PROPERTIES OF RECYCLED CROSSLINK POLYETHYLENE FILLED HIGH DENSITY POLYETHYLENE COMPOSITES

by

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LIST OF ABBREVIATION

AH	Ammonium hydroxide
FTIR	Fourier Transform Infra Red
HDPE	High density polyethylene
NA	Nitric acid
PVC	Polyvinyl chloride
Si	Silane
XLPE	Crosslinked polyethylene

LIST OF SYMBOLS

%	Percentage
°C	Degree celcius
cm^3	Centimeter cube
Eb	Elongation at break
MPa	Mega pascal
Tm_1	Melting point
W	Percentage of weight gain/loss
Wi	weight before immersion
Wt	weight after immersion
ΔH	Entalphy
ΔH_c	Crystalization entalphy
σ_y	Tensile yield strength

SIFAT BAHAN KOMPOSIT POLIETELINA SAMBUNG SILANG KITAR SEMULA POLIETELINA BERKETUMPATAN TINGGI

ABSTRAK

Sisa buangan polietelina sambung silang yang diperoleh daripada kabel elektrik berkuasa tinggi telah digunakan dan diadun ke dalam matriks polietelina berketumpatan tinggi. Oleh sebab kandungan gel yang tinggi (93%), kebolehan untuk menghasilkan sebuah adunan yang sebati sepenuhnya adalah amat tipis. Bagaimanapun disebabkan faktor tersebut, hasil buangan telah dipecahkan menjadi pengisi kecil. Pengisi kemudiannya diadunkan ke dalam polietelina berketumpatan tinggi untuk menghasilkan sebuah bahan komposit dengan kandungan 5, 10, 20, 15 dan 30 berat peratus. Sifat tensil, termal dan morfologi bahan komposit telah diperoleh. Bagaimanapun penambahan bahan buangan didapati tidak memberikan sebarang penambahan kekuatan kepada matriks polietelina berketumpatan tinggi. Kekuatan tegasan tensil komposit berkurangan apabila kandungan bahan terbuang meningkat dari 5, 10, 15, 20 dan 30%. Ujian ketahanan kimia telah dilakukan untuk memperoleh sifat tensil sebelum dan selepas direndam. Dua bahan kimia yang dipilih iaitu asid nitrik dan ammonium hidroksida telah digunakan. Sifat bahan komposit tersebut berkurangan banding dengan polietelina berketumpatan tinggi tidak terisi. Ujian ketahan kimia secara keseluruhanya telah menunjukkan kekuatan tensil bahan komposit berkurangan dengan peningkatan bahan terbuang dari 5, 10, 15, 20 dan 30% bersama bahan kimia kepekatan 50 dan 100%. Had putus pemanjangan bahan komposit menunjukkan tiada kesinambungan untuk sisa buangan berlainan kepekatan. Kadar pemanasan berlainan untuk DSC dari 5, 10 dan 15°C/min menunjukkan ko- penghabluran dengan penambahan sisa buangan dari 5, 10, 15, 20 dan 30%. Morfologi bagi bahan komposit tersebut menunjukkan pusat tumpuan tekanan dengan peningkatan bahan buangan 5, 10, 15, 20 dan 30%.

PROPERTIES OF RECYCLED CROSSLINK POLYETHYLENE FILLED HIGH DENSITY POLYETHYLENE COMPOSITES

ABSTRACT

Waste crosslinked polyethylene (XLPE) obtained from a high voltage electric cable was directly utilized, recycled and incorporated into a high density polyethylene matrix. Due to the high gel content (93%), the possibility of producing a completely miscible blend is quite unlikely. However due to that factor, the waste is break down into small filler. They are then compounded with HDPE in concentrations of 5, 10, 15, 20 and 30wt% to produce a composite material. The tensile properties, DSC and morphology of the composite were obtained. However, addition of the waste did not give any reinforcing properties to HDPE matrix. This is visible from the tensile properties of the composite where the tensile strength decreases as the waste concentration increase from 5, 10, 15, 20 and 30%. The elongation at break of the composite decreases as the waste concentration increases from 5, 10, 15, 20 and 30%. The chemical resistance test was done to obtain the tensile properties of before and after immersion. The two chemicals selected are nitric acid and ammonium hydroxide. The tensile strength of the composite decreased compared to virgin HDPE samples. Chemical resistance properties show that overall the tensile strength of the composite decreases with increasing waste concentration from 5, 10, 15, 20 and 30% with chemical concentration of 50 and 100%. For elongation at break of the composite, the value shows irregularity for different waste concentration. Different heating rates of 5, 10 and15°C/min of the DSC scans shows co-crystalization with increasing waste content form 5, 10, 15, 20 and 30%. The morphology of the composite shows stress

concentration sites due to the waste sticking to each other with increasing waste content from 5, 10, 15, 20 and 30%.

CHAPTER 1

INTRODUCTION

1.1 Polymeric Crosslinked Waste Disposal

Solid waste disposal is one of the major problems faced in Malaysia who is rising in terms of economic growth as well as increase in population (Hassan *et al.*, 2000). Increase in population speeds up the process of urbanization causing an increase demand in basic utilities like electric supply. In addition, rapid urbanization affects current cities which have to cater increase needs therefore implying upgrade and replacements in these types of services. This results in disposal of crosslinked polymeric waste which gives a huge blow to the nearly crippled waste disposal sites (Hassan *et al.*, 2000). As a result, waste is incinerated to save on land used for waste disposal. Crosslinked waste materials exist in the form of scraps like crosslinked PE which is produced by crosslinking LDPE using hydrogen peroxide with crosslinking degree of 60- 80% (Drake, 2010). Due to its excellent dielectric properties, it is commonly used as insulators for medium and high voltage cables.

The main insulation material used in cable manufacturing is crosslinked polyehthylene (XLPE). Nowadays crosslinked polyethylene (XLPE) is the most widely used polymer material in extruded cable insulation. It has largely replaced paper/oil insulation in medium and high voltage cables because of its simple structure, easy manufacturing, and low cost (Vaughan *et al.*, 2003).

Common methods which are used to crosslink polyethylene are electron irradiation and chemical crosslinking process (Callister, 2006 and Bartnkias *et al.*, 1983). In chemical crosslinking process, addition polymerization reaction takes place involving peroxide and a bridge molecule. Polymerization chains are formed and joined together by multi ended bridge molecule which are crosslinked. The crosslinking introduced into the material causes some properties to increase significantly. Apart from excellent electrical insulating properties, electron irradiated or chemically crosslinked polyethylene has increase impact toughness (Bartnkias *et al.*, 1983). However, given the added advantage of this material such as increased chemical resistant and excellent dielectric properties, the disposal of crosslinked waste material is a compelling environmental issue (Tamboli *et al.*, 2003 and Isa *et al.*, 2005)

1.2 Problem Statement

Based from an unofficial collaboration from a local manufacturer and power supply company, specifications for medium and high voltage cables are very strict and only minimum allowance (cable dimension) are allowed for the insulation layer during production process. Also, during production, the copper conductor face defect as in diameter out of specification, discolour and oxidize. Therefore, this cable produced is scrap entirely and not recycled.

The waste XLPE is then burnt and the copper is scrapped and sold to third party where they will re- process it to be used in other applications. From industry point of view, they have to minimize loss especially on scrap material. XLPE waste could not be reprocessed and this is considered as a high loss where it will increase in process cost which will then minimize profit.

Industrial approach to recycling polymeric waste is to crush into smaller pieces and composite again with virgin base material to be used again. Problem arises because XLPE waste is thermoset and re- compositeing again is not possible. That is the main reason why the waste is scrapped and burnt. Scrapping process also involve cost because it has to be out sourced to third party.

1.3 Direct utilization

Re- use the waste in cable insulation again is diminished because it has become a thermosetting material and could not be reprocessed. Aligned with that, waste XLPE is viewed as a normal rigid material like wood where it could not be melted to produce other material but it could be cut and shaped into other products like filler. Utilizing the waste crosslinked PE as filler in polyolefins could be advantageous, given that sufficient compatibility between filler and matrix would exist (Yamaguchi *et al.,* 2002). By decreasing the matrix of the composite, it could decrease in usage of virgin material as well as decreasing material cost.

Crosslink polyethylene has good chemical resistance properties (Abdul Rahman, 2006) which are advantageous when incorporating into a melt blend with reducing matrix content and increasing filler content. This highlights its potential use in gross pollutant traps which uses high density polyethylene as its main construction to filter gross pollutant waste from post consumer waste water. For this application, the GPT is exposed to chemicals which are present in the waste water. Although HDPE has good chemical resistant properties (Cornelia *et al.*, 1993), addition of the waste could produce a value added product as well as reducing the amount of HDPE used.

1.4 Study constrains

The study is based on an unofficial collaboration with Daya Polymer Sdn Bhd and Tenaga Nasional Berhad. Therefore the study uses an industrial approach with scientific interpretation based on the requirements of the manufacturer which is relatively straight forward; waste recycled and composite without any additional process to maintain efficiency. The requirement from the supplier is stressed on the processing aspects (thermal properties) and producing a value added product. In addition, the cable waste supplied is limited due to the copper material which is a strictly controlled material where the cable is scrapped as a whole (copper and XLPE). The manufacturer is looking into possibilities to set up a recycling line where they could get value added product from the insulation layer instead of incinerating it.

1.5 Possible setbacks

In order to do so, the XLPE waste needs to undergo a few processes before it could be utilized. For a complete cable form, the cable needs to strip from to obtain the XLPE. Here it must be stripped by means of mechanical method i.e. cutting. This proves to be one of the set back in directly utilizing this material. This process is lengthy and time consuming. The incorporation of waste XLPE could provide stress concentration sites because it could not melt entirely and mix with the matrix. This stress concentration sites therefore could decrease the mechanical properties of the composite especially its tensile properties. The crosslink materials which are not entirely melted into the composite could decrease the appearance of the composite. Apart from that, the size of the crosslink waste has to be control and if too large it could prove to be a difficult for small dimension products. Crosslinking the matrix could prove in helping to increase the properties of the composite but could also be a setback. As discussed previously, crosslinking will decrease the ductility of the composite therefore limiting the possible application of the blend where ductility is preferable compare to brittle.

Direct utilization of waste XLPE could prove to be satisfying since it would bring a good deal to surroundings by decreasing land fill consumption and also as an alternative to incineration of the XLPE waste. In addition, this method might be time consuming but it is safe because it uses no dangerous chemical as stated earlier using the de- crosslinking method.

1.6 Objective of study

The objective of this study is to;

i) To obtain the tensile properties of the waste XLPE/HDPE composite with increasing waste content.

ii) To obtain the thermal properties of the composite by means of thermoscans and its processing characteristics

iii) To obtain the chemical resistant properties of the composite for a value added product

CHAPTER 2

LITERATURE REVIEW

2.1. Polymeric waste

Urbanization has given significant effects towards the vast diversity of a growing population. Other than bringing developments in terms of better and efficient living experiences, it also gave rise to many problems mainly in pollution. There are several types of common environmental pollution which are air, water and land (Hill *et al.*, 2010). Land pollution concentrates on the excessive waste produced and un-properly disposed. As a result, we see many litter and waste laying around in common streets and places where human activity is at a peak. Polymers are useful material which provides a wide diversity of application due to its cost efficiency and ease in processing (Ryan et al, 1998). Therefore it has become a vital ingredient in providing ease in living for our society nowadays. However the growing need for polymers in everyday live has brought forward some drawbacks mainly in terms of disposing of it. Polymeric wastes are commonly found in waste or any landfills. They are usually in forms of bags, bottles and containers. This polymeric waste is currently a common issue in any nation. The main reason which is the root to this problem is the inability of a polymeric waste to degrade at a short period of time. This will result in it being left abundant in landfills and it is space consuming.

In the eyes of a common person, this is terribly a disadvantage since the waste is known to be utterly useless and is a nuisance. However, if looked closely, this problem could be arguably an advantage especially to industries where plastic is its bread and butter. The plastic waste could be recycled and incorporated to virgin plastic and a new product is produced. However this is easier said than done because recycling a plastic product is proved to be a hassle. The main problem lies in the sorting and cleaning of the polymer waste. Therefore, polymer or plastic recycling is focused commonly on post consumer and industrial scraps because of ease in collection and reprocessing. Basically there are five different polymers that contribute to the total amount of domestic plastic waste, namely polyethylene, polypropylene, polystyrene, polyvinyl chloride and polyethylene terephthalate (Chanda *et al.*, 2007).

Polyethylene is a type of thermoplastic which is commonly used in the production of plastic bags, detergent and milk bottles. Based on their differences in density and branching structurally, polyethylene could be classified as high density polyethylene, low density polyethylene and linear low density polyethylene which exhibits different characteristics physically and chemically (Fried *et al.*, 2003). Polyethylene could also be crosslinked with the presence of a crosslinking agent and initiator (Sen *et al.*, 1992, 1993, Kao *et al.*, 1986, Palmlof *et al.*, 1991, Narkis *et al.*, 1985; and Turcsanyi *et al.*, 1990) and is commonly used as main material in electric cable manufacturing. They are used because of its high electrical insulating properties. Stepping back towards the issue on plastic waste, crosslinked polyethylene (XLPE) waste is considered as hard to recycled since it has thermosetting properties where once formed it could not be reprocess which could risk it towards degradation. It has no prone towards melting since it crosslinking in its structure and being a waste, it has high risk of being crosslinked almost completely due to exposure to environment. In addition, elastomeric products like rubber which are widely used in automotive industry also contribute to the polymeric waste problem. Natural rubber is crosslinked before it could be utilized to produce new products to ensure that it has increased physical and chemical properties.

As a result, recycling these types of material is indeed a problem. Mainly, this material is incinerated to produce energy (Lee *et al.*, 2008). But since this could also lead towards polluting the environment, it is an unwise solution. Being a crosslinked material it provide several advantages in its properties which are discussed further in the next topic. Incorporating it into a polymer melt blend could help somehow increase the properties of the matrix. However further analysis is needed to be done to further confirm this idea. With that problem statement, this study is aimed at reviewing methods and solutions to overcome this problem which is present in the current environment.

2.2 Gross Pollutant Traps

In Australia, the local municipal council have practice the usage of pollutant traps in their water ways. These traps are their first line of defence in their wastewater management system. The concept of the trap is fairly simple where it filters the water through a series of traps and nets. These inventions manage to clean up to 95% of gross pollutant which are present in their water ways. Examples of manufacturer which produce gross pollutant trap (GPT) are Rocla, Humes and Baramy.

In Malaysia, several locations have been installed with GPT like Putrajaya, Klang Valley and Kota Tinggi. The main issue that arises during the installation is the cost that the product bares. For example, in Kota Tinggi, the local municipal council (MDKT) had to pay an amount of RM200, 000 for the product (Utusan, 2008).

The main construction material for these GPTs is concrete. However, polymer based GPT are also available and is based on high density polyethylene (HDPE) material. HDPE is used due to the chemical resistant properties and its capability to be used in a sub surface environment. Addition of the crosslink waste could decrease the amount of HDPE use therefore being cost efficient and create a value added product from crosslinked waste.

2.3 Crosslinking in Polymeric Material

Crosslinking is achieved by means of two methods which are chemically or physically (Flory, 1953, Mori, 1997, Coran 2003, and Marrykutty *et al.*, 2003). Crosslinking is also available in elastomeric materials (Flory, 1953; Mori, 1997; Conan, 2003; Abi *et al.*, 2003 and Marrykutty *et al.*, 2003) where sulphur is introduced to promote crosslinking in its chains which enhances the properties of natural rubber. This process is known as vulcanization where it improves the properties of the natural rubber physically (Amiya *et al.*, 2002) and chemically (Xiaohong, 1998).

By far, two methods are commonly used to chemically crosslink a polyethylene which are peroxide (Loan, 1963 and Edward *et al.*, 1984) and silane (Atkinson and Cicek, 1983; Shieh, 1998; Tsai, 1998; Liu, 1999; Shieh *et al.*, 2001 and Chuang, 2001). Radiation crosslinking (Erbun and Orhun, 2007 and Squire and Turner, 1972) is part of physical crosslinking where the polyethylene is exposed to high energy gamma rays for a certain period of time to achieve crosslink.

2.3.1 Peroxide Crosslinking Method

Peroxide induced crosslinking has to be operated at high vacuum, and it is difficult to control the thickness of the products (Kuan *et al.*, 2005). It is achieved by introducing a crosslinking agent which is peroxide to induce crosslinking within the polymer structure as shown in Figure 2.1.

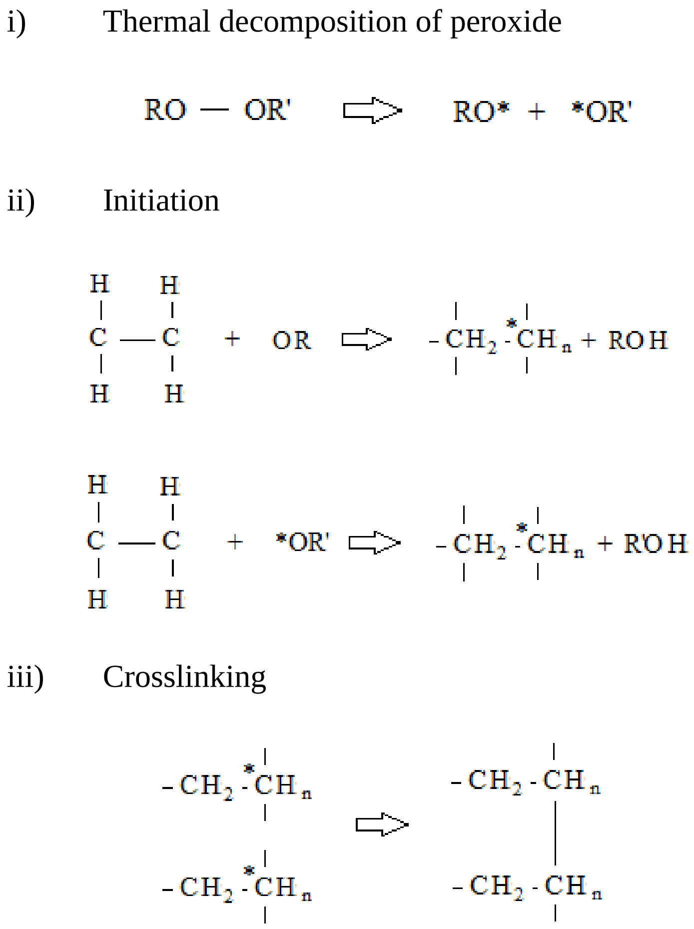

Figure 2.1: Peroxide induced crosslinking chemical reaction representation (Khonakdar *et al.*, 2003)

During the initiation reaction (Figure 2.1), the peroxide generates free radicals upon heating. Then the radical abstracts a hydrogen atom from one carbon atom from the PE chain. This produces a reactive carbon atom then forms crosslinking bond with another reactive carbon atom thus forming stable carbon-carbon bond. Izumi *et al.* (1996) and Kato and Miyashita (1988) reported that two adjacent bonds with such condition form crosslink.

2.3.2 Silane Crosslinking Method

In crosslinking polyethylene with silane, it is first grafted followed by hydrolysis to Si-OH groups and condensation to form Si-O-Si bonds as shown in Figure 2.2 (Beltran and Mijangos, 2000). Unsaturated hydrolysable alkoxysilanes are grafted into the polyolefin first. They are then undergone a catalyzed crosslinking process and shaped into desired product. According to Hidalgo *et al.* (1996), Rodriguez and Gilbert (1997), Shieh and Liu (1998), Shieh and Hsad (1999) and Shieh and Chang (2001). Peroxide crosslinking method involves the usage of a peroxide agent to initiate the hydrogen abstraction process at elevated temperature.

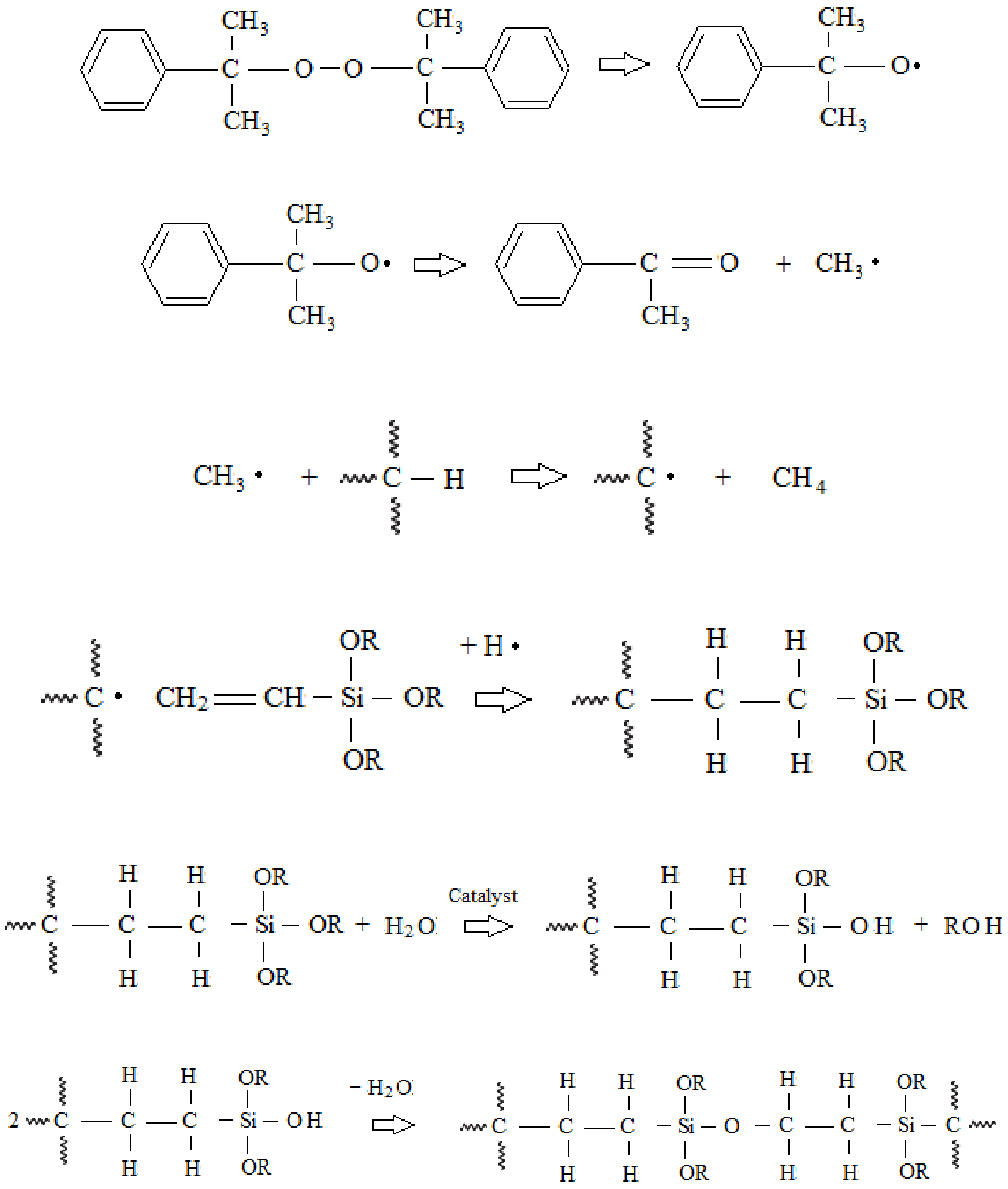

Figure 2.2: Silane crosslinking chemical reaction representation (Kuan *et al.*, 2005)

The process generates free radicals with free electron which then abstract the carbon atom from the polyolefins chain. The reactive localized radical will then abstract another hydron from another polyolefin strand. Then a carbon- carbon bond will occur for stability (crosslink).

2.3.3 Processing Methods on Producing Crosslinked Polyethylene

By far, the most common method used to produce silane crosslinked polyethylene is by extrusion method. The composites are mixed prior before extrusion to obtain a uniform distribution before being extrude.

For peroxide method, the crosslinked material is produced by reaction with peroxide at high temperature and pressure. High pressure is needed since the process produces methane by product. If no high pressure is present, the gas will exit the material and produce pores which could decrease the properties of the product. Peroxide is a heat sensitive material and precise temperature and process control is needed during the production. The material is risked to premature curing which could lead to decrease in properties and appearance of the product.

For silane grafted polyethylene, the grafting process takes place during mixing in the extruder and crosslinking occur during the extrusion of the melt. Crosslinking occur during immersing the composite in hot water or expose to hot moisture after extrusion. This further increase the gel content of the composite and this is known as a two step process. In a one step process, the product is produced directly i.e. cable, tube with crosslinking taking place immediately. This process sounds rather straight forward but is complicated since an efficient process control and machinery is needed.

2.4 Mechanical Properties of Silane Crosslinked Polyethylene

The mechanical properties of XLPE are affected greatly by the degree of crosslink that is available within its structure. Increase in gel content (crosslinking available) increases the tensile strength of the material but decreases the elongation at break. Other properties such as flexural strength and notched impact strength decreases as the gel content increases. The addition of crosslink reduces slippage (Figure 2.3) of the polymer chains which result in decrease of elongation but increases the tensile strength. The crosslinks impose restrictions towards the movement thus increasing the amount of force for it to break or fail.

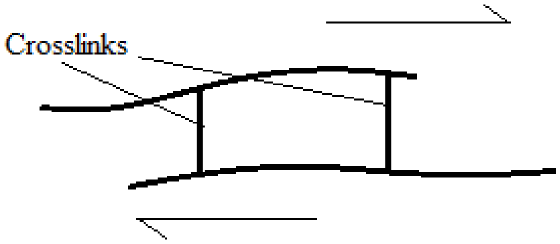

Figure 2.3: Crosslinks reduce slippage of the material at a structural level

2.5 Thermal Properties of Silane Grafted Polyethylene

The introduction of tertiary carbon bonds in the system decreases the thermal properties of the material. For instance, the decomposition temperature of crosslinked polyethylene system decreases as the gel content increases (Khonakdar *et al.*, 2003). In addition, the melting temperature of the crosslinked material decreases with increasing gel content. The introduction of crosslink within the structure causes the crystalinity of the material to decrease hence increasing amorphous region in the material on a structural level. Crosslinks play the role of defect centers, which impede the folding of macromolecular chains and thus decrease the sizes of the lamellar crystals (Khonakdar *et al.*, 2003). Increasing in amorphous region will therefore causes the glass and melting temperature to decrease compared to the virgin material.

2.6 Mechanical Properties of Waste Crosslinked Polymeric Material

Crosslinked polymeric materials like crosslinked polyethylene with high crosslinking degree shows decrease in mechanical properties like the elongation at break, tensile strength and tensile strength (Yusuf *et al.*, 2007). Restrictions imposed by the crosslink junctions, proves to be the reason why the mechanical properties of the material decreases. The restrictions causes stretching of the polymer segments are limited resulting decrease in elongation.

However, for elastomeric material, the restrictions provide an added advantage towards its mechanical properties. They are amorphous in nature (molecular chains twisted and coiled) and when it is stretched, it could elongate more than its original size. The crosslink acts as anchor points and prevents slippage from occurring at the chains (William and David, 2011). But with high crosslink density, the rubber hardens and become brittle.

2.7 Thermal Stability and Chemical Resistance of Crosslinked Polyethylene

Introduction of crosslinks into a polymer structure reduces the thermal stability. For example, introduction of crosslinks into a polyethylene system recorded that the degradation temperature is lower compared to neat polyethylene (Khonakdar *et al.*, 2003). Same goes for melting temperature where increasing crosslink content decreases the melting temperature. This is due to the increasing amount of tertiary carbon atoms with increasing crosslink density. As for melting temperature, the presence of crosslink affects the crystallinity of the composite where decrease in crystal size is experienced. As a result, the melting temperature decreases for increasing crosslink density.

Commonly, HDPE is used in water related applications like water pipes and water tanks. The main advantages of this material is that it is cost efficient, light weight and has long shelf life (50 years). Due to the good chemical resistance properties of HDPE, they are commonly used in this type of application. Being exposed to water, degradation process still takes place (Ildiko *et al.*, 2008). HDPE is also used in holding tanks like chemical and water tanks.

For instance, in pipes the material is exposed to chlorinated water (supplier) and waste water (post consumer). Several reports studied on the effect of chlorinated water on polymeric materials (and all concluded that the exposure decreases the mechanical properties of the composite. This property also enables HDPE to be used as a storage or holding tank for chemical (Gareth *et al.*, 1999).

Post consumer waste water specifically household waste water exposes the material towards acid and alkalis like detergent, bleach and household cleaning products. They are not as crucial compared to industrial waste water. However, prolonged exposure towards chemical degradation may decrease the properties of the material in terms of mechanical properties and physical appearance.

Chemical degradation is where the polymer reacts with the chemical at its surroundings. The reaction results in breaking of double bonds which alter the structure of the polymer. This results in the decrease of mechanical properties like tensile strength. Commonly, Fourier Transform Infrared Spectroscopy is used to analyze degradation in polymer composite. The altered structure could be analyze and compared with un- exposed material. The structural changes could be obtain by FTIR and confirm the degradation process.

2.8 Application of Crosslinked Polymeric Materials

Crosslinked polymeric materials are used in many everyday applications. Crosslinking provides improved properties of the polymeric material physically and chemically. For example, crosslinked rubber is used in producing tyres for automotive applications. Without crosslinking, natural rubber is brittle and could not be used in many applications. Crosslinked polyethylene is used in electric cable (Orton and Hartlein, 2006) manufacturing where it becomes the core of the cable providing high levels of electrical insulations (Ruben *et al.*, 2009) and low electric loss (Malik *et al.*, 1998). The cable ranges from high voltage cable, medium voltage cable and low voltage cable. These cables are mainly used at sub- stations for power distribution. The cables usually have few layers depending on its application surrounding. For example, for sub-surface application, the cable is armoured with steel wire to further protect the cable core as well as the insulation. Some cables have flame retardant capabilities which are required for offshore application. Crosslinked polyethylene is also used as insulation in auto- wire manufacturing for automobile application. In addition, it is also use in power cable manufacturing. Power cables are mostly used as power distribution for heavy industries and machineries. It is also made into tubes used for plumbing (Society of Plastic Engineering, 1998) and fire protection applications (Hemant, 2008).

2.9 Methods of Recycling Crosslinked Waste by Direct Utilization

Due to the high level of crosslinking available in the waste, the material could not be directly reprocessed to produce a new product. For example, scrap XLPE cannot be recycled directly by reprocessing due to the crosslinking that is available (Tamboli *et al.*, 2004). But from a different point of view, it could be treated like any conventional material like wood where it could be utilized directly to produce or incorporated into a new product.

Utilizing it covers a broad scope where the most obvious usage of the crosslinked material is incorporating it into a polymer matrix producing a polymer matrix composite. This gives it an added advantage because of in nature it is still a polymeric material thus giving it compatibility with the matrix system. Compared to other types of fillers like mineral fillers (Liang and Yang, 2007; Metin *et al.*, 2004; D'Almeida and DeCarvalho, 1998; and Pukanszky *et al.*, 1989) which are of different material than the matrix, they tend to exhibit incompatibilities like agglomeration

(Ariffin *et al.*, 2006; Fuad *et al.*, 1995; and Rothon, 1999) and pre-treatments (Khunova *et al.*, 1993; Maiti *et al.*, 2002; and Doufnoune *et al.*, 2008) of the fillers are usually needed before processing.

Incorporating it into a polymer matrix system is a worthwhile since it could be a method to minimize the amount of crosslinked polymeric waste that is available. When the crosslinking is at a maximum, the material tends to be brittle (Tamboli *et al.*, 2004). For common application like cable insulators, the gel content is around 60-89% (Caronia *et al.*, 2003) and constant application could cause the gel content to increase up to 95% which result it to be hard and brittle. Due to its brittleness, the crosslink material could be subjected to grinding i.e. filler production. A few publications (Shigiro *et al.*, 2003 and Uematsu and Ogiwara, 2000) have recorded the use of a pulveriser to create particles which could be used as filler in a composite material. The filler is then incorporated into a polymer matrix to produce a polymer matrix composite. Several publications (Shigiro *et al.*, 2003; Uematsu and Ogiwara, 2000) recorded that the filler gave significant reinforcing capabilities where there is an increase in impact strength but decrease in elongation.

In the same context, crosslinked polymeric materials which are of elastomeric base (Marykutty *et al.*, 2000)are also pulverized into smaller sizes and incorporated into a polymer matrix of elastomer base like natural rubber (Rajaleksmi and Rani., 2002; Campbell *et al.*, 1978; Mullins, 1978) to produce a new product. These waste includes tyre (Aman *et al.*, 2011; Zainal and Ismail, 2011), scraps (Yan *et al.*, 2003; Ravinchandran and Natchimuthu, 2005) and by- products of rubber factories (Thaniya and Sirinthrar, 2009; Kaosol and Wandee, 2009).

Overall, the properties which are exhibit by this type of composite system show promising results physically and chemically. Incorporation of crosslinked polyethylene into a polyethylene matrix shows increased impact strength but reduced percentage of elongation at break (Tamboli *et al.*, 2004) which is quite similar to the properties of crosslinkedpolyethelene. However, the incorporation of crosslinked filler did not affect the tensile strength, flexural strength, and modulus. The authors also concluded that the crosslinked filler may affect the matrix of the composite by forming networks. This has yet to be proven yet since there is no data indicating of such phenomena. Such phenomenon is where a certain amount of crosslinking is promoted into the matrix system of the composite thus improving overall properties (Ratner *et al*,.2003). In addition, the melted crosslinked skin provided good interfacial towards the matrix thus improving the properties. Crosslinked skin here refers to the uncrosslinked parts which are present but at a low level.

2.10 Methods of Recycling Crosslinked Waste by Chemical Methods

Chemical methods simply refer to the de- crosslinking of a crosslinked polymeric material. Here, the process involves removing the crosslinking between the polymer chains by exposing it to extreme conditions involving elevated pressure and temperature. For elastomeric composites, the process is known as de- vulcanization (Goodyear, 2010; Alexandre-Franco *et al.*, 2010 and Sato *et al.*, 2004). De-vulcanization aims at removing the crosslinks which are available and making it more easy to re-process into a new product. In the same context, same process is also applied to waste crosslinked polyethylene (Cho *et al.*, 2009; Yong *et al.*, 2012; Masaaki *et al.*, 2005; and Lu and Hentschke, 2002) to break the crosslinking in the material. It is subjected to extreme conditions in mediums of water or an alcohol until the crosslinks breaks and the thermoplastic is obtained. However, this method has its drawbacks since specialized equipment is needed and the extreme conditions prove to be costly. In addition, the process sometimes is not successful where the crosslinking is still available or reformed after the process is ended (Kojima *et al.*, 2003).

2.11 Crosslinked Polymeric Waste Composite

Crosslinked polymeric waste could still be utilized to form new products like incorporating it into a HDPE matrix. The methods available are proactive and practical especially for direct utilization. Tamboli *et al.,* (2003) produced a HDPE filled with waste crosslink foam. They concluded that the waste crosslinked polyethylene foam is compatible with HDPE. Also, addition of waste foam as a filler to virgin PE influenced the properties of base HDPE in a manner similar to crosslinking of PE reducing the percentage elongation at break without significantly affecting the tensile strength, flexural strength, and modulus.

Even though the waste XLPE material could not be used again as same as the previous application, it is still a value added product and this provides us with a solution in reducing and utilizing crosslinked polymeric waste which are available. This development of a value added product could be one of the ways in utilizing this waste. Being an ethylene base product, it should have no difficulties blending together with the matrix composite. The enhancement characteristics of XLPE in terms of thermal and chemical resistance could increase the properties of the melt blend composite. There is a possibility that the waste XLPE could crosslink the matrix of the composite and enhances the properties of the blend as discussed previously in the topics above. The waste could bear a low level of crosslink initiators left in its system that could help in crosslink the matrix. Being a crosslink material it could also provide a resistance barrier; first line of defence when subjected to extreme conditions mechanical or chemically before affecting the matrix of the composite.

CHAPTER 3

METHODOLOGY

3.1 Material

High-Density Polyethylene resin was purchased from Titan Petrochem (M) Sdn Bhd with a grade name of Titanex HB0972. The density of this resin is 0.949 g/cm3 and the melt flow index (MFI) is 10 g/10min. Waste crosslinked PE filler is obtained from a waste high voltage cable as shown Figure 3.1 and 3.2.

Figure 3.1: Cross section of cable sample obtained from TNB Berhad

Figure 3.2: Cable sample obtained from TNB Berhad

The cable sample was obtained from TNB Stor Bkt Tambun, Pulau Pinang. According to the TNB, the cable was in use before being damaged by jacking machinary due to unauthorized construction works. Investigation is still ongoing and details are classified. Samples of 3 inches long were given for the purpose of this study (Figure 3.3). The sample was cut using a high speed saw by a TNB technician. Table 3.1 shows the construction layer of the cable.