Recycling rubber for automotive weather seals engineering essay

With increasing concern about environmental protection and sustainable development, more and more researches are considering rubber recycling. Crumb rubber, which is mechanically broken down from waste tyres rubber into a particulate solid, is an effective method of recycling and more applications of this need to be found. The incorporation of the crumb rubber into EPDM-based automotive weather seals is one of the potential applications and can lower the cost of the final product. One aim of this project is to determine how much tyre crumb can be added to an EPDM-based weather seal compound without largely affecting mechanical properties and surface quality. The other aim is to identify whether sulphur cure or peroxide cure results in better properties.

LITERATURE REVIEW

Introduction of Rubber and Tyres

Since French scientist Charles Maria de la Condamine brought the first samples of rubber to Europe from his travels in South America in 1736, rubber has been introduced to Europe for more than 200 years. However, rubber only became a technically significant material, successfully utilised in industry when an American scientist Charles Goodyear discovered sulphur vulcanization of rubber in 1839 [[1]]. Today, rubber, as one class of widely used materials, plays an important role in modern engineering technology and pursues new possible applications. According to the International Rubber Study Group, the world consumption of rubbers exceeded 20 million tonnes in 2005 [[2]].

The vast majority of the global production of natural and synthetic rubber is used in tyres. Shown in , a tyre is composed of rubber materials, carbon black fillers and some fibrous materials which provide mechanical strength to optimise the tyres [[3]]. Natural rubber (NR), polybutadiene rubber (BR) and styrene butadiene rubber (SBR) are the main elastomers used to manufacture automotive tyres. These three rubbers are briefly described in the following sections.

Natural Rubber (NR)

The structure of NR is shown below:

NR consists of over 99. 99% of linear cis€1, 4€polyisoprene, since trans-1, 4-polyisoprene has plastic properties. NR accounts for about one third of total global consumption of rubber. As a non-polar rubber, it can be easily blended with a large number of other non-polar rubbers such as EPDM. The strain crystallization property of NR vulcanisates supplies high tensile strength and very good tear resistance, as well as its high elastic rebound, low hysteresis and low heat build-up in dynamic deformation, which make it suitable for producing automotive tyres [[4]].

Polybutadiene Rubber (BR)

The structure of BR is shown below:

With very similar structure to NR, BR is the simplest synthetic rubber and has some analogous properties of NR. BR is also a non-polar rubber. In the rubber industry, more than 90% of BR production is used in tyres. Because BR has good abrasion resistance, it has been widely used in a large range of tyres including tread compounds, carcass, sidewall and bead compounds. Especially, BR tyres are quite useful to improve ice traction in winter [].

Styrene-Butadiene Rubber (SBR)

The structure of SBR is shown below:

The annual consumption of SBR is the biggest in synthetic rubber. With good dynamic fatigue resistance, aging resistance and abrasion resistance, SBR is mostly used in tyre compounds. SBR compound is better used for light truck tyres rather than heavy truck or high speed tyres, since SBR has higher dynamic heat build-up than NR and BR [].

Rubber/Tyres Recycling

The vulcanization of rubbers improves their mechanical strength and makes them better to use in many applications. However, unlike thermoplastic materials, rubber vulcanisates which possess a three-dimensional crosslink structure cannot be melted and are hard to reprocess. The European Tyre Recycling Association estimates that there are approximately 250 million tyre arisings accumulated per year in the European Union (EU), which equals to 2. 6 million tonnes of waste tyres. Worldwide, the generation of new arisings is estimated to be 1 billion tyres every year [,[5]]. Therefore, rubber recycling, especially waste tyres recycling, is a tough problem which needs to be resolved, since environmental protection and sustainable development are the biggest issues in the world today.

Recycling Methods

Today, a great number of researchers have investigated numerous approaches including pyrolysis and incineration, reclaiming, grinding, pulverization, microwave and ultrasonic processes to solve the recycling problem effectively [[6]]. However, earlier methods such as pyrolysis and incineration cause health hazards and air pollution, as toxic wastes are produced during burning. Reclaiming could badly affect the quality of the final products. Microwave and ultrasonic processes are more expensive for rubber recycling. Considering economic and environmental factors, modern grinding technique seems to be an acceptable approach for recycling waste rubbers [[7]]. This method reduces the particle size and the surface area, and makes waste rubber usable in the vulcanized state []. One recycling application of the technique is to fabricate crumb rubber by using it with virgin polymers.

Current Recycling Situation

shows the evolution of tyre recycling in the European Union from 1992 to 2005 estimated by the European Tyre Recycling Association. With increasing concern about the environment and the development of recycling techniques, the recycling situation experienced a dramatic increase. The proportion of recycling of waste rubbers and energy use steadily grew while landfilling of tyres was substantially reduced. In 2004 – 2005, the European Union recycled almost 1 million tonnes of car and truck tyres, which reached nearly one-third of annual arisings in Europe

In addition, two European Commission Directives: The Waste Landfill Directive (1999) [[8]] and The End of Life Vehicle Directive (2000) [[9]] were put into force to ban the landfilling of tyres by 2006 and encourage the recycling of tyres. Actually, both the EU and most other countries have already attempted to control the management of tyres demonstrates the disposition of scrap tyres and main application in the U. S. in 2007. The majority of scrap tyres were used as tyre-derived fuel (TDF) for energy recovery. About 2. 5 million tonnes of scrap tyres were utilised for TDF in the U. S. in 2007. Another large portion is in civil engineering for road and construction applications, which consumed roughly a half million tonnes of scrap tyres in 2007

The second largest application for recycling scrap tyres is ground rubber (crumb rubber). This simple and environmentally friendly technique consumed 789. 1 thousand tonnes of scrap tyres in the U. S. in 2007. The ground rubber market is promising and is expected to experience growth in the future This project is concerned with the recycling of tyre rubber as crumb rubber.

Crumb Rubber

Normally, crumb rubber refers to rubber particles recycled from passenger vehicle and truck scrap tyres without any reclaiming process being carried out [[10]]. As previously mentioned, grinding is a favourable method to manufacture crumb rubber. Generally, there are three approaches to grind waste rubbers: (1) ambient grinding, which produces relatively large crumb with 0. 85 mm to 2. 54 mm particle size; (2) cryogenic grinding, which makes much finer particle from 0. 25 mm to 0. 8 mm; and (3) wet-ambient grinding, which can manufacture particle size reaching about 0. 12 mm. The particle size of the most often used crumb rubber ranges between about 0. 3 mm to 2 mm[11]. A finer particle of crumb rubber makes it suitable for good processing and producing relatively smooth extrudates However, the price increases exponentially with the fineness of the crumb rubber particle [[12]].

As one type of successful technique for waste rubber recycling, crumb rubber has several applications. shows recent markets and applications for crumb rubber in North America estimated by the Recycling Research Institute. The largest applications include rubber-modified asphalt used to improve the properties of road construction, and moulded rubber products such as carpet underlay, flooring material, dock bumpers, roof walkway pads, rubber tiles and bricks In addition, playground and other sports surfacing markets also have a dynamic demand for crumb rubber.

Recently, more and more crumb rubber with finer size was applied to automotive parts: tyres and sealing, for example. The biggest advantage of this technique is that it can lower the material cost, as well as reducing cure time. Therefore, this market is expected to have a substantial growth potential.

Automotive Weather Seal

One possible new application for crumb rubber is to add virgin rubber and mix them homogeneously to manufacture automotive weather seals and lower the cost of the product. Automotive weather sealing is extensively utilised in window seals, door seals, trunk seals, and sometimes hood seals of vehicles. Generally, automotive weather seals, which have a rod-like shape and may be hollow in section, are made of rubbers or thermoplastic elastomers.

Automotive weather seals are essential for motor vehicles, although they are just the small parts of automotive components. Automotive weather seals not only need to protect the passenger area from water entering during any kind of weather conditions and commercial vehicle washing, but also minimize the noise of the wind inside the car. For door seals applications, automotive weather seals are of great significance in determining the door closing effort and the cosiness of operation of the door [[13]]. According to a testing report from Ford Motor Company, approximately 35-50% of the force or energy to close the front door is comprised by seal resistance. Weather seal materials are designed and manufactured with complicated characteristics including compression deformation, high extensibility and compressibility [[14]].

The materials from which automotive weather seals are made should have adequate mechanical properties such as good toughness and abrasion resistance. Good weather resistance is extremely important and they should be resistant to cleaning and anti-freeze fluids. In addition, good surface quality is indispensible where the weather seals are visible.

Compounds

EPDM compounds are supposed to be one of the most appropriate materials to produce automotive weather seals. shows some properties of automotive window seals made by EPDM compound. Aside from EPDM rubber, the compounds mainly include filler, plasticizer and curing agent [[15]].

Ethylene-Propylene Diene (EPDM) Rubber

EPDM rubber as a type of synthetic rubber refers to a copolymer of ethylene and propylene, and a small quantity of diene, using catalysts of the Ziegler-Natta Type One type of structure of EPDM is shown below:

Since ethylene-propylene (EPM) rubber has a saturated molecular structure and is hard to crosslink, a third monomer, a diene, which resides in sidegroups of polymer chains, is added to offer double bonds and result in unsaturation to improve the vulcanisation of the rubber.

Three most often used dienes in commercial EPDM rubbers are shown below:

Dicyclopentadiene

(DCP)

Ethylidene Norbornene

(ENB)

Trans-1, 4 Hexadiene

(HX)

Generally, a suitable termonomer contains two sets of double bonds which have different reactivities. One needs to copolymerize with remaining EPM in polymer chains; the other with a higher reactivity can be vulcanized with sulphur to form a three-dimensional crosslinked structure. ENB is the most common and effective termonomer nowadays

Since main polymer chains of EPDM rubber are entirely saturated, as well as their non-polar character, chemical inertness and low brittle point temperature, these favourable properties make EPDM rubber possess excellent resistance to ozone, oxidation and ultraviolet radiation, and good resistance to abrasion and cracking

In addition, EPDM has the lowest specific gravity in all the rubbers and good compatibility with other additives. EPDM can be extended with a great number of fillers and oils without deteriorating the properties substantiallyTherefore, this decreases price and can improve processability.

Filler

Since a discovery in the early twentieth century illustrated that carbon black, which is produced by incomplete combustion of many organic substances, could be largely accepted by natural rubber to improve its mechanical properties, carbon black has been the most common filler in rubber compounds during the past few decades [[16]].

Carbon black is an inexpensive material and normally very small (20-50 nm) and spherical in shape. According to the production process, carbon black was classified as furnace black, channel black and thermal black. Today furnace black is extensively used in most rubber compounds such as EPDM Carbon black could occupy approximately one-third the volume of EPDM compounds, which can comparatively lower the prices of final products.

When added to EPDM rubber, carbon black improves its strength by reducing the mobility of the polymer chain. Therefore, mechanical properties such as hardness, tensile strength, toughness, and abrasion resistance are enhanced. These reinforcing properties achieve a particularly good adhesive bonding with rubber molecules. Additionally, the uniformly distributed particles can efficiently reduce plastic deformation

Carbon black also improves the chemical properties of the material. It will increasingly block out the ultraviolet light through into the EPDM rubber, and thereby carbon black increases the resistance to oxidation and weathering [[17]].

Plasticizer

When EPDM rubber is mixed with carbon black filler, the stiffness of the compounds is increased. After the compounds are vulcanized, a cross-linked structure will form between molecular chains, which can make the product too hard for normal utility [[18]].

The main function of the plasticizer is to weaken the secondary bonds such as van der waals force between molecules in polymers, thereby reducing the attraction between polymer chains, which make the segments of polymers easy to move. Consequently, hardness and modulus of the compounds decrease while flexibility increases. Additionally, plasticizer also can improve the compatibility between additives in the compounds [[19]].

Generally, plasticizers are categorised as mineral oils, natural products and synthetic plasticizers. Mineral oils have an extensive utility due to relatively cheap price and good compatibility with non-polar rubbers. Vegetable oils can lower the processing viscosity and improve the tackiness or filler dispersion of the rubber compounds

Table 1 Compatibility of Mineral Oils with Various Types of Rubber

ã€€

NR

BR

SBR

EPDM

Paraffinic

+

+

+

+

Naphthenic

+

+

+

+

Aromatic

+

+

+

â-‹

Highly aromatic

+

+

+

â-‹

+ compatibility good, â-‹ conditionally compatible

Table 1 Compatibility of Mineral Oils with Various Types of Rubber represents four types of mineral oils' compatibility with different rubbers. Non-polar mineral oil plasticizers are compatible with non-polar rubbers; paraffinic oils are especially compatible with saturated rubbers such as EPDM. The content of mineral oils used in rubber compounds ranges between about 5-30 phr. In some compounds such as EPDM, larger contents up to 100 phr are being utilised

Curing Agent

The function of a curing agent is to convert rubber molecules into a network by the formation of a crosslinked structure, which makes rubber change from a thermoplastic to an elastic state and improve its mechanical properties. The ultimate cure states depend on the process of the vulcanization and the choice of the vulcanization chemical. EPDM rubber can be vulcanized by either sulphur or peroxide.

Sulphur

Elemental sulphur has remained the most important and widely used vulcanization agent for rubber. For soft rubber the dosages of about 0. 25-5 phr are used, and for hard rubber 25-40 phr of sulphur are sufficient. EPDM rubber can be cured by sulphur because a termonomer offers unsaturated bonds reacting with sulphur to form a three-dimensional structure. The desired dosage of sulphur depends on the type and quantity of termonomer in the EPDM rubber. For ENB-EPDM, about 1. 2-1. 5 phr of sulphur are added. In order to obtain the required fast cure rate and high cure states, a combination of some accelerators is essential Accelerators such as tetramethyl thiuram disulphide (TMTD), N-tert-butyl-2-benzothiazylsulfenamide (TBBS), mercaptobenzothiazole (MBT), dibenzothiazyl disulfide (MBTS) and zinc diethyl dithiocarbamate (ZDC) are mostly utilised in several researchers' work to achieve the synergistic effect with curing agent to make the compounds crosslink easily

Peroxide

Another vulcanization agent is peroxide, which has been known for a long time for crosslinking. Normally, peroxides are used to crosslink most saturated rubbers such as ethylene-propylene (EPM) and silicone rubber.

Peroxides can crosslink the EPDM rubber if the ethylene concentration is high enough, since the methyl group in polypropylene reduce crosslinking reactions with peroxides and can lead to chain scission. Therefore, at least 50 mole percentage of ethylene is required to obtain a high degree of crosslinking. For the termonomer selection, DCP-EPDM gives a higher cure rate than other termonomers. In addition, activators are indispensible for peroxide cures

Table 2 Properties of EPDM Rubber Crosslinked by Sulphur and Peroxide

Rubber grade

EPDM,

EPDM,

sulphur crosslinked

peroxide crosslinked

Tensile

M

L/M

Strength

Resistance to

M

L

tear propagation

Resistance

M

L

of abrasion

Compression set

8

4

at room temperature %

Heat resistance

200

220

after 5h â„ ƒ

Working

140

150

temperature â„ ƒ

L: low; M: medium; H: high

In comparison with sulphur-cured EPDM, peroxide-vulcanized EPDM shows the better heat resistance and the lower compression set even at high temperatures while it has the lower tensile strength, tear strength and abrasion resistance, as well as mostly a higher cost (see Table 2 Properties of EPDM Rubber Crosslinked by Sulphur and Peroxide).

Blending Crumb Rubber into Compounds

The project aim is to add a certain amount of crumb rubber into EPDM compounds for automotive weather seal applications without significantly affecting mechanical properties and surface quality. Most crumb rubber comes from automotive tyres which are mainly made of NR, BR or SBR. Unfortunately, crumb rubber may unfavourably affect the surface quality of the product and is not quite compatible with EPDM rubber. However, NR, BR, SBR and EPDM are all non-polar rubbers, so EPDM can theoretically blend with them. No papers were found in the literature concerning the use of tyre crumb rubber in EPDM compounds for use in automotive weather seals. Nevertheless, several relevant articles concerned with similar projects were found and are discussed in the following sections.

Mixing Schedule

Similar research by Jacob et al. using ground EPDM vulcanisate with EPDM compound in a window seal application illustrated a possible mixing process of crumb rubber and rubber compound matrix. Firstly, virgin material was put into the mixer and melt, accompanying with carbon black, paraffinic oil, paraffin wax, brown factice and other additives. Then, crumb rubber was added and mixed. After sheeting out, accelerators and curing agent were added and mixed into the blends efficiently in a second stage. As in the automotive weather seal application, the final product was obtained by extruding or sheeting out the blends of crumb rubber and EPDM compounds. The formulations used in Jacob’s researchfor window seal composition is illustrated in Table 3 Formulations Used Adding EPDM Crumb Rubber into EPDM Compound .

Table 3 Formulations Used Adding EPDM Crumb Rubber into EPDM

Compound	Ingredients, phr
EPDM	100
Ground EPDM vulcanisate	0 – 200
ZnO	5
Stearic acid	1
GPF carbon black	120
Paraffinic oil	70
Paraffin wax	10

Brown factice

10

TMTD (accelerator)

1. 2

MBT (accelerator)

1. 2

ZDC (accelerator)

2

Sulphur

1. 5

Accelerator

During the mixing process, proper selection of accelerators is of great importance and can help to achieve crosslinks between crumb rubber and rubber compound matrix. Taking NR ground tyre rubber as an example, the mechanism of this crumb rubber crosslinked with EPDM compounds is quite similar with NR/EPDM blends. One research investigated the influence of accelerator type on NR/EPDM blends indicated that TBBS and MBTS could provide good cure compatibility between the NR and EPDM phase. Besides that, TBBS offered a high cure state and good mechanical properties for the blends as well. Although TMTD could give a high cure rate, it caused cure incompatibility and poor tensile strength of the blends [[20]]. Table 4 demonstrates the effect of accelerators on mechanical properties of NR/EPDM blends.

Table 4 Mechanical Properties of NR/EPDM Blends with Different Types of Accelerator

Accelerator type

TBBS

TMTD

MBT

MBTS

Tensile strength, MPa

48. 1

48. 6

41. 6

42. 5

Elongation at break, %

576

470

705

703

Modulus at 100 % elongation, MPa

0. 8

0. 9

0. 7

0. 7

Hardness, Shore A

48. 1

48. 6

41. 6

42. 5

Tear strength, kN m-1

16. 7

15. 2

18. 0

17. 9

Rebound resilience, %

35. 8

34. 5

33. 6

33. 6

Compatibiliser

As reported previously, a compatibiliser such as maleic anhydride grafted polypropylene, maleic anhydride grafted EPM or EPDM could enhance adhesion between crumb rubber and the compound matrix focused on a compatibility study of NR/EPDM blends and found that the incorporation of 10 phr of EPDM-g-MAH copolymer as a compatibiliser into NR/EPDM blends could largely improve their compatibility by creating a number of crosslinks between the NR and EPDM components. This resulted in a better homogeneous phase distribution and the rheological property of the rubber blend was significantly enhanced as well. In addition, the mechanical properties such as tensile and tear strength were greatly increased when compared with non-compatibilised rubber blends. Another researcher also found that a zinc oxide activator interacted with a compatibiliser to produce an ionic crosslink, which made blends bind more effectively

Crosslinking between EPDM and tyre crumb rubber

As stated before, two approaches can be used to crosslink crumb rubber to EPDM compounds, and one is sulphur curing. Since NR, BR and SBR are unsaturated rubbers, sulphur can crosslink the double bonds in crumb rubber with the unsaturated bonds in termonomer of EPDM. Therefore, tyre crumb rubber can possibly be crosslinked into an EPDM compound matrix using a sulphur cure system.

Another method to cure crumb rubber with EPDM compounds is peroxide curing. Research by Wagenknecht et al. reported that they blended NR ground tyre rubber with polypropylene elastomeric alloys and used peroxide curing to crosslink the crumb into the matrix. The mechanism of chemical reaction in their research is quite similar to what could happen in my project because EPDM is chemically very similar to polypropylene. The steps of reaction are given in Figure 1.

(a) initiator decomposition; (b) macroradicals formation; (c) grafting onto rubber surface

Figure 1 Reactions during melt mixing

Selection of crumb rubber

The appropriate size and content of the crumb rubber must be added into EPDM compounds for automotive weather seal applications if the compound is to have good enough mechanical properties and surface quality. The effect of particle size and crumb content is discussed in the following two sections.

Size of crumb rubber

The size of the crumb rubber is of great importance, since the proper size makes crumb rubber have a good dispersion in compounds so that mechanical properties would not be largely affected. Normally, as an ingredient in a sealing compound, crumb rubber needs a particle size not more than 630 Î¼m Wagenknecht et al. used an average size of 400 Î¼m ground tyre rubber to blend successfully into polypropylene elastomeric alloys. They also found that a cryogenic-ground crumb rubber not only met the requirement of size, but also provided a smooth surface after extrusion . Other researchers found that crumb rubber aggregated easily, so they concluded that an ultrasonic technique would be another way to make crumb disperse well and reach a smaller particle size which was range from 5 to 100 Î¼m. In this way, the deterioration in some mechanical properties on incorporation of ground rubber was marginal, especially for tensile strength and elongation at break which remained nearly the same . However, the cost of the final product increases due to the expensive crumb rubber with finer size and costly processing equipment.

Content of crumb rubber

The content of crumb rubber added into the EPDM compound matrix is another significant issue which needs to be taken into consideration. Jacob et al. compared 0, 50, 100 and 200 phr ground EPDM vulcanisate added into the EPDM compounds and found the content of crumb rubber could affect some properties of the compounds. The effect of crumb content on physical, rheometer and mechanical properties is given in Table 5. They reported that the increasing load of the crumb rubber resulted in an increase of the compounds viscosity and the die swell, which made the processability weaker and the surface smoothness of the compounds extrudates impaired (see Error: Reference source not found), respectively.

Table 5 Effect of Crumb Content on Physical, Rheometer and Mechanical

Properties

Crumb rubber, phr

0

50

100

200

ML(1+4) at 120 â„ ƒ

24

29

37

49

Scorch time t5, min

9. 9

8. 8

8. 0

7. 2

MH – ML, dN m

7. 99

6. 75

5. 47

3. 76

t90, min

10. 6

10. 9

10. 6

10. 7

Tensile strength, MPa

6. 37

6. 30

6. 67

6. 33

Elongation at break, %

489

488

518

472

Modulus at 100 % elongation, MPa

2. 06

1. 85

1. 77

1. 69

Hardness, Shore A

57

56

54

51

Abrasion loss, cm3 h-1

2. 5

2. 8

2. 8

3. 1

Tear strength, kN m-1

32. 4

27

25. 6

22. 8

Jacob et al. also explained that with the incorporation of the crumb rubber the scorch time reduced due to the migration of accelerators from ground EPDM vulcanisate to the EPDM compound matrix. On the other hand, the minimum rheometric torque (ML) increased because crumb improved the compound viscosity, whilst the maximum rheometric torque (MH) and âˆ†torque (MH – ML) decreased owing to the migration of sulphur from compound matrix to ground rubber, which resulted in reduction of the crosslink density and the cure rate. These phenomena are illustrated in Error: Reference source not found.

F0 = no crumb rubber; F50, F100, F200 = 50, 100, 200 phr crumb rubber

Additionally, some mechanical properties of the compounds such as hardness, modulus, abrasion resistance and tear strength gradually decreased with the content of crumb (see Table 5 Effect of Crumb Content on Physical, Rheometer and Mechanical Properties). Hence, an appropriate content of crumb rubber not only can lower the price of the final product, but also keep the mechanical properties from large deterioration.

Research Gap

As one type of recycling rubber, crumb rubber is cheaper than EPDM compounds, and therefore the project is focusing on the incorporation of the ground tyre rubber normally made from NR, BR or SBR with EPD