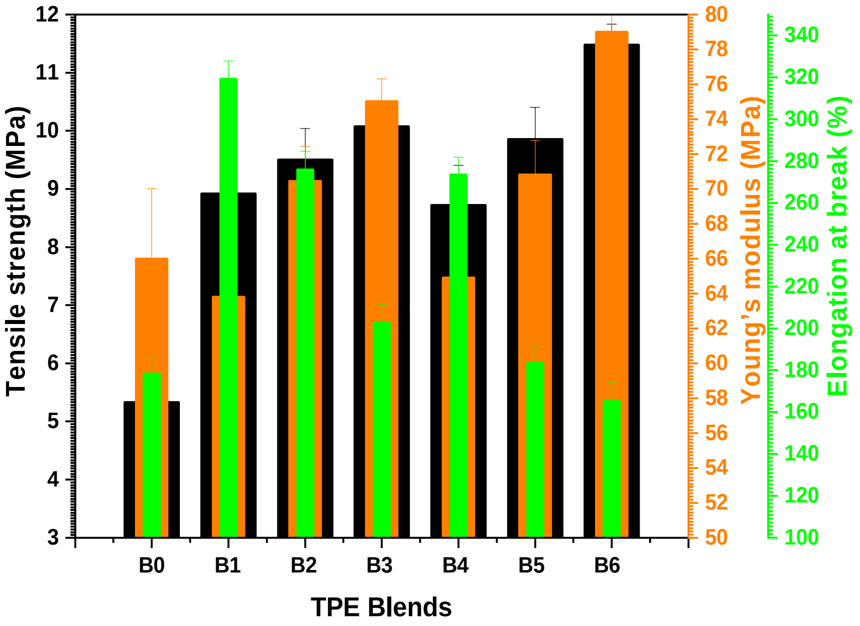


Figure III.9 Tensile strength, Young's modulus, and elongation at break of the control NBR/PP blend, and those of the CA_{25}, and CA_{50}-containing TPE blends.

Figure III.9 shows a trend of increased tensile strength and modulus and a decrease of the elongation at break. This means that the addition of CA_{25} and CA_{50} increased the capacity of the blends to withstand the tensile load and therefore led to an enhanced mechanical resistance.

On the other hand, it is noted that the increase of tensile strength and modulus increased with increasing the ENR content as there are more functional groups in CA_{50} than those in CA_{25}. In addition, the hydroxyl group in both CA_{25} and CA_{50} participated also in improving the interactions, diminishing hence the interfacial tension between the blend constituents. Another plausible interpretation of these results is that the crosslinked structure in the CA imparted a reinforcing effect. This correlates well with the mixing behavior discussed earlier where it was observed that the torque value increased after the addition of CAs for NBR/PP TPE blends.

III.6 Conclusions

In this chapter, the following conclusions were drawn:

1. The FTIR analysis revealed that upon blending, ENR reacted with PP-g-MA and produced ENR-grafted-PP with an ester and acid-based linkage. The results of ^{1}H-NMR revealed that the CA was insoluble and did not dissolve in the different solvents but swelled only. This could confirm the fact that blending of ENR with PP-g-MA lead to a crosslinked structure.
2. The Histograms of the NBR/PP blends containing the compatibilizers showed a moderate increase of the torque value when the CAs were added. This increase was attributed to the interactions that developed with the blend constituents through the functional groups of ENR and PP-g-MA. It was found that higher torque levels were obtained with a higher extent of the CA concentration.
3. The presence of compatibilizers at different concentrations caused an improvement in the mechanical properties of NBR/PP TPE blends compared with the control 50/50 NBR/PP blend without compatibilizer. This was reflected by the increase of tensile strength and Young’s modulus and a decrease of the elongation at break with the increase of the amount of the CA.

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[5] Polypropylene-graft-maleic anhydride maleic anhydride ~1.2 wt. %; Compatibilizer in polymer blends and alloys. https://www.sigmaaldrich.com/catalog/product/aldrich.

General Conclusions

General Conclusions

The objective of this work was to investigate the effect of the addition of a 50/50 blend of ENR/PP-g-MA as a compatibilizing agent on the rheological and mechanical properties of a 50/50 NBR/PP thermoplastic elastomer blend.

The following results were obtained:

1. The FTIR analysis revealed that upon blending, ENR reacted with PP-g-MA and produced ENR-grafted PP with an ester and acid-based linkage. This crosslinked reaction was confirmed during the preparation of the compatibilizer by the rise of the mixing torque noted when ENR was added to PP-g-MA. Confirmation of this reaction was obtained also from the ^{1}H-NMR characterization since dissolving the CAs in hot xylene produced a swollen gel.
2. Evidence to suggest compatibilization was then observed from the Brabender plastograms of the NBR/PP blends containing the compatibilizers. The Histograms showed a moderate increase of the torque value when the CAs were added. This increase was attributed to the interactions that developed with the blend constituents through the functional groups of ENR and PP-g-MA. From the histograms, it was also found that, compared to ENR_{25}; the ENR_{50}-based CA caused a reinforcing effect by increasing the viscosity which was reflected by the value of the final torque.
3. The mechanical properties results confirmed the enhancement of the interphase interactions for NBR/PP TPE blends. This was reflected by the increase of tensile strength and Young’s modulus and a decrease of the elongation at break with the increase of the amount of the CA.

Recommendations

Recommendations

For an eventual continuation of this work, it would be beneficial to further investigate:

1-Study of the chemical structure of the individual CAs as well as that of the resulting TPE using a solid-state NMR.

2- Study the effect of the dynamic vulcanization

3-Extend the study to:

3-1 A rigid type of TPE; for example, a 50/50 NBR/PP using a lower MFI grade of PP.
3-2 Another type of TPE such as a blend of another synthetic rubber with a polyolefin.
3-3 The use of other compatibilizing agents.

Abstract

The objective of this work is to study the effects of the incorporation of a 50/50 blend of Epoxidized Natural Rubber / Polypropylene-grafted maleic anhydride (ENR/PP-g-MA) as a compatibilizing agent (CA) for a thermoplastic elastomer based on a 50/50 Nitrile Rubber / Polypropylene NBR / PP blend on the rheological and mechanical properties.

Several formulations of this type of elastomer containing different concentrations of CA (from 5 to 15 Phr) were prepared by mixing in the molten state Nitrile Rubber and Polypropylene using a Brabender plasticorder. The rheological behavior was examined by means of a Brabender plasticorder. The mechanical properties were determined by the tensile measurements.

The Brabender plastograms as well as FTIR analysis revealed that upon mixing ENR reacts with PP-g-MA and a crosslinked structure results. Evidence of compatibilizing effects was obtained from an improved mechanical properties; which was attributed to a reduction of the interfacial tensions and an enhanced interphase interactions imparted by the CAs.

Keywords: Nitrile Rubber, Polypropylene, Thermoplastic Elastomer, Epoxidized Natural Rubber, Polypropylene-grafted Maleic Anhydride, Compatibilizing Agent.

Résumé

L'objectif de ce travail est d'étudier les effets de l’addition d’un mélange de Caoutchouc Naturel Epoxydé/Polypropylène greffé par l’anhydrid maléique (ENR/PP-g-MA) en tant qu’agent compatibilisant (AC) sur les propriétés de l’elastomer thermoplastique à base du mélange Caoutchouc Nitrile/Polypropylène (NBR/PP). Les différents mélanges étudiésont été préparés à l’état fondu en utilisant un mélangeur BRABENDER.

Pour évaluer l’influence de l’AC, plusieurs techniques d’analyse ont été utilisés ; notamment la rhéologie par le Plastographe Brabender et détermination des propriétés mécaniques par l’essai de traction.

Le suivi des plastogrammes au cours de la préparation des AC a révélé que l’ENR réagit avec le PP-g-MA et produit une structure réticulée. Cette structure a été confirmée grâce à l’analyse par FTIR.

Les résultats ont montré que l’effet compatibilisant a été obtenue vu l’amélioration des propriétés mécaniques. Ceci a été attribué à la réduction des tensions interfaciales et l’augmentation de l’adhésion interphases causées par les agents compatibilisant.

Mots clés : Caoutchouc Nitrile, Polypropylène, Elastomère Thermoplastique, Caoutchouc Naturel Epoxydé, Anhydride Maléique,Agent Compatibilisant.

ملخص

الهدف من هذا العمل هو دراسة تأثير دمج ايبوكسيد المطاط الطبيعي/ البولي البروبيلين المطعم بالأنهيدريد ماليك (PP-g-MA/ENR) بنسبة 50/50 كعامل توافق (CA) للمطاط الصناعي الترموبلاستيكي المتكون من خليط المطاط النتريلي/البولي بروبيلين PP/NBR 50/50 على الخصائص الريولوجية و الميكانيكية. تم تحضير عدة تركيبات من هذا النوع من اللدائن المحتوية على تراكيز مختلفة من عامل التوافق CA (من 5 إلى 15 Phr) عن طريق خلط المطاط النتريلي والبولي بروبلين في الحالة المنصهرة باستخدام جهاز من نوع برابندر(Brabender).

الخصائص التي تمت دراستها إضافة الى منحنيات البرابندر شملت دراسة السلوك الريولوجي للعينات كما تم أيضا دراسة الخصائص الميكانيكية عن طريق اختبار الشد.

أظهرت دراسة المنحنيات البيانية أثناء تحضير(CAs) أن ENR يتفاعل مع PP-g-MA وينتج بنية متشابكة. تم تأكيد هذا الهيكل المتشابك من خلال تحليل FTIR.

أظهرت هذه النتائج أيضا أن تأثير التوافق تم الحصول عليه من خلال تحسين الخواص الميكانيكية. يعزى ذلك إلى انخفاض التوترات البينية بين الأسطح وزيادة التصاق الطور البيني الناتج عن أجهزة التوافق.

الكلمات المفتاحية: المطاط النتريلي ،البوليبروبلين ،المطاط الطبيعي الترموبلاستيكي، ايبوكسيد المطاط الطبيعي ،البولي البروبيلين المطعم بالأنهيدريد ماليك، عامل التوافق.