

**PROCESSING CHARACTERISTICS, PHYSICAL
PROPERTIES AND MORPHOLOGICAL STUDY OF
POLYPROPYLENE (PP)/RECYCLED ACRYLONITRILE
BUTADIENE RUBBER (rNBR) BLENDS**

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UNIVERSITI SAINS MALAYSIA

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by

GALPAYAGE DONA DILINI GALPAYA

**Thesis submitted in fulfillment of the requirements for the
degree of Master of Science**

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A1(i) Comparison of Properties of Polypropylene (PP)/Virgin Acrylonitrile Butadiene Rubber (NBR _v) and Polypropylene (PP)/Recycled Acrylonitrile Butadiene Rubber (NBR _r) Blends <i>(Polymer-Plastics Technology and Engineering, 2009,48, 440-445)</i>	170
A1(ii) The compatibilizing effect of epoxy resin (EP) on polypropylene (PP)/ recycled acrylonitrile butadiene rubber (NBR _r) blends <i>(Polymer Testing, 2009,28, 363-370)</i>	171
A1(iii) The comparison effect of natural weathering on properties of recycled acrylonitrile butadiene rubber (NBR _r)/polypropylene (PP) and virgin acrylonitrile butadiene rubber (NBR _v)/polypropylene (PP) blends <i>(Journal of Applied Polymer Science, Accepted by 10th May 2009)</i>	172
A1 (iv) Electron-beam irradiation of polypropylene (PP) and recycled acrylonitrile butadiene rubber (rNBR) blends <i>(Journal of Vinyl and Additives Technology, Accepted by 15th June 2009)</i>	173

A1 (v) Effects of Dynamic Vulcanization on Tensile Properties, Morphology and Natural weathering of Polypropylene/Recycled Acrylonitrile Butadiene Rubber (PP/NBRr) Blends 174
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A1(vi) Thermoplastic elastomer based on polypropylene (PP)/ natural rubber latex modified recycled acrylonitrile butadiene rubber (rNBR_{LM}) blends 175
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Appendix 2 International Conference Presentation

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(Oral presentation, 2nd USM-Penang International Conference for Young Chemists, 18-20 June 2008, Penang, Malaysia)

A2(ii) Properties of thermoplastic elastomer based on polypropylene/recycled acrylonitrile butadiene rubber blends 177
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Appendix 3 National Conference Presentation

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LIST OF ABBREVIATIONS

CBS	N-Cyclohexyl-2-benzothiazole sulfonamide
DCP	Dicumylperoxide
DGEBA	Diglycidyl ether of bisphenol-A epoxy resin
DTMPTA	Ditrimethylol propane tetraacrylate
EB	Electron Beam
ENR	Epoxidized natural rubber
EPDM	Ethylene- propylene diene terpolymer
EVA	Ethylene Vinyl acetate
FESEM	Field Emmission Scanning Electron Microscope
FTIR	Fourier-transform infrared spectroscopy
IPN	Interpenetrating Polymer Network
IRSG	International Rubber Study Group
MIDA	Malaysian Industrial Development Authority
MT	Metric Tonnes
NBR	Acrylonitrile Butadiene Rubber
NBR-RCOOH	Carboxylated Acrylonitrile Butadiene Rubber
NR	Natural Rubber
PA 6	Polyamide 6
PE	Polyethylene
PfMs	Polyfunctional monomers
Ph-PP	Phenolic modified Polypropylene
PP	Polypropylene
PP-g-MAH	Polypropylene graft maleic anhydride
rNBR	Recycled acrylonitrile butadiene rubber
rNBR _{LM}	Natural rubber latex modified rNBR
TMPTA	Trimethylolpropane triacrylate
TMTD	Tetramethyl thiuram disulfide

TPEs	Thermoplastic elastomers
TPOs	Thermoplastic olefins
TPVs	Thermoplastic vulcanizates
UV	Ultra Violet
vNBR	Virgin acrylonitrile butadiene rubber
WTD _{ML}	Latex modified waste tyre dust blends
ZnO	Zinc oxide

LIST OF SYMBOLS

cm	Centimeter
°C	Degree Celsius
E_b	Elongation at break
T_g	Glass-transition temperature
g	Grams
Kg	Kilograms
kGy	Kilo Gray
T_m	Melting point
μm	Micrometer
mA	Milliampere
MeV	Megaelectron volt
mm	millimeter
MPa	Mega Pascal
MT	Metric Tonnes
nm	Nanometer
Nm	Newton meter
php	Parts per hundreds plastics
phr	Parts per hundreds rubber
rpm	Revolutions per minute
S	Seconds

**CIRI-CIRI PEMROSESAN, SIFAT FIZIKAL DAN KAJIAN MORFOLOGI
ADUNAN POLIPROPILENA (PP)/GETAH AKRILONITRIL BUTADIENA
TERKITAR SEMULA (rNBR)**

ABSTRAK

Penggunaan sarung tangan lateks nitril menunjukkan peningkatan di seluruh dunia kerana ia mempamerkan sifat fizikal yang unggul, tidak mengandungi protein larut air berbanding sarung tangan lateks getah asli dan kebolehtahanan yang baik. Justeru itu, setiap hari jumlah sarung tangan nitril yang terpakai dan terbuang sedang meningkat dengan mendadak. Oleh yang demikian, adalah penting untuk mencari teknik yang kos efektif, sesuai dan tidak mencemarkan alam untuk menggunakan semula bahan terbuang ini. Termoplastik elastomer baru yang berasaskan getah akrilonitril butadiena (NBR) kitar semula (sarung tangan nitril) dan polipropilena (PP) sebagai matrik telah dihasilkan bagi mengatasi masalah ini. Adunan PP/NBR telah disediakan melalui teknik penyebatian leburan dengan menggunakan mesin pencampur dalaman “Haake Rheomix Polydrive R 600/610” pada suhu 180°C dan kelajuan rotor 60 rpm. Sebanyak enam siri adunan dalam kondisi berlainan telah disediakan dan diselidik. Siri pertama adalah untuk membandingkan sifat adunan PP dan NBR kitar semula (rNBR) dengan PP dan NBR tulen (vNBR). Siri-siri yang selebihnya tertumpu kepada penyelidikan kesan agen penserasi dan penyambung silangan bagi meningkatkan prestasi akhir adunan. Teknik pemprosesan, sifat tensil, sifat pembengkakan, analisis FTIR dan morfologi adunan telah dikaji dengan mengubah komposisi adunan sebagai rujukan. Degradasi adunan apabila didedahkan kepada pencuciaan bagi tempoh masa 3 bulan dan 6 bulan telah diselidik. PP/rNBR memerlukan tork yang lebih tinggi bagi penyebatian leburan berbanding PP/vNBR. PP/vNBR mempamerkan sifat tensil yang lebih baik berbanding PP/rNBR. Sifat

rintangan minyak bagi adunan PP/rNBR adalah lebih baik berbanding PP/vNBR. Satu penemuan menarik yang perlu diberi perhatian ialah kebolehtahanan PP/rNBR yang lebih baik terhadap degradasi oleh pendedahan kepada cuaca persekitaran berbanding PP/vNBR. Pemvulkanan dinamik mengakibatkan peningkatan dalam sifat tensil dan rintangan minyak. Nilai tork penstabilan bagi adunan yang ter Vulkan secara dinamik adalah lebih tinggi dan ini boleh dianggap sebagai petunjuk kepada kualiti penyebatan yang lebih baik. Mikrograf SEM menunjukkan bahawa penyerakan rNBR di dalam matrik PP adalah lebih baik dalam sampel ter Vulkan. Tambahan pula pelekatan di antara kedua-dua fasa adalah lebih baik. Adunan yang ter Vulkan secara dinamik menunjukkan sifat rintangan degradasi pencucaan yang lebih baik berbanding sampel yang tidak ter Vulkan. Apabila adunan didedahkan kepada radiasi alur elektron hampir semua sifat dan aspek yang diselidik terutamanya sifat tensil, rintangan minyak dan morfologi telah menunjukkan peningkatan. Sifat rintangan terhadap degradasi pencucaan adunan yang terdedah kepada radiasi adalah lebih rendah berbanding dengan adunan yang tidak terdedah kepada radiasi. Ini mungkin disebabkan oleh degradasi rantai polimer apabila terdedah kepada radiasi.

Resin “diglycidyl ether of bisphenol-A epoxy (DGEBA)”, “polypropylene graft maleic anhydride (PP-g-MA)” dan rNBR terubahsuai dengan latek getah asli (rNBR_{LM}) telah digunakan sebagai agen penserasi untuk meningkatkan prestasi PP/rNBR. Sifat tensil dan morfologi PP/rNBR telah meningkat akibat peningkatan keserasian antara PP dan rNBR. Penserasian adunan dengan DGEBA dan PP-g-MA membawa kepada peningkatan rintangan minyak manakala apabila rNBR_{LM} digunakan, sifat rintangan minyak berkurang berbanding dengan adunan tanpa agen penserasi.

PROCESSING CHARACTERISTICS, PHYSICAL PROPERTIES AND MORPHOLOGICAL STUDY OF POLYPROPYLENE (PP)/RECYCLED ACRYLONITRILE BUTADIENE RUBBER (rNBR) BLENDS

ABSTRACT

The consumption of the gloves made out of nitrile latex has been increasing worldwide due to their excellent physical properties, non existence of leachable proteins unlike in natural rubber latex gloves and durability. As results of this, an enormous quantity of used and waste nitrile gloves are generated daily. Therefore, it is important and worthwhile to find out a cost effective, suitable and environmentally friendly method to reuse this waste material. Hence, a new thermoplastic elastomer blend was developed using recycled acrylonitrile butadiene rubber (NBR) (nitrile gloves) with polypropylene (PP) as the plastic base material. Blends of PP/NBR were prepared by melt mixing using a Haake Rheomix Polydrive R 600/610 mixer at 180°C with the rotor speed of 60 rpm. Six series of blends under varying conditions were prepared and investigated. The first series was to compare the properties of blends of PP and recycled NBR with blends of PP and virgin NBR. The rest of the studies were aimed at investigations of the effects of compatibilization and crosslinking behaviour on the properties of the blends with the intention of improving the blend properties. Process development, tensile properties, swelling behavior, FTIR analysis and morphological characterization of blends were investigated with the variation of the composition of the blend. Degradation of the blends by means of natural weathering was studied for a period of 3 months and 6 months. PP/ rNBR blends required higher torque for melt mixing than that of PP/vNBR blends. PP/vNBR blends exhibited superior tensile properties and finer morphology compared to that of PP/rNBR blends. The oil resistance properties of

PP/rNBR found to be better than that of PP/vNBR blends. It is interesting to note that PP/rNBR blends have superior ability to withstand natural weathering compared to PP/vNBR blends. Dynamic vulcanization of the blend resulted in improved tensile and oil resistance properties compared to unvulcanized counterpart. Stabilization torque of dynamically vulcanized blends exhibited higher value indicating better mixing of the blend. This result was confirmed by the SEM study that showed better dispersion of rNBR in the PP matrix and improved adhesion between the two phases. Dynamically vulcanized blend showed superior weathering properties compared with the controlled unvulcanized blends. When the blend was exposed to electron beam irradiation all properties examined, namely tensile properties, oil resistance properties and morphology have shown improved properties. Weathering properties of the irradiated blends were found to be inferior to that of unirradiated blends which may be the result of excessive degradation of the material due to irradiation.

Diglycidyl ether of bisphenol-A epoxy resin (DGEBA), polypropylene grafted maleic anhydride (PP-g-MA) and natural rubber latex modified rNBR ($rNBR_{LM}$) were used to compatibilize the PP/rNBR blends. It was found that the tensile properties and morphology of PP/rNBR blends were enhanced due to the improvement in blend compatibility. The compatibilization of blends with DGEBA and PP-g-MA resulted in improving the oil resistant properties whereas with $rNBR_{LM}$ resulted in poor oil resistance compared to uncompatibilized PP/rNBR.

CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1. Introduction

Thermoplastic elastomers (TPEs) have emerged as a highly demanding class of polymeric materials and already started replacing many other conventional materials in various applications. With the exception of their dual characteristics of vulcanized elastomer and thermoplastic properties, the possibility of adjusting their properties by different routes has caused TPEs to be a versatile class of materials.

Low cost and attractive properties such as superior mechanical strength, light weight, corrosion resistance, applicability at elevated temperatures, ability to be tailored for specific engineering applications are some of the properties of TPE which may not be found in any other materials. The most important feature of TPEs is the repeated recyclability up to several times without significant loss of properties (Naderi et al., 1999).

Basically, a TPE consists of at least two polymeric phases. A hard thermoplastic phase is combined with a softer elastomer phase, and the properties of the resultant TPE will be derived from the properties of each of the two phases individually and from the extent of interaction between these phases (Arnold & Rader, 1992). There are many possible combinations of plastics and elastomers of TPEs that could be developed in accordance with the expected properties of the final material.

Polypropylene (PP) is a linear hydrocarbon polymer and the typical density of the PP is 0.9 g/cm^3 . The products based on PP are very significant commercially due to the advantages of being low in both density and the cost. Additionally, its

crystalline structure and high melting point results in resistance to solvent and high temperature (Holden, 2000). Acrylonitrile butadiene rubber (NBR) has excellent oil resistant properties over a wide range of temperatures. NBR is also well known for its superior strength, excellent resistance to abrasion, water, alcohols and heat. Disadvantages of NBR are poor dielectric properties and resistance to ozone (Yasin et al., 2002). As such, blends of acrylonitrile butadiene rubber/polypropylene are an important class of TPE material which exhibit excellent oil resistant properties as a result of the presence of NBR and excellent mechanical and processing characteristics due to the presence of PP. They can be successfully used for high temperature, oil resistance applications (George et al., 1995).

The importance of recycling of waste materials generating from industries worldwide has become significantly important in the recent past mainly due to environmental reasons. The rubber manufacturing industry also faces a major challenge in this regard. As such, scientists are compelled to find the satisfactory ways and means to deal with the enormous quantity of waste rubber goods generated by the industry which may lead to severe environmental problems unless they are disposed properly. Rubber wastes are usually generated during the processing of the products and from the disposal of post-consumer products.

It has been seen significant increase in the production of nitrile gloves all over the world during the last couple of years due to its ability to resist puncturing, tearing and abrasion as well as non existence of leachable allergenic proteins unlike in natural rubber latex. Similarly nitrile gloves possess excellent resistance to many chemicals like solvents, greases, oils, and alkali solutions. They also withstand water permeability, and are less likely to absorb water in damp conditions (<http://www.dontheglove.com>).

According to the statistics of International Rubber Study Group (IRSG), the world synthetic rubber production and consumption in 2007 was 13.5 million of MT and 13.2 million of MT, respectively. The Malaysia's synthetic rubber consumption in 2007 was 0.13 million of MT and it is 0.98% of world's synthetic rubber consumption. According to Malaysian Industrial Development Authority (MIDA), there are 60 glove manufactures in Malaysia in 2007 and their production capacity in 2007 was 20,390.94 million pairs (Malaysian Rubber Statistics). Among them the production capacity of nitrile glove from three of the leading companies in Malaysia in year 2007 was 1,100, 882 and 780 million pieces, respectively (Rubber Glove, 2007).

Currently, nitrile gloves are used widely by the healthcare industry as the natural rubber latex-free examination glove as the choice for nurses and doctors. Nitrile gloves are known for providing protection to various chemicals like chemotherapy drugs. In addition, nitrile examination gloves provide excellent barrier protection providing three times more puncture resistance than NR latex gloves. Due to its durability, an excellent abrasion resistance and cut and puncture resistance nitrile glove is mostly used in industrial applications such as automotive and chemical industries. In addition, nitrile gloves have begun replacing natural rubber latex gloves in the recent past in the sanitary and cleaning applications because its surface is highly resistant to degradation unlike NR gloves. Transportation and security sectors especially for screening activities at the airports use nitrile gloves to a great extent.

As a result of enhanced use of nitrile gloves significant quantities of used nitrile gloves and rejects are generated worldwide daily. As such, it would be of immense important to the industry to find an appropriate method to recycle and reuse

these waste materials. Numerous techniques have been developed to solve the problem and to find more effective ways to utilize waste rubber. These include reclaiming, surface treatment, devulcanization, etc. Mechanical grinding of gloves would be one of the simplest recycling methods of conversion of used gloves into any useable form of reclaimed rubber in the powdered form (Zulkepli et al., 2009). Blending the reclaimed forms with another polymeric material to form a blend is one of the most effective methods of utilizing the reclaimed rubber for any industrial applications. Among various thermoplastic elastomers (TPEs), blends based on polyolefins are an important class of engineering materials (Rajalekshmi et al., 2005).

Therefore; this study is focused on the development of a new class of TPE material by blending PP with waste nitrile gloves generating from the nitrile glove manufacturing industry. It is hopeful at the end; the final product developed would find useful applications in the automotive and chemical industries.

Even though blending of PP with NBR looks to be a very attractive as a way to obtain new TPEs with excellent oil resistance, good mechanical properties and easy processability, these blends are found to be highly incompatible. PP and NBR are very dissimilar polymers. Therefore, the physical and chemical interactions across the phase boundaries are very poor, giving rise to a very weak interphase. In addition, the low interfacial adhesion increases the chances of the formation of large voids at the interphase (Soares et al., 2006). Joseph et al. (2006) have studied the melting behavior of the PP/NBR blends with DSC. They have found that temperature at the onset of melting ($T_{m,onset}$) and melting temperature (T_m) of PP were not affected by blending. Further, percentage crystallinity (X_c) remained almost unaffected by the addition of NBR. This indicated a lack of interaction of the PP and NBR phases. It was very analogous to the behavior of incompatible blends. Soares et al., (2006) have

reported that PP/NBR blends exhibited an increase of free volume size because of the strong incompatibility between the blend components on their study by positron annihilation lifetime spectroscopy (PALS). George et al. (1999) have observed that the negative deviation of the viscosity of the PP/NBR blend by their study of rheological behavior of the blends. This is also an indication of incompatibility of the system. As such, drawbacks of PP/NBR blends arising from incompatibility of the two phases need to be resolved, to achieve good mechanical properties of the blend and to improve the cost efficiency of the bulk production. Therefore, it is important to improve the compatibility of the two polymeric phases of the blend to achieve better homogeneity and morphology for improved and desired mechanical properties (Joseph et al., 2006). Several compatibilizing systems in TPEs have been studied to achieve such desired properties for practical applications. The use of maleic anhydride functionalized PP (PP-g-MAH) and carboxylated NBR (NBR-RCOOH) as a compatibilizing system was investigated by Soares and co workers (2006) and found that there is an improvement in tensile and swelling properties of PP/NBR blends. PP/NBR blends with phenolic modified polypropylene (PP-g-Ph) as a compatibilizer show better resistance to tearing than uncompatibilized counterpart due to the reduction in particle size of dispersed NBR domains (George et al., 1996). The enhanced tensile properties and finer morphology were resulted in compatibilizing NBR/EVA blends by partially hydrolyzed EVA in combination with oxazoline-functionalized-NBR (Soares et al., 2004). Another way of improving the properties of TPE blends is to introduce crosslinks in the rubber phase of the blend. This can be done by vulcanization of the rubber phase either through dynamic vulcanization or by irradiation techniques.

Considering the increasing trend of the use of TPEs in outdoor applications, it is of fundamental importance to determine their weathering behavior which is quite dependent of the chemical structure of the constituent polymers in the blend. Most polymers are usually vulnerable to harmful effects from the environment. This includes attack by chemical detergents, oxygen, humidity, harmful anthropogenic emissions and atmospheric pollutants such as nitrogen dioxide, sulfur dioxide and ozone and physical stresses such as heat, mechanical forces, radiation and ablation (Pielichowski & Njuguna, 2005). As such, polymer blends need to be tailor made to depending upon the product application; particularly in outdoor applications the blend needs improved weathering resistance properties.

1.2. Objectives

The main focus of this study is to develop a new thermoplastic elastomer (TPEs) using polypropylene and recycled acrylonitrile butadiene rubber and thereby to find a suitable solution to the existing problem of disposing the nitrile rubber waste material generated from nitrile rubber based product industries. It is also expected to manufacture advanced material with superior mechanical properties using these wastes in different compositions with PP in the blend. The cost reduction of the final product is the other objective due to the use of cheap waste generated from the nitrile rubber industry.

The main objectives of this work are:

- To compare the effect of virgin acrylonitrile butadiene rubber (vNBR) and recycled acrylonitrile butadiene rubber (rNBR) at different blend ratios in PP/NBR blends on the process development of the blend, morphology, tensile properties, swelling behavior, and natural weathering.

- To study the effect of dynamic vulcanization on the ultimate properties and natural weathering behaviour of newly developed PP/rNBR thermoplastic elastomer.
- To evaluate the property improvement of the blend by electron beam irradiation and its effect on polymer degradation.
- To determine compatibilizing effect of diglycidyl ether of bisphenol-A epoxy resin (DGEBA) and maleic anhydride graft PP (PP-g-MA) on the properties of developed PP/rNBR blend.
- To study the effect of modification of recycled NBR with natural rubber latex on the processing, the physical properties and the morphology of the developed TPE.

CHAPTER 2

LITERATURE REVIEW

2.1. Polymer Blend

Since the beginning of the plastics industry it has been recognized that blending yields materials with property profiles superior to the features of the individual components. The blending of polymers provides a means of producing new materials, which combine the useful properties of all of the constituents (Utracki, 2000). The technology of blending is now advancing at a rapid pace. The ability to combine existing polymers into new compositions with commercial utilities offers the advantage of reduced research and development expense compared to the development of new monomers and polymers to yield a similar property profile. An additional advantage is the much lower capital expense involved with scale-up and commercialization. Another specific advantage of polymer blends versus new monomer/polymer compositions is that blends often offer property profile combinations not easily obtained with new polymeric structures. Blending technology is more useful in the field of plastics recycling. It is estimated that about one third of all commercially produced polymer materials are blends of two or more polymers.

Polymer blend could be defined as a mixture of at least two macromolecular substances, polymers or copolymers, in which the ingredient content is higher than 2 wt% (Utracki, 1998). Preparation of polymer blends can be done by melt mixing, latex blending, solution blending, partial block or graft polymerization as well as interpenetrating polymer network (IPN) technology. Melt mixing is the most widespread method of polymer blend preparation in practice. It is important that the

size of the dispersed phase be optimized, considering the final performance of the blend (Horak et al., 2007).

Polymer blends can be classified with many parameters such as number of components (binary, ternary etc), type of constituent (thermoplastic, thermosetting or elastomer), nature of the polymer architecture (graft or block polymer), compatibility among the constituent (compatible, incompatible), and method of producing (physical or chemical blending). Among the listed parameters, type of constituent is the most commonly used indicator. It has classified the polymer blends into three main categories;

(i) Plastics-plastics blends

(ii) Elastomer-elastomer blends

(iii) Plastics-elastomer blends

As this research is more about the plastics-elastomer blends, the other two will not be discussed further here.

2. 2. Thermoplastic Elastomers (TPEs)

Thermoplastic-elastomer blends/Thermoplastic elastomers (TPEs) have become a technologically important class of material in recent past years. TPEs have many of the elastomeric physical properties of rubbers, e.g., softness, flexibility, resilience but they are processable as thermoplastics. TPEs can be able to process using conventional thermoplastic processing techniques such as injection molding, extrusion. TPEs can also be completely reprocessable without any considerable loss in properties or processing characteristics due to recyclability of their scrap and rejects (Holden, 2000; Walker, 1986).

A TPE consists of at least two polymeric phases. They generally exhibit a phase-separated system in bulk. A hard thermoplastic phase is combined with a soft elastomer phase, and the properties of the resulting TPE will be derived from the properties of each of the two phases and from the interaction between these phases. The two phases may result from simple mixing of two different polymers, as in a blend of a hard thermoplastic with a soft elastomer (Arnold & Rader, 1992). The hard phase gives these TPEs their strength and the elastomeric phase provides elasticity and flexibility to the system.

The performance characteristics of a TPE depend on the melting point (T_m) of the hard thermoplastic phase and the glass-transition temperature (T_g) of the soft elastomeric phase. The useful temperature range of a TPE is between T_m and T_g and the TPE displays its desirable elastomeric properties within this range. At temperature above T_m the thermoplastic phase melts and the TPE becomes fluid and can be processed by usual thermoplastic techniques. Below T_g the TPE becomes brittle and loses all of its useful elastomeric properties (Arnold & Rader, 1992).

2. 2.1. Properties of TPEs

The properties and characteristics of TPEs are strongly dependent on constituents of the TPE, molecular weight, relative amount of hard and soft segment and processing history. The changing of hard segment will influence the crystallinity of the materials, similarly the soft segment type influences on the phase separation and hence physical properties of the final. The performance characteristics of TPE also depend on the weight fraction of crystallinity of hard phase and its T_m and the T_g of the soft phase. The useful temperature range for a TPE is between T_m and T_g .

Within this range it is elastomeric, below the range it is brittle and above the range the hard phase melts.

The majority of TPEs function as rubber at temperature as low as -40°C or even lower as measured by their brittle point. The upper temperature limit is determined by the maximum temperature at which it can give satisfactory retention of tensile stress-strain and hardness properties. TPEs generally extend to high elongation and often in some cases with residual elongation or permanent set. Their set properties are in between elastomers and thermoplastics. As the temperature rises in TPE, modulus and strength decrease due to softening of hard domain. In the vicinity of softening point the properties decrease drastically and the material cannot be used as TPE. Most of the TPEs are in the high rubber hardness range. Most TPEs have fair to good compression set resistance at ambient temperature. The resistance of a TPE to different chemicals is greatly influenced by its chemical similarity to the fluid. The resistance to many oils and greases is high for more polar TPEs. The electrical properties of styrenics, thermoplastic olefins (TPOs) and thermoplastic vulcanizates (TPVs) are very good. Their non polar nature allows their use as a primary electrical insulation (Dutta, Bhowmick & Choudhury, 1997).

2. 2.2. Applications of TPEs

TPEs find uses in virtually all the applications where thermoset rubbers are used with the exception of pneumatic vehicle tires.

TPEs mainly TPOs are widely used in automotive industry due to their excellent combination of properties, wide range of service temperature, resiliency, ease of processability and colourability and so on. TPOs are mostly use in exterior body applications such as filler panels, bumper covers, fender extensions, lower

fascias, flexible front, rear panels, corner panels and sight shields. TPOs are used to make some interior automotive parts such as steering wheel, horn pads, seat-belt housings, bushing etc. The TPEs are largely used as insulation and jacketing materials where environmental and heat resistance are required. The electrical characteristics such as low dielectric constant, high electrical resistance, high dielectric strength of TPOs coupled with abrasion resistance and ability to use in a wide range in temperature and in a variety of environmental conditions provide an excellent market potential in wire and cable applications. TPEs are especially PP/EPDM useful in electrical applications. Flame retardant TPEs are available for electrical uses requiring rubber which do not support combustion. Due to their abrasion resistance and flexibility of TPOs, they are used in mechanical applications such as fabric coating, hoses, seals, gasketing in a great extent. The good chemical resistance to hot water and detergents is very important in appliance applications for instance hose, seals and gaskets for washers, dryers and refrigerators. A growing number of uses is being found for TPEs in food processing equipment, beverage dispenser pumps, peristaltic pump tubing, syringe stoppers, catheters and hospital tubing and sheeting. Other application areas include clutch parts, wheels, molded feet, housewares, toys, sporting goods, shoe soles and footwear as well as medical and pharmaceutical goods (Walker, 1986; Harper, 1992). Figure 2.1 shows some of the commercially available TPEs products.



Strips and Hoses



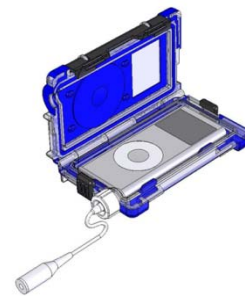
Shoe sole

<http://www.made-in-china.com/>



Forefoot Relief Pad

<http://www.nectardesign.com>



Drypod Nano Case

<https://www.drtodds.com/>



Air valves

<http://www.gkplastics.net/gate-valves.html>

Figure 2.1. Some of the TPEs products

2.3. Polypropylene (PP)

Polyolefins are the main industrial polymers which are based on low-cost petrochemicals or natural gas and the required monomers are produced by cracking or refining crude oil. Based on economics, the four major polyolefins with outstanding growth rate are polyethylene, polypropylene, polyvinyl chloride and polystyrene (Ulrich, 1993). PP is similar to polyethylene in structure except for the substitution of one hydrogen group with a methyl group on every other carbon. This change allows for the preparation of different stereoisomers, namely, syndiotactic, isotactic and atactic chains. PP is synthesized by the polymerization of propylene monomer that is derived from petroleum products. The repeating unit of polypropylene is given below.

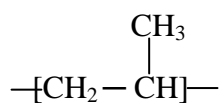


Figure 2.2. Repeating unit of polypropylene (Pasquini, 2005)

Different behavior can be found for each of the three stereoisomers. Isotactic and syndiotactic PP can pack into a regular crystalline array giving a polymer with more rigidity where as atactic PP has a very small amount of crystallinity due to its irregular structure, thus it behaves as a soft flexible material. The isotactic PP is the most commercially important form (Pasquini, 2005). Commercial polymers are about 90-95 percent isotactic. The amount of isotacticity present in the chain will influence the properties. As the amount of isotactic material increases, the amount of crystallinity will increase resulting in increased modulus, softening point and hardness.

Even though polypropylene is similar to polyethylene in many respects, they differ in some significant properties.

- PP is harder and has higher softening point, T_g and melting point.
- PP is less resistance to degradation but it has better environmental stress cracking resistance. The decreased degradation resistance of PP is due to the presence of tertiary carbon in PP, allowing for easier hydrogen abstraction compared with PE.
- PP is more resistance to cracking and bending

Polypropylene has many applications such as in automotive uses, packaging applications and etc. Some of the automotive applications are dome lights, kick panels, car battery cases, mount and engine covers. Elastomer filled PP is used for bumpers, fascia panels, and radiator grills in automotive industry. Also PP is used in house ware applications and in the outer tank of washing machines. PP films are used for carpet backing and sacks. Fibres prepared from PP are used in both woven and nonwoven fabrics (Baker & Mead, 2002).

2.4. Acrylonitrile butadiene rubber (NBR)

Acrylonitrile-butadiene rubber or also known as nitrile rubber is a family of unsaturated copolymers of acrylonitrile and various butadiene monomers such as 1,2-butadiene, 1,3-butadiene and, there being considerable variation in the ratio of these two monomers.

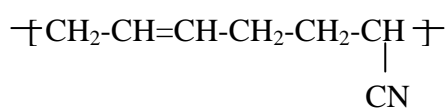


Figure 2.3. Repeating unit of acrylonitrile butadiene rubber (Blow, 1998)

The actual level of acrylonitrile in the polymers varies from nearly 50 per cent for the very high range to about 18 per cent for polymers of low acrylonitrile content (Ulrich, 1993). As the acrylonitrile content is increased so the molecule becomes less hydrocarbon and more polar. The primary properties affected are the T_g and the solubility parameter which both increase with increasing percentage of acrylonitrile content (Blow, 1998; Brydson, 1978). Also, the level of acrylonitrile content has an important effect on the properties of the final product.

As acrylonitrile content increases (Blow, 1998):

- Oil and solvent resistance improves
- Tensile strength increases
- Hardness increases
- Abrasion resistance increases
- Permeability decreases
- Heat resistance improves
- Low temperature resistance becomes poorer
- Resilience decreases
- Plasticizer compatibility decreases
- Compatibility with phenolic and PVC resin increases

The major technical advantage of the nitrile rubbers over general-purpose rubbers is resistance to oil and fuel. However; they have other properties that become important in specific applications such as resistance to gases, to abrasion, to heat, and to many solvents and chemicals as well as compatibility with certain resins (Lufter, 1964; <http://www.answers.com/topic/nitrile-rubber>). Disadvantages are poor dielectric properties and poor resistance to ozone (Ulrich, 1993).

2.4.1. Uses of Nitrile Rubber

NBR is used in the automotive industry to make fuel and oil handling hoses, seals, and grommets. NBR's ability to withstand a range of temperatures from -40°C to 120°C makes it an ideal material for extreme automotive applications (<http://www.answers.com/topic/nitrile-rubber>). Other automotive applications include shaft seals, bushings, gaskets, carburetor parts and oil-filter gaskets. Another large user of nitrile rubber is the oil-drilling industry such as blowout preventers, drill-pipe protectors, pump piston elements and rotary drilling hose (Blow, 1998). Nitrile rubber is also used to create moulded goods, cements, adhesives, sealants, footwear, sponge, expanded foams and floor mats. Nitrile rubber is used in plastic modifications to improve impact strength and flexibility (Morton, 1995). NBR latex is used in glove manufacturing industry in a great extent.

2.4.2. Nitrile gloves

Nitrile gloves are made of a synthetic polymer formed by combining the monomers acrylonitrile, butadiene and carboxylic acid. Each monomer contributes a unique property. Acrylonitrile provides penetration resistance from a number of solvents and chemicals such as hydrocarbons oils, fats and solvents. The chemical resistance and stiffness of the glove increase as the acrylonitrile concentration increases. Natural rubber on the other hands is not very resistance to chemicals. Butadiene adds softness and flexibility and contributes the elasticity of the glove. Carboxylic acid contributes to the tensile strength or the tear strength of the glove. By changing the composition of these monomers the characteristics of the glove can be changed. Many of the chemicals used in manufacturing nitrile gloves are the same as those used for manufacturing latex gloves (Nitrile gloves, 2003). Generally, nitrile

gloves exhibit tensile strength inferior to that of natural rubber gloves. Nitrile gloves are more expensive than natural rubber gloves. (Disposal medical gloves: the basic; <http://www.mrepc.com/publication/pub1/pg1.pdf>). Table 2.1 is given the comparison of nitrile gloves and natural rubber latex gloves (McPherson & Shamis, 2007).

Table 2.1. The comparison of nitrile gloves and natural rubber latex gloves

Nitrile gloves	NR latex gloves
<ul style="list-style-type: none"> • Inherently static dissipative 	<ul style="list-style-type: none"> • Inherently insulative
<ul style="list-style-type: none"> • Consistent in composition and cleanliness 	<ul style="list-style-type: none"> • Composition varies day-to-day and from season to season
<ul style="list-style-type: none"> • Durables and stands up to rigorous cleaning 	<ul style="list-style-type: none"> • Not as durable as nitrile
<ul style="list-style-type: none"> • Excellent chemical protection over range of chemicals, good performance with solvents 	<ul style="list-style-type: none"> • Limited protection over range of chemicals
<ul style="list-style-type: none"> • Not significantly affected by UV light or heat 	<ul style="list-style-type: none"> • Easily degraded by UV light and heat without the proper additive
<ul style="list-style-type: none"> • Lower elastic memory: retains approx. 50% of stretch force for extra comfort during long wearing periods 	<ul style="list-style-type: none"> • High elastic memory: 85% of stretch force over a short time period causing user hand fatigue

Table 2.1. Continued

Nitrile gloves

- Synthetic product with no natural latex proteins
- Quickly approaching feel (comfort) advantages of latex

NR Latex gloves

- Natural rubber latex protein allergens increase risk of Type I hypersensitivity
- Traditionally offers a comfortable feel

2.5. PP/NBR blend

Blends of NBR and PP combine the oil resistance properties of NBR and the excellent mechanical and processing characteristics of PP. The blends can be successfully used for high temperature oil resistance applications.

However these blends are found to be incompatible and immiscible. The incompatible blends are characterized by a two-phase morphology, narrow interphase, poor physical and chemical interactions across the phase boundaries and poor mechanical properties (George et al., 1995). Their overall performance depends on the properties of the individual components, the morphology and the interfacial properties between the phases (Liu & Huang, 2001). Therefore, it is crucial to improve the compatibility of these blends in order to use them for commercial applications. Compatibilization and dynamic vulcanization of immiscible blends lead to better compatibility and properties.

2.6. Compatibilization

A process of modification of interfacial properties of an immiscible polymer blend, resulting in formation of the interface and stabilization of the desired morphology, thus leading to the creation of a polymer alloy is known as compatibilization (Utracki, 1990 & 1998). There are three functions of the process:

- (i) To reduce the interfacial tension in the melt, thus engendering the finer dispersion
- (ii) To make certain that the morphology generated during the alloying stage will not be destroyed during high stress and strain forming
- (iii) To enhance adhesion between the phases in the solid state, facilitating the stress transfer across the boundaries, hence improving the mechanical properties of the final.

In practice, It is likely that all these effects will occur to some extent with addition of a particular compatibilizer (Bonner and Hope, 1993 & Utracki, 1998)

Generally, the materials used as compatibilizers are

- block of graft copolymers having segments identical to the components of blends and/or specific interactions with them
- functionalized polymers which have specific reactions or interactions with the component polymers
- by the addition of low molecular weight materials

(Utracki, 1998; Liu & Huang, 2001; Bonner & Hope, 1993).

The compatibilization of PP/NBR blend was investigated by many researchers (Soares et al., 2006; Joseph et al., 2006; George et al., 1996; George et al.,

1995). Soares et al. (2006) investigated the compatibilizing effect of PP-g-MAH on physicochemical properties of PP/NBR blend. They have reported that the concentration of compatibilizer corresponding to 2.5% resulted in a maximum on tensile strength and a minimum on the percent change of weight after toluene swelling. Further, they have observed that there was a continuous improvement of elongation at break as the amount of PP-g-MAH in the blend increase. Joseph and co workers (2006) have studied the melting and crystallization behavior of PP/NBR blends in the presence and absence of compatibilizers and fillers. They have found that phenolic modified PP (Ph-PP) and maleic modified PP (MAH-PP) permitted finer dispersion, provided a measure of stability against gross phase segregation and resulted in improved interfacial adhesion. Further they have observed compatibilization had an appreciable effect on melting temperature (T_m) and crystallization temperature (T_c) of PP. The melt rheological behavior of PP/NBR blend has been investigated by George et al., (1999). Their studies showed that the compatibilization of the blend with Ph-PP was found to increase the viscosity of the system, indicating an increase in interfacial interaction. According to their findings, as the compatibilizer concentration increases the domain size decreases and shows a leveling-off at high concentration.

In this study an attempt has been made to investigate the compatibilizing effect of polypropylene graft maleic anhydride (PP-g-MAH), Diglycidyl ether of bisphenol A (DGEBA) and natural rubber latex modified rNBR on the PP/NBR blend.

2.6.1. Polypropylene grafted maleic anhydride (PP-g-MAH)

Maleic anhydride (MAH) modified polyolefins are the most important class of functionalized polyolefins in commercial applications, due to the unique combination of low cost, high activity, and good processibility. They are the general choice of material in improving compatibility, adhesion, and paintability of polyolefins. Among them, MAH modified polypropylene (PP-MAH) is the most investigated polymer, which has found applications in glass fiber reinforced PP, anticorrosive coatings for metal pipes and containers, metal-plastic laminates for structural use, multilayer sheets of paper for chemical and food packaging, and polymer blends (Lu et al., 1998). PP-g-MAH is a highly reactive compound, which is often used as compatibilizer or adhesion promoter in various polymer systems (Szazdi et al., 2005).

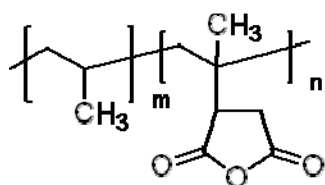


Figure 2.4. Chemical structure of polypropylene grafted maleic anhydride

2.6.2. Diglycidyl ether of bisphenol A (DGEBA)

DGEBA is a liquid diepoxide, the reaction product of bisphenol A with an excess of epichlorohydrin.

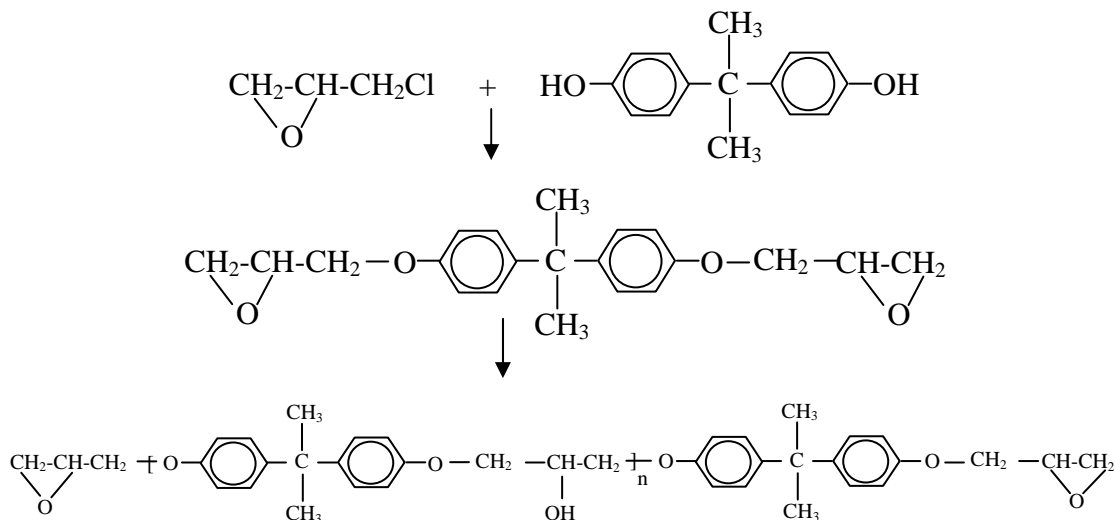


Figure 2.5. 2,2 -bis[4-(2',3'-epoxypropoxy)phenyl]propane/ Diglycidyl ether of bisphenol A (DGEBA) (Varma and Gupta, 2000)

Epoxy resins are characterized by the presence of a three-membered ring containing two carbons and an oxygen. Epoxy resins contain two chemically reactive functional groups, epoxy and hydroxyl. The epoxy group is highly reactive because of its three-membered ring structure and can be opened by a variety of nucleophilic and electrophilic reagents. Low molecular weight epoxy resins are mostly cured via the epoxy group. High molecular weight epoxy resins can cross-link via reaction with both epoxy and hydroxyl functionality depending on the choice of curing agents and curing conditions.

DGEBA is used extensively in industry due to its fluidity, processing ease, and good physical properties of the cured resin. The presence of glycidyl units in these resins enhances the processability but reduces thermal stability. The glass

transition temperature of the cured resin is relatively low, <120°C limited use in high performance applications (Varma and Gupta, 2000).

2.6.3. Natural rubber latex

Natural rubber is a polymer of isoprene, most often cis-1,4-polyisoprene with a molecular weight of 100,000 to 1,000,000. Typically, a few percent of other materials, such as proteins, fatty acids, resins and inorganic materials are found in natural rubber (Wikipedia-Natural rubber). Natural rubber is a nonpolar polymer. Besides that, natural rubber latex is also known to possess adhesive properties, low viscosity and low surface tension. Taking these facts into account, an attempt has been made to improve the interaction between PP and NBR by coating the NBR particles with natural rubber latex.

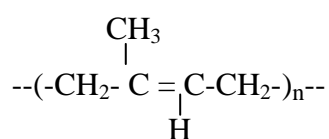


Figure 2.6. Chemical structure of 1,4-cis- polyisoprene

Awang et al. (2008a) have studied the processing and properties of PP-latex modified waste tyre dust blends (PP/WTD_{ML}). According to their findings, all examined properties of the blend such as tensile properties, swelling index in solvent and oil improved with the modification of WTD by NR latex. Better dispersion of WTD_{LM} in the PP matrix was observed. The thermogravimetric study has revealed that the modification did not alter the thermal properties of the blend.