

**CHARACTERIZATION AND PROPERTIES OF  
RECYCLED POLYPROPYLENE (RPP)/  
CHLOROPRENE RUBBER (CR) BLENDS**

**NURUL AZRA BINTI BAKARUDDIN**

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**Characterization and Properties of Recycled  
Polypropylene (RPP)/Chloroprene Rubber (CR)  
Blends**

by

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## LIST OF ABBREVIATIONS, SYMBOLS, SPECIALIZED NOMENCLATURES

1, 2-PB	1, 2-polybutadiene
AAc	Acrylic acid
ABS	Acrylonitrile butadiene styrene copolymer
ASTM	American Society for Testing and Material
BMI	M-phenylene-bis-maleimide
CBS	N-cyclohexylbenzothiazole-2-sulphenamide
CIIR	Chlorobutyl rubber
CPE	Chlorinated polyethylene
CR	Chloroprene rubber
DCP	Dicumyl peroxide
DMA	Dynamic Mechanical Analysis
DOP	Di-octyl phthalate
DSC	Differential scanning calorimetry
EBA	Poly(ethylene-co-butyl acrylate)
ENR	Epoxidized natural rubber
EOC	Ethylene octene copolymer
EOR	Ethylene-1-octene copolymer
EP	Epoxy
EPDM	Ethylene propylene diene terpolymer
EPM	Ethylene propylene copolymer
EPR	Ethylene propylene rubber
FTIR	Fourier Transform Infrared Spectroscopy

GMA	Glycidyl methacrylate
GTR	Ground tyre rubber powder
HDPE	High density polyethylene
HVA-2	<i>N,N'</i> - <i>m</i> -phenylenebismaleimide
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
LNR-6	Liquid natural rubber
MA	Maleic anhydride
MAc	Maleic acid
MAPP	Maleic anhydride grafted polypropylene
MBS	2-morpholinothiobenzothiazole
MgO	Magnesium oxide
MNR	Maleated natural rubber
NBR	Acrylonitrile butadiene rubber
NR	Natural rubber
PA	Polyamide
PA6	Polyamide 6
PA12	Polyamide 12
PC	Polycarbonate
PE	Polyethylene
PEBAX	Copolymer ethylene propylene diene
PEO	Poly(ethylene-octene) copolymer
PET	Polyethylene terephthalate
POE	Polyethylene octene elastomer
POM	Polyoxymethylene

PP	Polypropylene
PS	Polystyrene
PTT	Poly(trimethylene terephthalate)
PUR	Polyurethane
PVC	Polyvinyl chloride
RPP	Recycled polypropylene
RR	Recycled rubber
RTR	Reclaimed tire rubber
SAN	Styrene acrylonitrile copolymer
SBS	Styrene butadiene styrene copolymer
SEBS	Styrene ethylene butylene styrene block copolymer
SEM	Scanning electron microscope
$T_g$	Glass transition temperature
$T_m$	Melting temperature
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TMTD	Tetramethylthiuram disulfide
TMTM	Tetramethylthiuram monosulfide
TPEs	Thermoplastic elastomers
TPOs	Thermoplastic polyolefin blends
TPUs	Thermoplastic polyurethanes
TPVs	Thermoplastic vulcanizates
Tris	Trimethylolpropane methacrylate
WRP	Waste rubber powder
WTD	Waste tyre dust

$X_b$	Crystallinity of blend
ZnO	Zinc oxide
$\Delta H_f$	enthalpy of fusion of blend

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## **Pencirian dan Sifat Adunan-Adunan Polipropilena Kitar Semula (PKS)/Getah Kloroprena (GK)**

### **ABSTRAK**

Elastomer termoplastik adunan-adunan polipropilena kitar semula (PKS) dan getah kloroprena (GK) telah dikaji. Adunan-adunan polipropilena tulen (PP)/getah kloroprena telah digunakan untuk perbandingan. Adunan-adunan disediakan dengan menggunakan pencampur bilah-Z pada suhu 180°C dan kelajuan rotor pada 50 rpm. Kesan nisbah adunan-adunan ke atas sifat-sifat tensil, sifat-sifat pembengkakan, morfologi dan sifat terma juga telah dikaji. Didapati dengan meningkatnya kandungan GK di dalam adunan-adunan PP/GK dan PKS/GK telah meningkatkan pemanjangan pada takat putus dan indeks pembengkakan manakala kekuatan tensil, modulus Young dan penghabluran didapati berkurang. Adunan-adunan PP/GK telah menunjukkan sifat-sifat tensil dan terma yang lebih baik berbanding dengan adunan-adunan PKS/GK. Kajian morfologi adunan-adunan PP/GK menunjukkan interaksi antara muka yang lebih baik berbanding dengan adunan-adunan PKS/GK. Kesan pemvulkanan dinamik ke atas sifat-sifat adunan-adunan PKS/GK menunjukkan kekuatan tensil, pemanjangan takat putus, modulus Young dan penghabluran yang lebih tinggi tetapi peratus pembengkakan yang rendah. Pengserasi, maleik anhidrida polipropilena (MAPP) dan maleik anhidrida (MA) telah digunakan untuk meningkatkan sifat tensil adunan-adunan. Penambahan MAPP atau MA telah meningkatkan kekuatan tensil, modulus Young, pemanjangan pada takat putus dan penghabluran adunan-adunan. SEM mikrograf permukaan patahan tensil adunan-adunan PKS/GK dengan pemvulkanan dinamik, MAPP atau MA menunjukkan interaksi antara muka dan lekatan di antara GK dan PKS telah meningkat. Kehadiran MAPP atau MA di dalam adunan-adunan PKS/GK menunjukkan ketahanan terhadap bahan kimia yang lebih baik.

## Characterization and Properties of Recycled Polypropylene (RPP)/Chloroprene Rubber (CR) Blends

### ABSTRACT

*The thermoplastic elastomer of recycled polypropylene (RPP) and chloroprene rubber (CR) blends were studied. Virgin polypropylene (PP)/chloroprene rubber blends were used as comparison. The blends were prepared by using Z-blade mixer at temperature 180°C and rotor speed of 50 rpm. The effect of blend ratios on tensile properties, swelling behaviour, morphology and thermal properties were investigated. It was found that increasing of CR content in PP/CR and RPP/CR blends increased the elongation at break and swelling percentage but decreased in tensile strength, Young's modulus and crystallinity. The PP/CR blends indicated higher tensile and thermal properties than RPP/CR blends. The morphology study of PP/CR blends showed better interfacial interaction as compared to RPP/CR blends. The effect of dynamic vulcanization on the properties of RPP/CR blends indicated higher tensile strength, elongation at break, Young's modulus and crystallinity but lower swelling percentage. The compatibilizers, maleic anhydride grafted polypropylene (MAPP) and maleic anhydride (MA) were used to enhance the tensile properties of blends. The addition of MAPP or MA has improved the tensile strength, Young's modulus, elongation at break and crystallinity of blends. The micrograph SEM of tensile fracture surface of RPP/CR blends with dynamic vulcanized, MAPP or MA showed the interfacial interaction and adhesion between CR and RPP has been improved. The presence of MAPP or MA in RPP/CR blends exhibited better chemical resistance.*

## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

Nowadays, many new high performance products are manufactured by melt blending of common polymers. Polymer blends are one of the most interesting and useful classes of materials, which offer a convenient and less expensive alternative to develop new type of materials that can be tailor-made to meet specific requirements (Chakraborty et al., 2008a). Blending of polymers has been widely investigated as a simple and practical means to obtain new materials with novel properties. The blending of different polymer pairs usually gives rise to new materials with properties that cannot be achieved from the individual components. The many attractive mechanical characteristics of polymer blends have made it desirable to choose these materials over individual materials for numerous types of applications such as in automotive industries, explosives, and load-bearing components. As the use of polymer blends increase, an understanding of the mechanical behaviour of these materials becomes vital for creating innovative and economical designs for various components (Abu-Abdeen & Elamer, 2010).

Materials that combine elastomeric properties with many of the attributes of thermoplastics have been available to industry for over twenty years. They provide opportunities for polymeric materials to satisfy the requirements of designers and users of a wide range of products across a whole industry. Therefore, a number of research

works have been focused on enhancing properties of these materials for a specific application and for a better combination of properties. The thermoplastic elastomers (TPEs) based on rubber and plastic blends are kind of those materials. They combine the excellent processing characteristics of thermoplastic materials at high temperature, and a wide range of physical properties of conventional elastomers at room and service temperatures. TPEs materials are reprocessable, display and have economic advantages (Coran et al., 1998). The TPEs are materials consisting of a relatively high volume fraction of fully elastomeric domains in a continuous thermoplastic matrix. This morphological feature is produced by the process of vulcanizing a rubber component during its melt mixing with a thermoplastic resin (Asami & Nitta, 2004). TPEs have been gaining importance because of their wide range application in such fields as automotive parts, household appliances, electrical equipment, industrial supplies, food contact systems and medical apparatus (Rader, 2003).

The most well-known materials used to prepare TPEs are olefinic thermoplastics, such as epoxidized natural rubber (ENR)/polypropylene (PP) blends (Nakason et al., 2006a), natural rubber (NR)/low density polyethylene (LDPE) blends (Bhowmick et al., 2001) and NR/linear low density polyethylene (LLDPE) (Dahlan et al., 2002). NR/high density polyethylene (HDPE) blends have also produced interesting TPE materials (Nakason et al., 2006b). This type of blend combines the excellent processing characteristics of HDPE and the elastic properties of NR which can be used in automobile components and other industrial applications.

Thermoplastic elastomer based on polypropylene (PP) has received much attention over the years. Some elastomers such as ethylene propylene rubber (EPR), styrene butadiene styrene copolymer (SBS), butyl rubber, and ethylene propylene diene terpolymer (EPDM) have been introduced into PP to improve the impact and toughness

of PP (Tang et al., 2009). PP is considered to be the best choice for blending with elastomers due to its high softening temperature of about 150°C and the low glass transition temperature of the blend. The blending of PP with various elastomers has been done by many researchers. Awang et al., (2008) investigated the effect of latex modified waste tyre dust (WTD<sub>ML</sub>) on tensile properties, swelling resistance, and morphology of PP/waste tyre dust (WTD) blends. They found that the presence of WTD<sub>ML</sub> in the blends enhanced the tensile properties and swelling resistance of PP/WTD<sub>ML</sub> blends, and the improvement in interfacial adhesion and dispersion of PP/WTD<sub>ML</sub> blends.

PP is one of the most common thermoplastic polymers used for blending with elastomers. The use and demand of PP is increasing at a very fast pace. Indeed PP can be produced from low-cost petrochemical raw material, making it an inexpensive thermoplastic, relative to others, while showing good processability and reasonably high mechanical properties. Because of its excellent molding processability and good mechanical properties, PP has been widely used in automobile, household appliance and construction industry.

The improvement of physical and mechanical properties of PP based blends can be achieved by addition of rubbers or elastomers into it. Elastomers such as Chloroprene rubber (CR) or Neoprene are used to enhance the toughness and impact properties of PP. There are some advantages of CR which they have good inherent flame resistance, moderate resistance to oil and gasoline, excellent adhesion to fabrics and metals, very good resistance to weather ozone and natural aging, good resistance to abrasion and flex cracking and very good resistance to alkalis and acids (Long, 1985). CR is used in different applications such as for automotive parts, wire and cable jackets, general industrial parts, sponge and construction materials for buildings and public works.

Thermoplastics contribute to the total plastic consumption by roughly 80% and are used for typical plastics applications such as packaging but also in non-plastics applications such as textile fibres and coatings (Dewil et al., 2006). PP is one of the most visible forms of waste in landfills due to its chemically stabilized state for long service life and high volume-to-weight ratio. The presence of recycled PP has increased significantly for economic and environmental reasons in today's society (Brachet et al., 2008). It becoming a common procedure for the automotive as well as in the packaging industry. Thus, blends of recycled polypropylene (RPP) with elastomer would have some environmental advantages. The use of RPP in the blends can substitute the virgin synthetic thermoplastic matrix and the end product would be cheap. However, the recycled plastics have less desirable properties compared to the same articles manufactured from virgin materials. RPP has lower fracture properties (Aurrekoetxea et al., 2001) and heat ageing (Gahleitner, 2002) compared to virgin PP. Although the properties of RPP are lower than virgin PP, the idea is to enhance the properties of the RPP sufficiently for an intended technical application without losing the ecological and economic advantages of the recycled material. Navarro et al., (2003) have used the RPP toughened with various types of elastomers in their studies. They found that elastomer can improved the toughness without compromising the processability and recycling capabilities of the blends.

Generally, blending of thermoplastic and elastomer has led to an immiscible blend, phase separation, low interfacial adhesion and poor mechanical properties. In order to improve the compatibility of this immiscible polymer blend, the addition of one or more compatibilizers, such as block and graft copolymers were used to reduce interfacial tension, decrease the size of dispersed phase and provide specific interaction between two phases (Li et al., 2009).

In recent years, the common methods have been studied to improve the interfacial adhesion of blends included the use of maleic anhydride grafted polypropylene (MAPP) and grafting of maleic anhydride (MA). MAPP is a very effective compatibilizer that has been to improve the interfacial interaction between the components and mechanical properties of polymer blends by introducing the polar groups on the nonpolar PP backbone that leads to better interfacial adhesion. The novel technique for preparing maleic anhydride grafted PP has been reported by Qiu et al., (2005). The MAPP contributed to modification of polyolefins and gives the advantages of solventless, lower process temperature, energy efficient, low cost and easily running process which yields the high purity MAPP.

The purposes of MA grafting is either to achieve a polarity match or to introduce reaction sites (Elmaghor et al., 2004). Various elastomers such as CR, EPDM, EPR and NR can be used as polymer for the grafting of MA. Melt grafting of MA onto elastomer backbone has also been done by many researchers to improve the compatibility between non-polar elastomers. Jose, (2005) reported the effect of compatibilization by using MA on the blends of polyamide 12 (PA12)/styrene ethylene butylene styrene block copolymer (SEBS). They found that the morphology of compatibilized blends exhibited finer and more uniform rubber dispersion than the uncompatibilized blends because of the interfacial chemical reactions. The mechanical properties of PA12/maleic anhydride-grafted-SEBS (SEBS-g-MA) blends also were superior to those of PA12/SEBS blends.

Ismail & Suryadiansyah, (2002) have reported the comparison of mechanical properties of PP/NR and PP/recycle rubber (RR) blends. The tensile strength and Young's modulus decrease with increasing rubber content but elongation at break exhibit opposite trends for both blends. It was found that PP/RR blends have higher

mechanical properties than PP/NR blends. However, these blends are immiscible and these combinations are known to cause reductions in both strength and stiffness of the blends. They also have poor mechanical properties due to the weak physical and mechanical interactions between the phases. Thus, several studies were done to attain a technological compatibilization, improving the mechanical properties of the blends.

Dynamic vulcanization is a route to new TPEs, which have properties as good or even, in some cases, better than those of elastomeric block copolymers. This method describes the process of vulcanization of the elastomer during melt-mixing with a molten plastic (Soto-Oviedo & De Paoli, 2006). Elastomers are vulcanized to give a particulate vulcanized elastomer phase of stable domain morphology both during melt processing and subsequently. The effect of the dynamic vulcanization is to produce compositions which have improvements in permanent set, ultimate mechanical properties, fatigue resistance, melt strength and thermoplastic processability (Hernández et al., 2008). Dynamic vulcanization and addition of compatibilizers to the blends were done by several researchers to improve the blend performance. Awang et al., (2007) studied the effect of dynamic vulcanization on tensile properties of PP/waste tire dust (WTD) blends. They found that the dynamic vulcanization improve the tensile properties of the blends and promoted good adhesion between the PP matrix and WTD. Huang et al., (2002) have prepared a blend of EPDM and nylon via dynamic vulcanization. The effects of curing systems and compatibilizers on the mechanical properties of EPDM/nylon blends were investigated. They found that EPDM/nylon blends using sulfur as curative has higher tensile strength and elongation at break than that of blends using phenolic resin or peroxide as curatives. The compatibilized EPDM/nylon blends with MA grafted EPR has a better performance compared with other compatibilizers containing acid group. Nakason et al., (2006c) used MAPP in

order to compatibilize the maleated natural rubber (MNR)/PP blends. It was observed that the incorporation of MAPP in the blends enhanced the interaction at the interface and improved the interfacial tension thus leads to decreasing size of dispersed domains of the minor phase (PP) in the MNR matrix.

## **1.2 Problem Statement**

The previous studies have reported the various blends of polypropylene with different types of rubber blends, but not many researches studied base on recycled polypropylene and rubber blends. The recycled polypropylene was used to reduce cost of blends and solve the environment problem of plastic waste. This research was focus to investigate the new blends from recycled polypropylene and chloroprene rubber blends.

## **1.3 Objectives of Study**

The primary objective of this study is to determine the feasibility of recycled polypropylene (RPP) in RPP/CR blends with different composition. The objectives of this research are:

1. To study the effect of different blend ratios of RPP/CR and PP/CR blends on tensile properties, swelling behaviour, morphology, and thermal properties.
2. To study the effect of dynamic vulcanization on the properties of RPP/CR blends.
3. To study the effect of different compatibilizers, maleic anhydride-grafted polypropylene (MAPP) or maleic anhydride (MA) on properties of RPP/CR blends.