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Management Engineering

Rubber in shoes: Role of technology and recycling based on a LCA analysis

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ABSTRACT

In the product's entire life cycle, waste is produced from raw material acquisition to use through manufacture, production to use. With the requirements of carbon reduction, environmental protection, the concept of life cycle engineering has been gradually deepened in various products and related industries. With the improvement of people's living standards, the consumption of footwear products is increasing day by day. At present, the waste footwear rubber products are mainly burned and buried, resulting in great waste of resources and environmental pollution. In order to meet the requirements of sustainable development, the whole life cycle of footwear products is investigated with the aim to reduce wastes and environmental pollution.

Based on the basic theory of the whole life cycle of the product, this study will analyze the whole life cycle of footwear rubber. Comprehensive consideration should be made on the raw material acquisition, manufacturing, consumption and recycling of rubber, so as to improve the utilization of resources and reduce environmental pollution and waste.

Recycling of waste footwear rubber is the key of this life cycle research analysis. Based on the study of the recycling of waste footwear rubber around the world, this thesis will discuss the proposed recycling methods and ways of footwear rubber, so as to solve the reasonable recovery or disposal of these materials. The whole life cycle of footwear rubber has great economic and social significance and broad prospects for development, with specific relevance in highly populated nations.

KEY WORDS

End-of-Life Management, Shoes Recycling, Product Recovery, Footwear Industry.

CHAPTER 1

1.1 - Introduction

Resource scarcity and environmental pollution are the common more relevant issues that the world is facing today. In order to achieve the strategic objectives of sustainable development, it is a matter of concern that how to make good use of resources, with special attention to recovery of any waste produced along the life cycle of any entity. In order to meet the requirements of the sustainable development of human society, how to maximize the use of resources and minimize the waste, has become the most concerned problem of government, manufacturing business and academia area. As early as in the process of industrialization, people began to pay attention to the problem of environmental pollution. The measures taken at that time were mainly focused on the "end-of-pipe" technology of waste, such as waste gas treatment, waste water purification, sound treatment, solid waste landfill and incineration. With the rapid development of science and technology, the promotion of new technology and new achievements and the application of new materials, new features, new types of modeling, a wide range of new products continue to emerge in large numbers. The existing waste disposal technology has been far away from meeting the requirements of the safe handling of current and future unpalatable products.

At the same time, due to the increasingly shortage of landfill site, the costs of gradual control of waste disposal are also increasing, people are increasingly aware of the importance of environment "beginning to prevent". So, some new concepts emerged in that time, such as the concept of product life cycle "from the cradle to the grave" and the strategy of sustainable development. Sustainable development is an inevitable choice for economic development, which requires people to use the basic idea of product life cycle to explore how to reduce and minimize waste and maximize use of resource. With the development of science and technology and the improvement of people's living standards, the consumption of materials is getting higher and higher, so that an increasing number of materials need to be eliminated and discarded, facing urgently the problem to develop methods to recover these materials with appropriate recycling technologies and strategies to favor their reuse. Footwear products are exemplary materials which require urgent attention.

1.2 - Sustainable development

1.2.1 - Introduction

Sustainable development refers to the development of both the ability to meet the needs of the people without compromising the ability of future generations to meet their needs[1]. In other words, it refers to the coordinated development of economy, society, resources and environmental protection. They are an inseparable system for the purpose of economic development and the protection of the atmosphere, fresh water, sea, land and forests and other natural resources and the environment, so that future generations can reach sustainable development.

Sustainable development implies the fulfillment of several conditions: preserving the overall balance, respect for the environment, and preventing the exhaustion of natural resources. Reduced production of waste and the rationalization of production and energy consumption must also be implemented. Sustainable development is presented as a more or less clean break from other modes of development, which have led and are still leading to worrying social and ecological damage on both a worldwide and a local scale.

In all cases, recycling of resources has been identified as one of the most important ways to achieve sustainable development.

1.2.2 - Three aspects of sustainable development

In order to be sustainable, development must combine three main elements: fairness, protection of the environment, and economic efficiency. Any sustainable development project must be based on a better-developed mode of consultation between the community and the members it comprises. The success of such a policy depends also on consumers accepting certain constraints and citizens observing certain requirements with regard to transparency and participation.

1. *Ecological aspect*

   It refers to minimizing damage to the environment. Although this principle is endorsed by all parties, due to the limitations of human scientific knowledge, there are diametrically opposed understandings for many specific problems, such as the use of nuclear power.

2. *Social aspect*

   It means still to meet the needs of mankind itself. The key word is development, only the continuous development in order to meet the needs of mankind. Sustainable development does not require mankind to return to primitive society, even though the damage to the environment at that time was minimal.

3. *Economic aspect*

   It means that it must be economically profitable. Sustainable development may involve improvements in the quality of life for many but may necessitate a decrease in resource consumption. Sustainable development can promote the long-term sustainable development of the economy

1.2.3 - Background of sustainable development

Since the 18th century European industrial revolution, the traditional industrial development model has become the dominant mode of economic development and has played a very important role in the modernization process. However, over time, the shortcomings of the traditional development model have increasingly revealed a series of issues.

First, the population has grown-up exponentially. The traditional development model has created a wealth of materials, but at the same time, it has also brought about the dramatic growth of the population. In this century, world population turned twice. According to the United Nations Population Division, on October 12, 2000, the global population was 6 billion and it is estimated that by 2030 will reach 10 billion. The explosion of population is the underlying cause of food shortages, over-consumption of resources and environmental degradation, and is the main predisposing factor for the plight of mankind.

Second, an excessive exploitation and consumption of natural resources was demonstrated. The traditional development model relies on uncontrolled consumption of natural resources, embracing a model of "high input, high consumption, and high pollution". The reason why such a development model was chosen, was that the material resources were considered infinite, assuming an infinite ability of man to conquer and transform nature. In fact, from the initial conditions of the traditional development model of operation, no evidence of "scarcity" of natural resources was proved or scarcity was not so obvious. However, with the development of industrialized society, the limited nature of natural resources gradually emerged.

Third, environmental pollution and ecological damage have dramatically increased. The traditional development model is the development model of "anthropocentrism". In modern times, the value of "anthropocentrism" is gradually replaced by the value of "natural centralism" and it becomes the mainstream value of social development. In the view of anthropocentrism value, natural resources are infinite, science and technology are omnipotent, and thus the possibility of satisfying human needs with the help of science and technology is infinite. This led to a series of problems such as ecological imbalance, environmental pollution and resource shortages, so that social development is facing a serious crisis.

The environmental problems that have arisen since industrialization have not only become a regional, but also a global problem, such as climate warming, ozone depletion, biodiversity decline, land degradation and desertification, acid rain, and so on. Because the traditional development model has been inevitably adopted in certain historical stages in all countries, human society is now facing into a non-sustainable "malignant development" state and the concept of sustainable development is gradually prevailing.

For a long time, sustainable development has been in the theoretical stage and how to truly achieve sustainable development in practice is a popular concern. The effective way to address the problem is now focused into the dominant idea of circular economy, collecting in this term are the design strategic models for international sustainable development of latest choice. The development of circular economy is considered an important way to achieve sustainable development.

1.3 - Circular economy

1.3.1 - Introduction to the circular economy

In general, the circular economy is referred to the material closed-loop mobile economy. It is essentially an ecological economy; it is a combination of clean production (CP) and comprehensive utilization of waste into one economy, so that the economic activities will change from the traditional single linear process “resource - product - waste" into a feedback process "resources- renewable resources"[2].

The principle of circular economy is "reduction, re-use, recycling" (

), to ease the contradiction between the limited resources and the infinite development of our society, in order to solve the increasingly negative impact of human activity on the Earth.

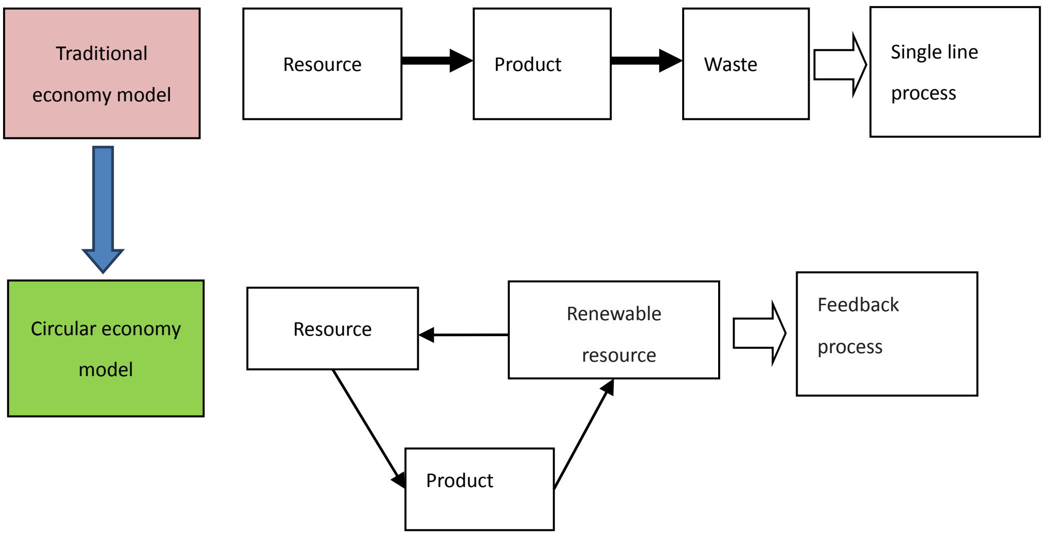


Figure 1. 1 - Flow chart of traditional economy compared with circular economy

This awareness has pushed policy makers to incentive the search of new solutions to mitigate pollution and reduce resource consumption. The world environmental policy is led by the European Union since Kyoto Protocol (1997); in facts, EU sets the most ambitious objectives for the internal industrial development agenda in the mid and long term[3]. The current reference document for the environmental legislation of the European countries is the 7th Environment Action Programme (7EAP), which entered into force in 2014 and sets the growth targets for 2020[4]. “Living well, within the limits of our planet” says the official slogan of the programme, as shown **Error! Reference source not found.**.These few words perfectly represent the logic of changing toward a sustainable production and recycling paradigms.

Figure 1. 2 - Official logo and slogan of the EU 7th Environment Action Programme.

The main points of the 7EAP, to be fulfilled before 2020, are the following:

I. Reduce the 20% of the Greenhouse gas emissions (30% if other developed countries pursue this objective), employ at least 20% of renewable energy, and reduce the 20% of primary energy consumption by improving efficiency.
II. Halt the loss of biodiversity and the degradation of ecosystems in European territory and restore them as far as possible.
III. Halt the loss of global cover loss (by 2030 at the latest) reducing of the 50% the tropical deforestation compared to 2008 level.
IV. Maintain or improve the status for all EU waters.
V. Achieve good environmental status in all marine waters (12 miles from coast).
VI. Achieve of air quality levels in all the Union territory removing any impact to human health and environment.
VII. Produce, use and recycle chemicals and materials in a way that minimize the significant adverse effects on human health and environment.
VIII. Prevent and reduce the impact of waste generation and management.
IX. Stimulate the transition to a Green and Circular Economy, pursuing the complete decoupling of economic growth and environmental degradation.
X. Strive to achieve a land degradation neutral world in the framework of sustainable development.

These points represent the most modern and advanced positions toward environmental protection, highlighting the importance of some concepts as “Human health and environment protection”, “Green Economy”, and “Circular economy”.

Also, United States of America put much effort in directions similar to the 7EAP, with the “Air, Climate and Energy Strategic Research Action Plan” (ACEStRAP), valid from 2016 to the 2019, even though it is less ambitious on certain targets.[5] Still, US nation keep sits role of a privileged speaker on some of the technologies that should promote human sustainable growth.

7EAP and ACEStRAP are the proof that finally the governments (of the most advanced countries) are taking seriously the priority of protecting environment to guarantee the long-term wellness of citizens. However, if the role of governments and policy makers is to set the general direction to be followed, the road must be traced by the actual responsible of the environmental impacts, which is industry, as pointed by **Error! Reference source not found..** The 20% of the GHG emission worldwide, which among the many anthropogenic impacts is particularly cumbersome as responsible of global warming, is ascribable to the industrial sector. A more detailed insight comes from the specific contributions of the manufacturing categories (**Error! Reference source not found.**).

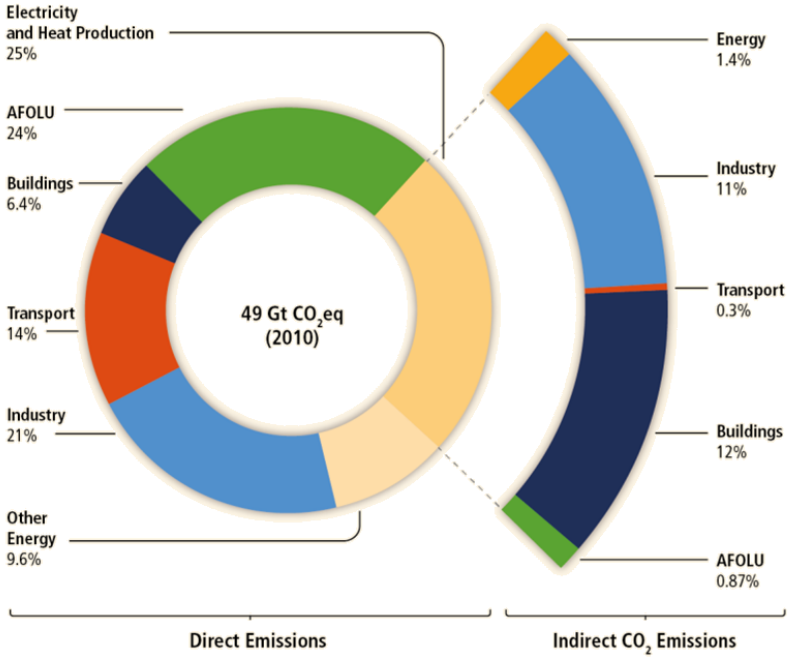


Figure 1. 3 - GHG emissions by economic sector adapted from ref. 4. The acronym AFOLU stands for "agriculture, forestry and other land use".

Interestingly, the areas related to chemical industry (waste treatment and chemicals production)[6] account by 30%: any improvement in this fields would hence result in the biggest benefits. Fortunately, this industrial sector has been developing for years the tools to implement the changes now formally required by the new green production paradigm. It was indeed within these manufacturing sectors that, following the continuous need to improve the plant efficiency while ensuring man and environmental safety was developed the first formulation of the "Human health and environment protection", "Green Economy", "Sustainable Development" concepts.[7]

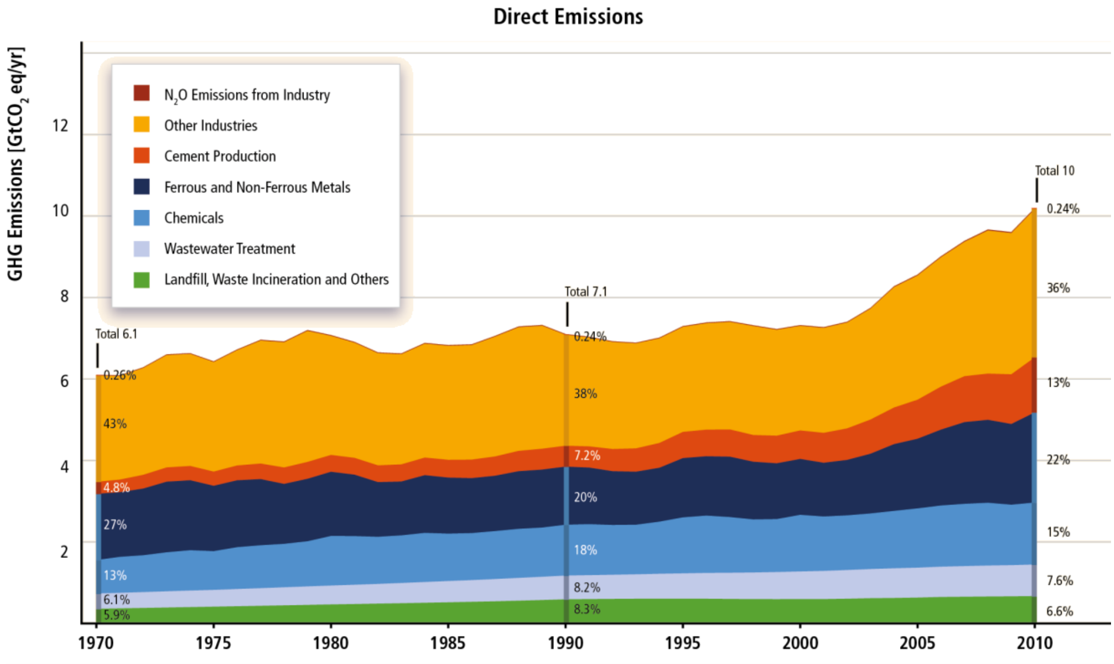


Figure 1. 4 - GHG emissions by manufacturing category adapted from ref. 4

Environment is therefore not only an industrial constraint, but is actually a leverage to relaunch the industrial competitiveness. In fact, developing countries, that currently underestimate the importance of pollution prevention against economic growth, will eventually understand the relevance of preserving human health and environment and will need sustainable solutions. It is therefore interest of western countries to be the market leaders and providers of Green Technologies for the Circular Economy.

In conclusion, the shift to Green Industry is a necessary action to be taken, even though it could appear challenging and requires the formulation of new concepts.

1.3.2 - Three principles of circular economy

- **Reduction**:

The principle of reduction in the economic activities is to pay attention to conservation of resources and reduce pollutants, which requiring less raw materials and energy inputs, to achieve the established production or consumption purposes. The principle of reduction in the performance of the production requires for the production of small size and light weight of the product, in order to achieve the purpose of reducing waste emissions.

- **Re-use:**

The re-use principle requires that the product and the packaging container be reused in the initial form, rather than being discarded at once. In other words, by extending the length of time for products and services, improve the efficiency of the use of products and services. Standardize the design of the product, and study the products of the removable and reusable, in order to achieve re-use of products.

- **Recycle:**

The recycle principle requires that the products produced can be reused into usable resources rather than useless garbage after the completion of their functions. The idea is to expand the supply of resources and reduce the final disposal capacity.

1.4 - Recyclable Resource

1.4.1 - Resource

Resources mainly refers to the natural resources, the main body for resources is mankind. In terms of leaving the human subject, all resources are meaningless. "The natural resources of the earth, such as water, air, mineral, land, energy (oil, coal, etc.) and various biological species, are the material basis for the survival and development of human beings and the biological world." Resource is the survival of human beings, access to nutrition, the source of life, but also the prerequisites of human beings survival and the prerequisites for human beings to improve the material, spiritual and cultural life. Harold believes that in modern society, the recycling of renewable resources, into new resources, the need for the following main conditions: 1.the number of waste recycling to form a scale effect; 2. the recycling of the use of renewable resources products to have a cost advantage; 3. ecosystem can achieve metabolism.

Resources can be divided into two categories: First, non-renewable resources, and second, renewable resources. Non-renewable resources refer to material resources that cannot be naturally formed or produced during a considerable period of time (within a million years) after being exploited by humans. It includes all kinds of metallic minerals, non-metallic minerals, rocks, solid fuel (coal, stone coal, peat), liquid fuel (oil), gaseous fuel (natural gas), etc.. Renewable resources refer to the material resources that can be continuously generated, grown and multiply by natural or artificial activities in a certain period of time (within a year or decades) after being developed and exploited by human beings, including surface water, soil, plants, animals and aquatic organisms.

1.3.2 - Recyclable Resource

Recyclable resources are a kind of renewable resources, that is, the products made from renewable and non-renewable resources that after the use of products can be re-used, refabricated, recycled, reprocessed or recovered. They include minerals and scrap as raw materials of steel, nonferrous metals, rare metals, alloys, inorganic non-metallic materials, plastic packaging and goods, rubber, natural and synthetic fibers, paper, etc..

From the perspective of industrial economics, Wu Xiansheng makes an interpretation of recyclable resources: he believes that recyclable resources are substances or products that can be used again under certain technical conditions. There are three points in this definition: the first, unused material cannot be called recyclable resources. Second, the existence of a certain value of the material may be the founding criteria for a recyclable resource. Third, the state of use has changed the object of recyclable resources and raw resources have changed, that is, the original use of a material has been replaced after it recycled.

1.5 - End-of-life footwear rubbers

1.5.1 - Introduction of footwear

With the growth of the world's population, economic development, the continuous improvement of people's living standards, the world's footwear production has increased significantly, from 1950 in 2.5 billion pairs to 2005 in 20 billion pairs. In 2015, continued to rise to 25 billion pairs. In EU, footwear consumption in 2005 reached 2.3 billion pairs. It is reported that the population in Germany is only 80 million, the annual sales of various shoes, up to 400 million pairs, which 5 times its population. Germans throw away 400 million pairs of shoes every year.

1.5.2 - Construction of footwear

The shoes consist or four main parts: the vamp, sock liner, insole, and outsole **(Error! Reference source not found.)**. The sole structure is quite complex, and in broad terms, it may include all the material that forms the bottom of the outsole, the midsole and the heel. In the narrow sense, only refers to the outsole, the general performances of the common soles are quite broad and include resistance to water, oils, and heat, good elasticity, comfortability, insulation, easy to absorb moisture, etc..

Figure 1. 5 - The four main parts of shoes

There are many types of materials used in the soles, which can be divided into natural materials and synthetic materials. Natural base materials include natural leather, bamboo, wood, etc.; synthetic base materials include rubber, plastic, rubber and plastics materials, recycled leather, flexible cardboard, and so on. Now, we just focus briefly on the rubber because this raw material has a crucial role in the footwear industry.

1.5.3 - End-of-life footwear solution

Due to the complexity of footwear products design and construction, it is technically difficult and time consuming to disassemble and separate footwear products into usable recycled material streams. For end-of-life footwear, mainly classified as domestic waste, mostly burned and landfill, resulting in a lot of pollution.

Barbieri, schwartbold, who systematically studied the Brazilian waste shoes pollution and environmental pollution, found that waste shoes have a greater pollution on the environment, will release toxic organic matter and heavy metals to soil. In Italy, Titano, Acerbic et al. studied the properties of waste footwear, studied its use of incineration and energy recovery and dust as a fertilizer. In Pakistan, Iqbal, Bhatti et al. studied the adsorption of cadmium ions, by using end-of-life shoes to remove cadmium ions from water. Zattera, Oliveira, who studied the performance of EVA waste shoes material evidenced when the polymeric component can be recycled.

In October 2007, Loughborough University organized and facilitated a seminar on "Footwear Recycling". This event brings together stakeholders in the footwear sector, including manufacturers, retailers, designers, recyclers, trade associations and government agencies, to discuss the current state of the German shoe cycle and to identify potential footwear product recovery Program to deal with the current footwear waste problem. The event is also designed to provide a forum to discuss the future direction of shoe recycling and how to overcome the obstacles to achieve footwear recycling strategy. These measures include: footwear reuse, recycling materials and incineration or gasification based on energy recovery. Thus, in recent years, the recycling of footwear products industry began to flourish. Germany has a company specializing in the recovery of end-of-life footwear products, called "Hanover end-of-life footwear recycling company." It has 11,000 recycling stations in the country. There are also some individual enterprises have also embarked on the recovery of end-of-life footwear, since the benefits of recycling end-of-life footwear is very considerable.

1.5.4 - The case study of Nike shoes

About the reuse of waste shoes, the famous footwear manufacturer Nike, play a very important role around all over the world.

On the one hand, Nike use environmentally friendly recyclable materials to replace the traditional materials produced footwear products. They cooperate with Norm Thompson; produce EK2.0 as eco-environmental awareness products, the characteristic of this product is that all multiple parts can be degraded, recycling and re-use. The bottom of the sole is made of environmentally friendly rubber, and 42% is made of recycled waste tire rubber, which absorbs the huge pollution and burial problem of the annual waste tires for the earth. Recycled leather parts will be refurbished; environmentally friendly rubber will be sent back to the manufacturing plant re-use; removable metal parts can be reused for new shoes or recycled to virgin material; polyester fiber inside can also be re-used for new polyester fiber commodity.

On the other hand, in the early 90s of last century, Nike carry out the old shoe recycling program, they encourage consumers to bring the old shoes back to the store, these shoes were recovered, and then broken and processed, the recycled materials were used for sports field construction. This project can promote consumers to bring a variety of brand of end-of-life shoes to Nike, so that Nike Company can create a new income. Waste shoes are also recycled to use of its materials into similar footwear products. Another part of the study was focused to reduce the pollution of end-of-life shoes burning, pretreatment before incineration, control of exhaust pollution and the full recovery of energy. In the past, due to the lack of implementation of the recycling plan, in the world, tens of thousands of sports shoes were mixed in ordinary living garbage every year and was sent to the landfill. Nike's statistics show that by the end of 2008, they had recycled 21 million pairs of sports shoes in the global, and now, in the United States, Nike can recycle about 2 million pairs of end-of-life sports shoes every year.

Figure 1. 6 - NIKE shoes taken apart into 3 parts

After the recovery of Nike shoes, each pair of shoes will be cut into three pieces - rubber outsole, foam insole and fiber upper, these slices will be sent to the grinding machine grinding, and then purified; or the shoes as a whole grinding into powder, and then through the separator to the grinding of the powder separation and processing into different uses of materials. Those shoes, after dismantling process, become into three kinds of high-quality wear-resistant materials. One is rubber particles, made of shoes outsole, can be used for plastic runway, gymnasium ground and other sports ground or even new Nike products; the other is the foam, made of shoes insole, can be used as a the carpet of outdoor basketball and tennis courts; the other one is the textile, which made of wear-resistant fibers, used to make the cushion, used in indoor plastic stadium and wood floor.

1.6 - Final comments - Thesis Objectives and Structure

At present, the problems of resources and ecological environment have become increasingly prominent.Sustainable development is one of the effective solutions to solve this kinds of the problems.

As an aspect of sustainable development, circular economy gives an effective way to develop economy with less consumption of resource. Circular economy is not a simple economic problem, not a simple technical issues and not a simple environmental issues, but to coordinate the relationship between man and nature, so that promote the whole society to development better, which requires the overall coordination of human culture, institutional innovation, technological innovation, structural adjustment and other social development.

The main objective of this study was to provide an updated and as far as possible complete techno-economic analysis of recycling possibilities for footwear products, analyzing the current technological alternatives.

Focusing on the structure of this thesis, the chapters are organized as follows:

Chapter 2 introduces the state of the art of the technologies for the production of alternative.

In Chapter 3, a realistic and sound conceptual flow sheet.

Chapter 4 presents the rubber mold technology and some main equipment used in rubber industry.

Chapter 5 introduces the process of separation of recycled rubber from footwear.

Chapter 6 presents some reclaim methods for recycled rubber.

Finally, Chapter 7 presents the summary of the whole thesis.

The chapters are provided of independent introduction and references, as they can be seen as distinct aspects of the same feasibility study. The general conclusions (Chapter 7) will finally recall the main achievements of this study, presenting the developments expected from the next future in this industrial area.

CHAPTER 2

RUBBERS

Rubber is a very important and irreplaceable strategic material, and it is closely related to human daily life. Rubber products are widely used in all aspects of human production and life, and the demand for rubber also showed an upward trend.

Rubber is an aliphatic elastomer, i.e. a flexible polymer. This means that the objects made with this material are capable of recovering from large deformations quickly and forcibly, and can be, or already is, modified to a state in which it is essentially insoluble (but can swell) in boiling solvent, such as benzene, methyl ethyl ketone, and ethanol toluene azeotrope". According to the different making ways, rubber can be divided into two types: synthetic rubber and natural rubber. In **Figure 2.1** is summarized the total consumption of the all types of rubber.

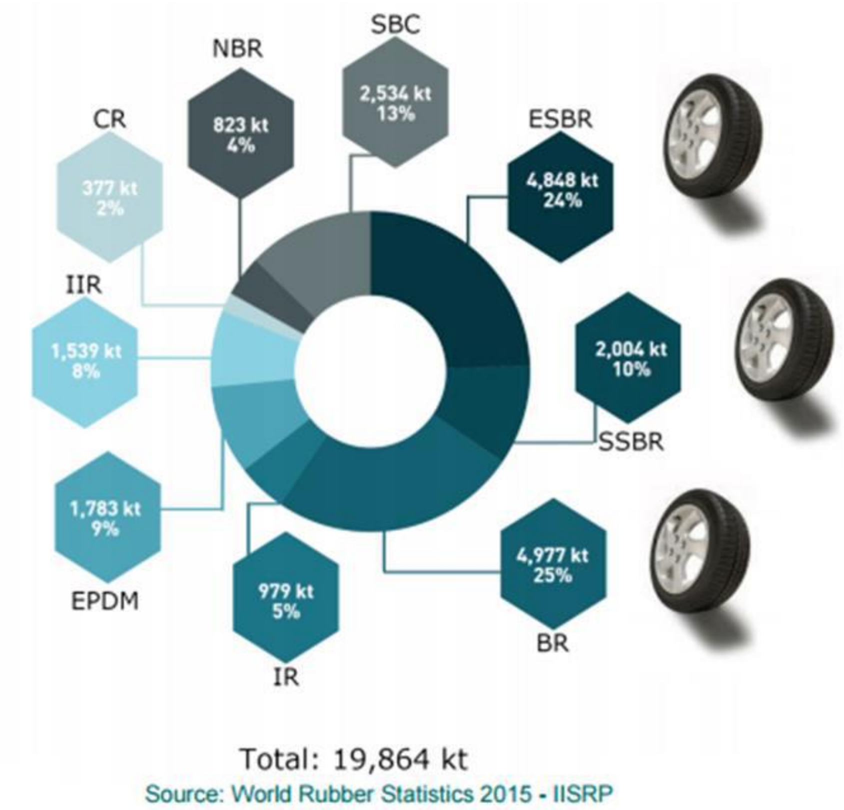
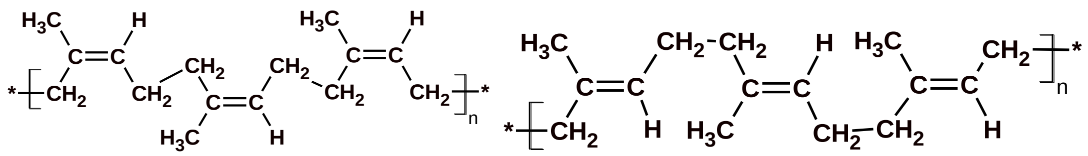


Figure 2. 1 - Global rubber consumption

2.1- Natural rubber

2.1.1- Introduction

Natural rubber, also known as India rubber or caoutchouc, is a natural macromolecular compound containing cis-1,4-polyisoprene (**Figure 2.2**) as the main component, the formula is $(C5H8)_n$, and 91% to 94% of its composition is rubber hydrocarbon (cis-1,4-polyisoprene), the rest is protein, fatty acids, ash, carbohydrates and other non-rubber substances. *Cis*-1,4-*polyisoprene* is a natural polymer which is most widely used as an elastomer owing its amorphous structure. Polyisoprene can also be created synthetically, producing what is sometimes referred to as "synthetic natural rubber", but the properties of synthetic and natural rubbers are different. Some natural rubber sources, such as gutta-percha, are composed of trans-1,4-polyisoprene, a structural isomer thatcrystallizes a room temperature, leading to a more rigid thermoplastic material[8].



a) b)

Figure 2. 2 - *Cis*- and *trans*-Isoprene repeating units of Natural Rubber (a) and Gutta-perca (b)

Properties of natural rubber (NR):

- *Physical properties*: Natural rubber has high elasticity, slightly plastic, with very good mechanical strength, low loss of hysteresis at room temperature. The heat generation is low at many times of deformation, so that the flex resistance is pretty good, and since it is a non-polar rubber, the electrical insulation performance is also very good.

- Chemical properties: Since rubber has unsaturated double bonds, the related materials show note worthy chemical reactivity towards light, heat, ozone, radiation, flexing deformation. Some metals (i.e. copper, manganese and others) can promote the aging of rubber. Intolerant aging is a fatal weakness for natural rubber.

There are various varieties of rubber tree, such as *Hevea brasiliensis*(Para rubber tree), *Landolphia heudelotis*(Congo rubber tree), Taraxacum kok-saghyz (Dandelion), *Parthenium argentatum* (guayule), whose rubber differs in purity and molecular weight. The major commercial source of natural rubber is the *Hevea brasiliensis*, that it is a member of the spurge family, Euphorbiaceae.

Hevea brasiliensis is native to the Amazon forest. It is a tall deciduous tree growing to a height of up to 40 m in the wild, but cultivated trees are usually much smaller because drawing off the latex restricts the growth of the tree. Its sap is the main source of natural rubber. This species perform well because it grows quickly in tropical zone, and it can produce lots of sap while cultured.

Para rubber trees were originally grown only in the Amazon rainforest. The increase in demand and the discovery of vulcanization procedures in last century led to a boom of rubber. By 1898, a rubber plantation was established in Malaysia. Today, most of the rubber trees plant in South and Southeast Asia. In 2011, the top three rubber producing countries are Thailand, Indonesia and Malaysia.

The sap is extracted from *Hevea brasiliensis* through a simple process. First, cut the rubber tree bar out of a small groove, install a deflector at the bottom of the tank, and place the container under the guide. So that the rubber sap will flow out from the small slot, along the small groove through the duct into the collection vessel (**Figure 2.3**).

Then, the sap is send to the factory to refine, solidification and drying to obtain the prepared rubber.

Figure 2. 3 - Extracting procedure of NR

2.1.2 - Global rubber consumption

In Central and South America, the history that people began to collect rubber can be traced back to 1600 BC. In 1876 the British explorer Henry Wickham brought back about 70,000 pieces of three-leaf rubber tree seeds from Parra and began to transplant the rubber trees to the areas of Congo, Liberia, Nigeria, Sri Lanka and so on. Thus Southeast Asia began to appear large-scale rubber farms. In the 1930s, Southeast Asia became the main production center for natural rubber.

Global rubber consumption has been on the rise since the 1960s. This is the result of the world's growing population and the rising world production, especially in the automotive industry.

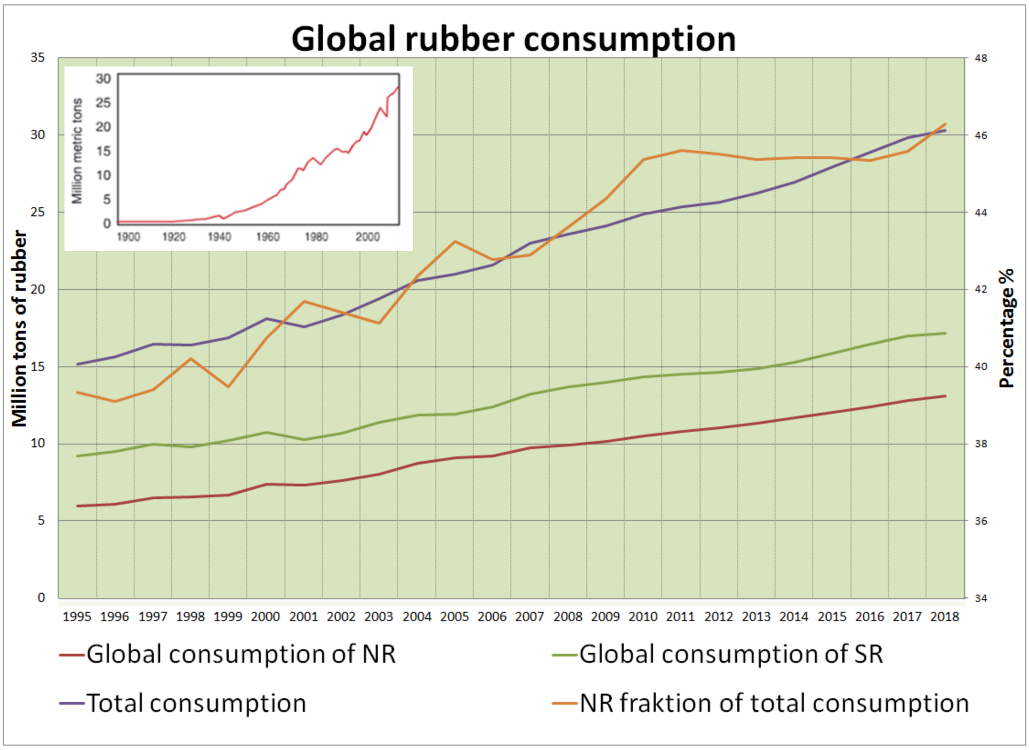


Figure 2. 4 - World total natural rubber consumption,1900–2018

According to the International Rubber Research Organization statistics show that in 2016, the world's rubber consumption reached 27.2 million tons, of which China's rubber consumption of 9 million tons, accounting for more than 33% of the world's rubber consumption. The International Rubber Research Organization predicts that the total rubber demand in 2020 will reach 31.5 million tons.

Thailand, Indonesia, Malaysia and India are the leading natural rubber production countries of rubber. From **Figure 2.5**, we can see that almost all the countries are Asian, especially Southeast Asian. Thus, Southeast Asia has become the center of the rubber industry.

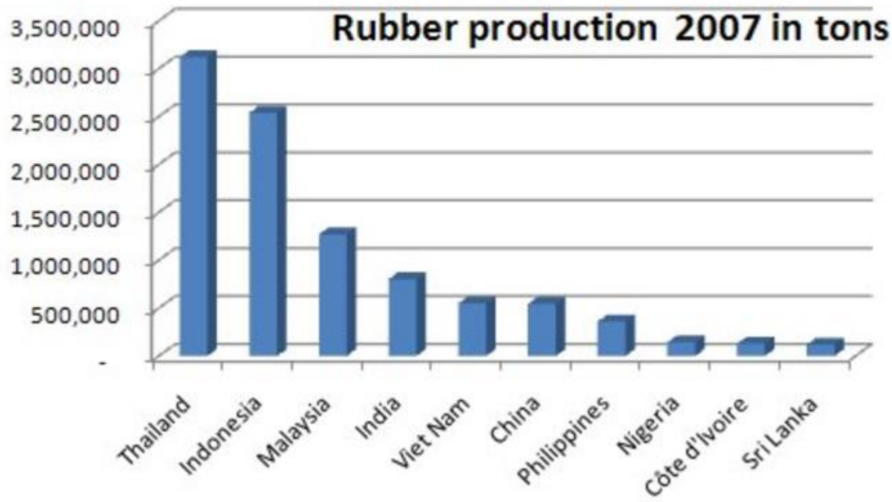


Figure 2. 5 - Rubber production in countries

However, rubber resources are extremely scarce. At present, the production of natural rubber is close to saturation, the world's natural rubber resources supply is facing a shortage situation, and its replacement - synthetic rubber constraints by the oil resources-do not appear easy. In the condition of increasingly shortage of oil resources, rubber production has been unable to large-scale growth. However, with people's production and living standards improved and, especially in recent years, the rapid development of the automobile industry and manufacturing industry, has induced an increasing demand for rubber. This situation in the short term is difficult to change, which severely limits development of relevant industry. Therefore, in this case, the recycling of rubber resources becomes particularly important.

2.2- Synthetic Rubber

2.2.1- Introduction

Synthetic rubber, as the name suggests, refers to any artificial, not naturally formed, polymeric material with elastic properties. These rubber-like materials consist of long polymer chains with high flexibility and flow ability. This class of polymers represents one of the three major synthetic materials and they are synthesized from sources such as coal, oil, and natural gas.

Synthetic rubber was born during the First World War with a small production owing to the urgent needs of the war. In the early 1930s, the synthetic rubber industry was established. From the 40's, a rapid development was made. The Second World War promoted the development of multi-species, multi-performance synthetic rubber industry. In1960s, synthetic rubber production began to exceed the natural rubber.

2.2.2 - Global synthetic rubber consumption

Synthetic rubber production in 1950 was only about 600 ktons, but starting from this year a progressive increase was observed mainly due to the rapid development of petrochemical industry. The production of synthetic rubber is increased by about 1000 ktons almost every 5 years.

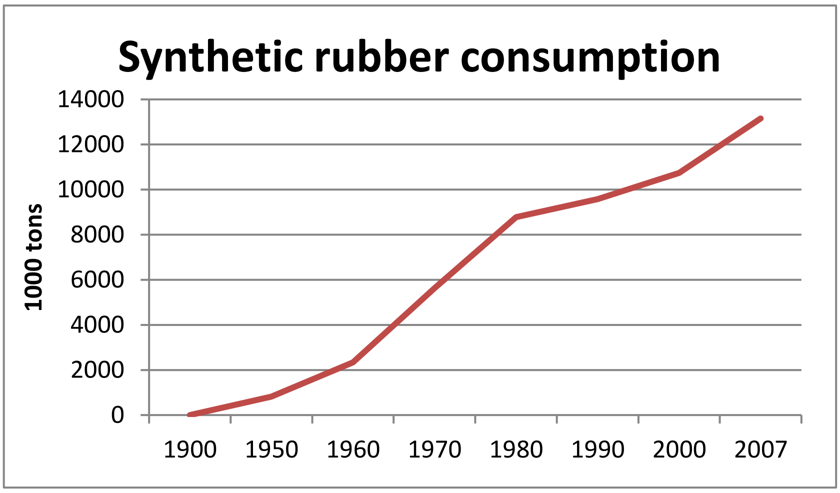


Figure 2. 6 - World total synthetic rubber consumption

In 1979, the production was about 9000ktons, reached its peak. The output began to decline in 1980s, the next few years stable at about 8000ktons, about twice the natural rubber production. Until now, the annual capacity of synthetic rubber is about 12Mt.

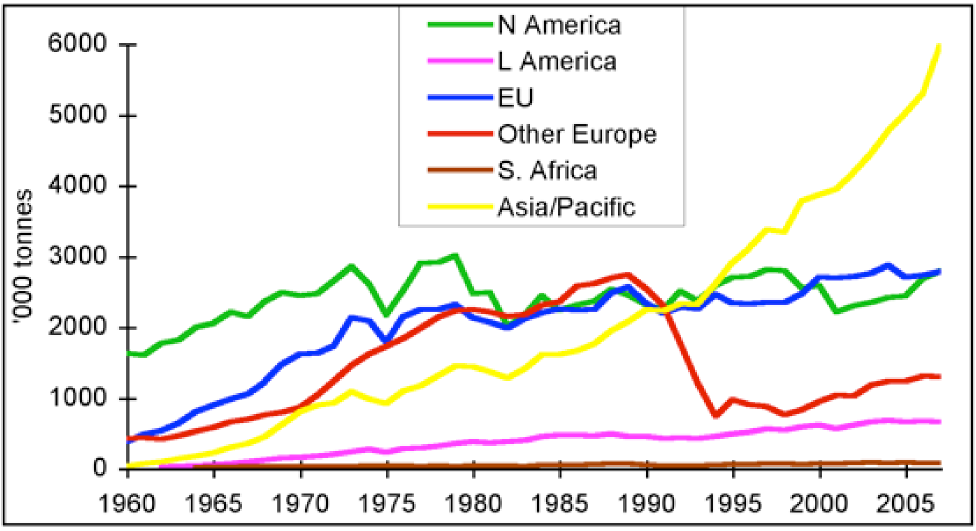


Figure 2. 7 - Synthetic rubber consumption by regional

After the Second World War, the synthetic rubber industry developed rapidly, especially in United States and other Western countries. However, from 1990s, Asia/Pacific dominates all other regions as far as total rubber consumption is concerned. In 2012, Asia/Pacific consumed 62% of world total rubber as compared to 15% for the European Union (EU), 11% for North America, 6% for Latin America, 5% for non-EU Europe and 1% for Africa.

Synthetic rubber is generally not as good as natural rubber, but it has high elasticity, insulation, air tightness, oil resistance, high temperature or low temperature performance, therefore, it is widely used in agriculture, industry, defense, transportation and daily life. Synthetic rubber is mainly used in the manufacture of automobile tires, tapes, hoses, rubber shoes, cables, sealing products, medical rubber products, adhesives and latex products. Moreover, it is widely used in the shoes soles.

2.2.3 - Main types of synthetic rubbers

Between the different synthetic rubbers available on the market, we will analyze n this thesis three types mainly used for foot wear rubber: Styrene/Butadiene Rubber (SBR),Butadiene rubber (BR), and Polyurethane (PU).

2.2.3.1 - Styrene/Butadiene Rubber (SBR)

The term styrene-butadiene or styrene-butadiene rubber (SBR) describes families of the most important synthetic rubbers; it copolymerized from butadiene and styrene. Their ratio influences the properties of the polymer and the performance at room temperature.

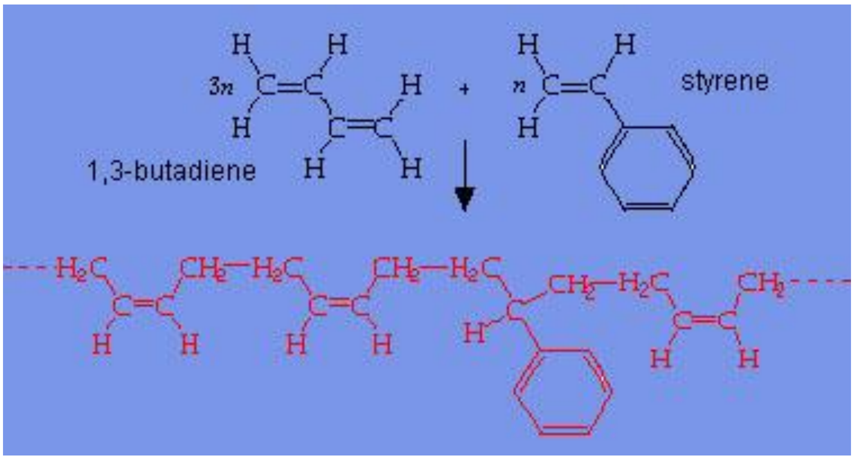


Figure 2. 8 – Monomers constituting SBR and related SBR polymer

Butadiene is the main raw material for the production of synthetic rubber (SBR, BR, nitrile rubber, chloroprene rubber). The presence of butadiene in a polymer entails three possible different configurations of the resulting double bond (**Error! Reference source not found.**). In the first and second unit, a carbon-carbon double bond with hydrogen atoms are on the same or on the opposite sides of the bond; in the vinyl unit, third and fourth carbon atoms are not in the centre and don't participate to the polymer chain structure[9], as shown in **Figure 2.9**

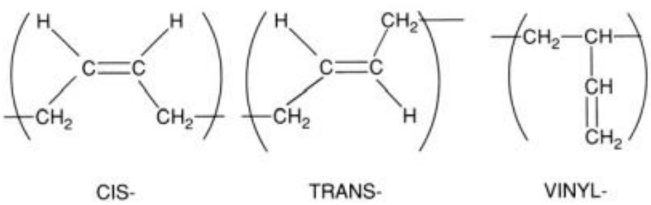


Figure 2. 9 - Isomer configuration of butadiene monomer in SBR and BR chains

The demand for SBR has been steadily increasing during the last 10 years, from 700,000 tons in 2007 to 120,000 tons in 2014(**Error! Reference source not found.**). A significant portion of this increase in demand for SBR was from the Asia-Pacific region, and the same trend is expected to continue in the near future.

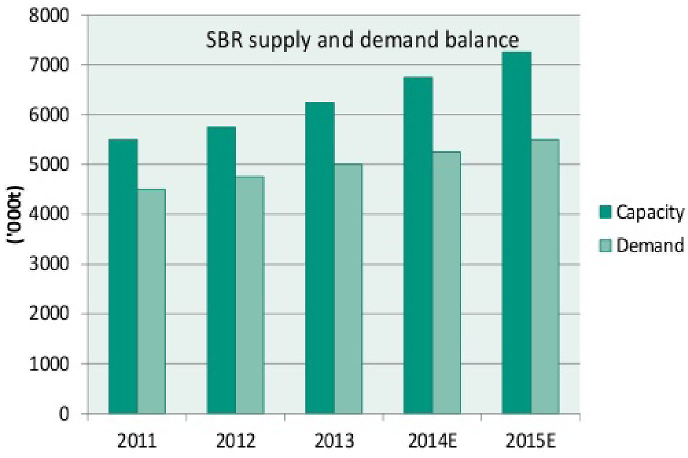


Figure 2. 10 - Production trend of styrene butadiene rubber (SBR)

According to the polymerization process, styrene-butadiene rubber is divided into emulsion polymerization (E-SBR) and solution polymerization (S-SBR).

E-SBR produced by emulsion polymerization is initiated by free radicals. Reaction vessels are typically charged with the two monomers, a free radical initiator, and a chain transfer agent such as an alkyl mercaptan. Solution-SBR is produced by an anionic polymerization process under strictly anhydrous and anoxic conditions. Polymerization is initiated by alkyl lithium compounds. Relative to E-SBR, S-SBR is increasingly favored because it offers improved wet grip and rolling resistance, which translate to greater safety and better fuel economy, respectively.

For footwear rubber, the application is mainly calls for E-SBR, although S-SBR is becoming more and more popular.

2.2.3.2 - Butadiene Rubber (BR)

Polybutadiene rubber is a kind of general synthetic rubber which is polymerized by using 1, 3- butadiene as the only monomer, its molecular formula is $(C_4H_6)_n$, chemical structure CH_2=CH-CH=CH_2. The most important type of polybutadiene rubber is solution polymerized high CIS butadiene rubber. The catalyst used in the production determines the type of polybutadiene product. According to the different catalysts can be divided into nickel, cobalt, titanium and rare earth polybutadiene rubber.

Table 2. 1 - Typical composition of polybutadiene based on the catalyst used

Transition Metal	*cis*(%)	*trans*(%)	vinyl (%)
Nd	98	1	1
Ni	96	2	2
Co	96	3	1
Ti	93	3	4
Li	10-30	20-60	10-70

- High-*cis* polybutadiene. Consists in a large amount of *cis* units (>92%) and few vinyl units (<4%); it is synthesized using the Ziegler-Natta catalysts and its properties vary depending on the metal used. These materials may have low to high mechanical resistance.
- Low-*cis* polybutadiene. Obtained using an alkyl-lithium catalyst (eg.N-butyl lithium), contains typically 36% of *cis* units, 54% of *trans* units and 10% of *vinyl*. Units. It is used as additive for other plastics.
- High-*trans* polybutadiene. Obtained with catalysts similar to those used for the high-*cis* and is a plastic lens material (non-elastic) that melts at 80°C. It's used in the production of golf balls.
- High-*vinyl* polybutadiene. Synthesized using analkyl lithiumcatalyst, it contains over 70% of vinyl units.
- Metallocene polybutadiene. Recently synthesized by Japanese researchers using a metallocene as a catalyst, it contains a proportion of *cis*/*trans*/*vinyl* units widely variable[10].

Polybutadiene rubber is the second largest synthetic polymer after the SBR. Compared with natural rubber and styrene butadiene rubber(SBR), the vulcanized butadiene rubber has excellent cold resistance, wears resistance and elasticity. Moreover, it has less heat generation and good aging resistance under dynamic load, and it is compatible with natural rubber, chloroprene rubber or nitrile rubber.

2.2.3.3 - Polyurethane rubber（Pu）

Polyurethane (PUR and PU) is a polymer composed of organic units joined by carbamate (urethane) links. Polyurethane polymers are traditionally and most commonly formed by reaction of a di- or poly-isocyanate with a polyol. Both the isocyanates and polyols used to make polyurethanes contain, on average, two or more functional groups per molecule. Typical examples are reported in **Figure 2.11**.

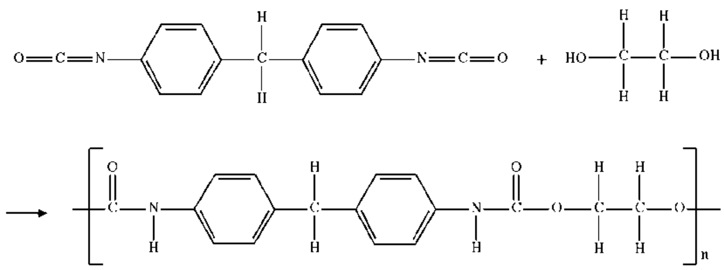


Figure 2. 11 - Representative structure of a polyurethane by addition of ethylene glycol to methylene diphenyl 4,4'-diisocyanate (MDI)

Polyurethanes belong to the class of compounds called reaction polymers, which include epoxies, unsaturated polyesters, and phenolics. Polyurethanes are produced by reacting an monomer containing two or more isocyanate groups per molecule ($R-(N=C=O)_n$) with a polyol containing on average two or more hydroxyl groups per molecule ($R'-(OH)_n$) in the presence of a catalyst or by activation with ultraviolet light.

Polyols can be polyether polyols, which are made by the reaction of epoxides with an active hydrogen containing compounds or polyesterpolyols which are made by the polycondensation of multifunctional carboxylic acids and polyhydroxyl compounds.

The mechanical properties of polyurethanes are highly adjustable. By controlling the ratio between crystalline hard segments and non-crystalline soft segments, polyurethanes can achieve different mechanical properties. So, products based on these polymers can have wear-resistance, temperature, sealing, noise, processing performance, and excellent degradation performance.

In 2007, the global consumption of polyurethane raw materials was above 12 million metric tons, the average annual growth rate is about 5%.

CHAPTER 3

THE TREATMENT PROCESS OF RAW RUBBER

Whether it is natural rubber or synthetic rubber, they are both needed to carry out a series of processing, in order to eventually apply to the actual production. Processes for processing rubbers include mixing, calendaring, extrusion and various operations commonly used as reinforcing additives, such as reinforcing fillers, stabilizers, flame retardants, colorants, plasticizers, etc., to incorporate chemical additives in rubber to optimize product performance and performance. For the materials of shoes sole, there are some main treatment processes.

3.1 - Vulcanization Process

"Vulcanization" comes from the original natural rubber(NR) products with elemental sulfur as a cross-linking agent. With the development of the rubber industry, now we can use a variety of non-sulfur cross-linking agent for cross-linking. Therefore, the more scientific significance of vulcanization should be "cross-linked" or "bridging", that is, the process that linear polymer through the role of cross-linking to get the formation of network polymer. Crosslink are bonds that connect one polymer chain to another[11]. From the physical property that is the process that plastic rubber is converted into elastic rubber or hard rubber.

The rubber that after vulcanization is called vulcanized rubber. Vulcanization is the last step in rubber processing; after that, we can get the practical value rubber products. In the network structure of the rubber, the density of the sulfur crosslinking bond (where the number of sulfur atoms is $n \geq 1$; and the number of uncrosslinked sulfur atoms is S_x or S_y) determines the degree of vulcanization.

3.1.1 - Definition of vulcanization

The unvulcanized rubber is called raw rubber. Raw rubber is very sticky, and it cannot maintain its shape after large deformation, so the applicable scope is small and it cannot apply to most of the rubber products. Vulcanization refers to the process that adds sulfur as crosslinking agent in rubber, so that the rubber macromolecules can react with sulfur in the condition of heating, cross-linked into a three-dimensional network structure.

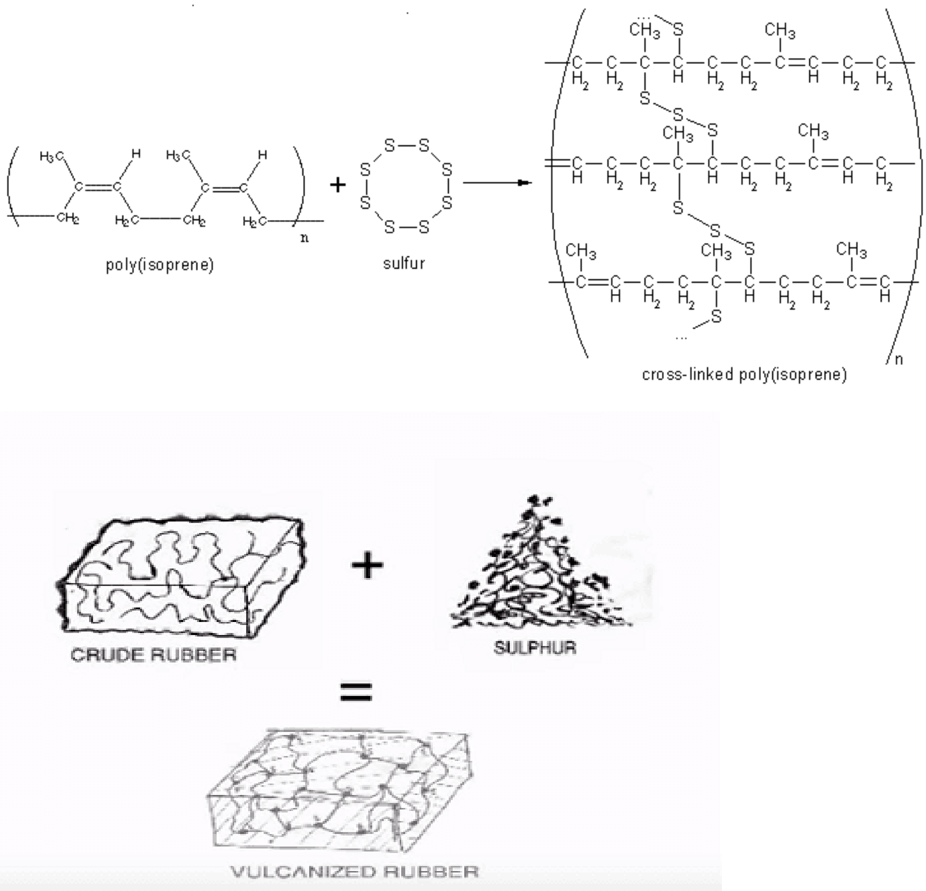


Figure 3. 1 - Schematic of vulcanization cross-linking process by sulfur

When sulfur is used, it can also be defined as the process that involves sulfur in cross-linking, and the process refers to the one or more sulfur atoms connected to the polymer chain to form a bridge structure. During this process, the contractile force of the polymer chains increases and the amount of permanent deformation remaining decreases. In general, vulcanization is to increase the strength and toughness of rubber and to reduce its plasticity[12].

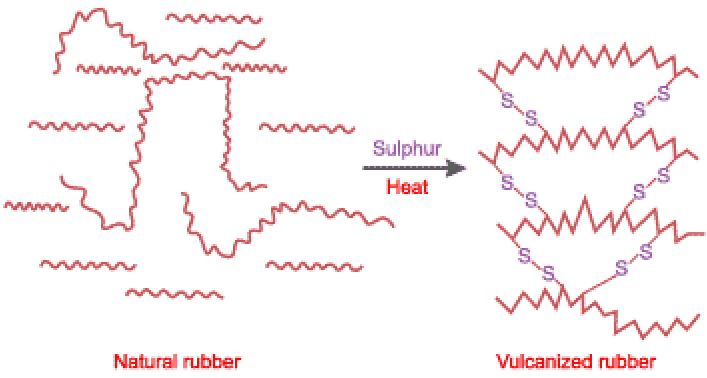


Figure 3. 2 - Schematic of the formation of cross-link network promoted by sulfur

3.1.2 - Vulcanization process

Through the measurement of the tensile strength of the compound, it can be seen that the whole vulcanization process can be divided into four stages: induction period of cure, precure, optimum cure and over cure (Natural rubber appears "back to the original" state).

During the induction period of cure, the crosslinking has not yet begun and the compound has good fluidity. This stage determines the ‘’scorch’’ of the compound and the processing safety. At the end of this phase, the compound begins to cross-link and lose liquidity. The length of this period is not only related to the nature of the raw rubber itself, but also depends on the additives used, such as the use of delayed accelerator can induce a longer scorch time and have a higher processing safety.

After the induction period of cure, the pre-cure stage is carried out at a constant rate. The degree of cross-linking for pre-cure is low, and even if at the end of this stage, the tear strength and elasticity of the compound cannot reach the desired level.

Upon reaching the optimum cure stage, the physical properties of the compound almost reach the optimum point or achieve a full balance of performance. After the optimum cure stage, it is the over cure stage. There are two cases:

a) natural rubber appears "back to the original" state (tensile strength decreased), and

b) most of the synthetic rubber (except butyl rubber) tensile strength continues to increase.

For any rubber, vulcanization does not only promote cross-linking, but also lead to fracture of molecular chain due to the effect of heat and other factors. This phenomenon runs through the entire vulcanization process. In the over cure phase, if the cross-linking is still dominant, the rubber is hard, the tensile strength continues to rise. NR rubber, on the contrary, softs at this stage and appear "back to the original" phenomenon

3.1.3 - Effects of vulcanization

The vulcanization process will has a great impact on the molecular structure of the polymer chains. There are some major effects of vulcanization:

a) Changes in physical and mechanical properties

The physical and mechanical properties of the rubber products are the outcomes of the molecular structure and the inside interaction of the dispersing agents. During the vulcanization process, the molecular structure changes, so that the physical and mechanical properties of the rubber are also changed. In the process of vulcanization, different structures of rubber show different trends of physical and mechanical property. Throughout the process, linear macromolecules gradually become a network structure. For natural rubber, plasticity decreases, tensile strength, hardness, and elasticity increases, while elongation, permanent deformation, heat and other properties consistently reduce. However, if the curing time is extended, the situation will be different, tensile strength and elasticity will gradually decrease while elongation and permanent deformation will rise. For synthetic rubber such as styrene-butadiene rubber, butadiene rubber and Nitrile Butadiene Rubber, its physical and mechanical properties in the vulcanization process has a similar change, but with the curing time continues to extend, the performance changes are relatively flat, such as for strength and other properties, it can be maintained for a long time when reaches the maximum value.

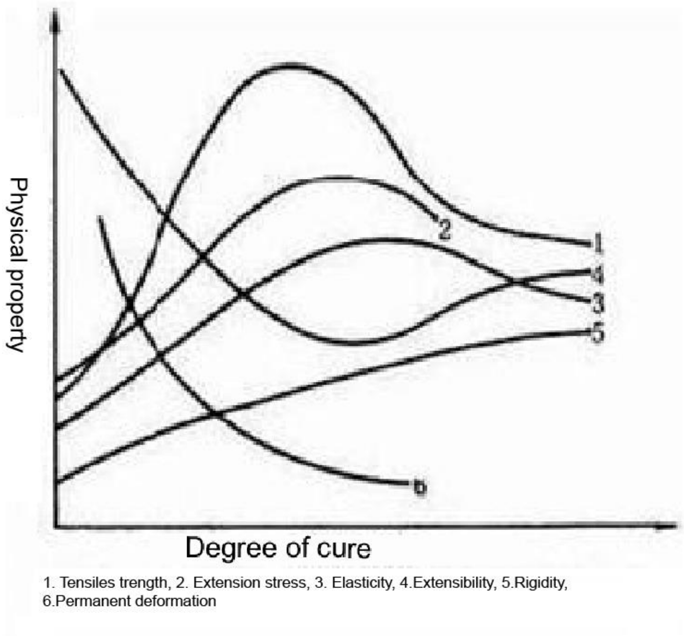


Figure 3. 3 - Dependence of Physical properties on degree of cure of Vulcanization

b) *Changes in physical properties*

In the vulcanization process, the cross-linking density of rubber has undergoes significant changes. With the increase of the crosslinking density, the density of the rubber increases, and the small molecules such as gas and liquid are difficult to move in the rubber, so that the breathability and the permeability is reduced. In the mean time, the relative molecular mass increases, solvent molecules are difficult to exist between rubber molecules, so that solvent can only make the vulcanized rubber swell, and the greater the degree of cross-linking, the smaller will be swelling. Vulcanization also improves the thermal stability and the temperature range of the rubber.

c) *Changes in chemical properties*

In the process of vulcanization, the cross-linking reaction always occurs at carbon atoms with relatively high chemical activities, which are the sites that are also susceptible to the aging reactions (commonly the double bonds or the allylic positions). After vulcanization, these sites have cross-linked, the molecular structure has changed and the aging reaction is difficult to carry out. When the rubber to form a network structure, it makes the low molecular diffusion becomes more hamper, the free radicals, resulting from the rubber aging, hardly spread, so that chemical stability of rubber is improved.

3.1.4 - Vulcanization methods

There are many different methods for vulcanization. The most important economic method is that after the curative agent is added to the rubber, treatment of rubber with high temperature and high pressure are applied. A typical method for vulcanization is that keeps the vulcanization temperature at 177°C for 10 minutes. This method employs a technique known as compression molding in which the rubber product is intended to use the shape of the mold. There are a number of other methods, for example, the use of hot air vulcanization or microwave heating vulcanization.

Five types of curing systems are in common use, operating through different mechanisms. They are:

1. Sulfur systems
2. Peroxides
3. Metallic oxides
4. Acetoxysilane
5. Urethane crosslinkers

We will describe in the following paragraph in more detail the sulfur based vulcanization owing to their relevance.

3.1.5 - Sulphur based vulcanization

Sulfur is a chemical element whose chemical symbol is Sandits in the periodic table and the atomic number is 16. It is a very common tasteless non-metallic material; pure sulfur appears as a yellow crystalline material. Sulfur can be found in different oxidation states, typically -2, 0, +4, +6, and so on. sulfur has several allotropes, of which the most important is the orthorhombic alpha sulfur(S8),cyclic molecule which opens when temperature increases to give a linear diradical polymeric structure. Due to the unpolar character, sulfur can be dissolved in rubber without any difficulties.

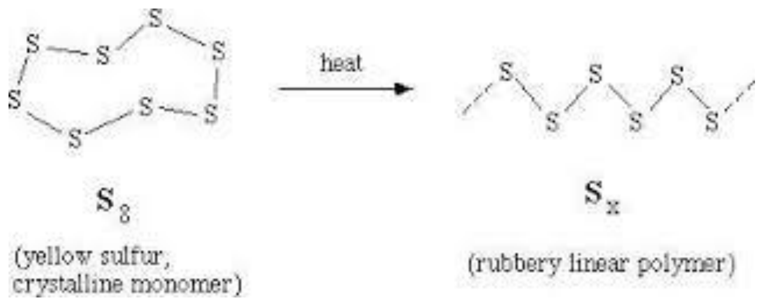


Figure 3. 4 - Opening of orthorhombic sulfur (S_8) by heating to polymeric sulfur (S_x)

So far, the most common method of vulcanization depends on sulfur. Sulfur is the oldest vulcanizing agent for unsaturated rubber used in rubber practice. The effective and rapid linkages with the crosslinking forms of the rubber macromolecules occur only in the presence of *accelerators* and activators. Sulfur itself is a slow curing agent. So, if these *accelerators* and activators are absent, the sulfur reacts very slowly with the rubber and combined with rubber in the form of a side cyclic structure rather than in the form of sulfur cross-linking. Even if natural rubber is used, a large amount of sulfur is required, as well as high temperature and long heating times.

3.2 - Additives for the vulcanization

Since the sulfur reacts very slowly with the rubber, additives are necessary for vulcanization. Only with vulcanization additives can the quality corresponding to today's level of technology be achieved.The additives can affect the kinetic parameters of vulcanization, such as temperature and time, and they also can affect the sulfur content required for the best network of vulcanizates.

The diversity of the desired vulcanization effect cannot be achieved with a single substance, so a large number of different additives are required. These additives include accelerators, activators such as zinc oxide and stearic acid and aging inhibitor. The accelerator and activator are catalysts. Aging inhibitors are used to prevent the vulcanization product from being degraded by heat, oxygen and ozone.

3.2.1 - Activators

Activators is any vulcanized active agent that increase in the activity of the accelerator, increase the rate of vulcanization and curing efficiency (i.e. increase the number of cross-linked bonds, reduce the number of cross-linked bonds in the average number of sulfur atoms), improve the performance of vulcanized chemicals. The typical active agents are zinc oxide and stearic acid, they can enhance the activation of vulcanization accelerator, improve the vulcanization effect of rubber.

3.2.2 - Accelerators

Vulcanization accelerator can decompose into active molecules when heated to promote rapid crosslinking of sulfur with rubber molecules at lower temperatures, to enhance the vulcanization of rubber, to reduce the vulcanization time, to reduce the amount of sulfur, and to improve the physical machinery of rubber performance. It can be divided into two categories: inorganic accelerator and organic accelerator. Currently the mostly used is organic accelerators. It has been found that the use of several accelerators together is better than the use of an accelerator alone. The characterization of the accelerator is mainly carried out from the aspects of vulcanization promoting properties and the physical and mechanical properties of vulcanizates. The vulcanization promoting characteristics mainly depend on the vulcanization rate, the scorch time, the vulcanization time, the vulcanization temperature and the anti-vulcanization reversion. The physical and mechanical property is mainly depends on the vulcanized rubber hardness, elasticity, tensile properties, friction properties and thermal aging properties.

In fact, the effectiveness of the accelerator depends on the physical and mechanical properties of the vulcanizate, the nature (type and density) of the crosslinking bond in the vulcanizate plays a decisive role in its application. The strength and dynamic mechanical strength of the vulcanizate depends not only on the performance of the polymer chain itself but also on the number of network support chains in the total cross-network. The cross-linking density determines the number of network support chains.

3.2.3 - Aging Inhibitor

Rubber molecules will react with oxygen, ozone and rubber structure will destroy, so that the mechanical properties of products will reduce, the life time will be shortened; this phenomenon is called rubber aging. Light and heat can promote the oxidation of rubber, thereby accelerating aging of rubber. By adding the substance which can resist, slow down the aging of rubber products, called aging inhibitor. There are two categories: physical aging inhibitor and chemical aging inhibitor.

Physical aging inhibitors are paraffin wax, ground wax, beeswax and stearic acid. Such substances can form a thin film on the surface of rubber products, to prevent oxidation of oxygen and rubber molecules, but also to block the light exposure.

Chemical aging inhibitors are more likely to react with oxygen than rubber. In the case, by adding chemical aging inhibitors, the oxygen into the colloid first react with the aging inhibitors, it can reduce oxygen contact with the rubber, so that effectively delay aging.

3.3 - Other additives

3.3.1 - Processing oils

To improve the elasticity, flexibility, ease of processing, easy to mix and other characteristics of rubber, usually need to add a specific processing oils to achieve the goals. In the actual use of rubber oil, because the different usages, the different physical and chemical properties of processing oil requirements, there are varieties kinds of processing oils. According to the composition of hydrocarbons can be divided into three primary categories: aromatic, naphthenic and paraffinic.

- Aromatic oils contain high levels of unsaturated rings, unsaturated naphthenic rings, and pendant alkyl and unsaturated hydrocarbon chains. The predominant structure is aromatic.
- Naphthenic oils have high levels of saturated rings and little unsaturation.
- Paraffinic oils contain not only high levels of naphthenic rings but also higher levels of alkyl pendant groups, unsaturated hydrocarbon pendant groups, and, most important, fewer naphthenic groups per molecule.

There are some main functions of processing oil

(1) it can significantly reduce the force between the rubber molecular chain, so that the powder-like additives and raw rubber can be a good infiltration, thereby improving the mixing process;

(2) it can make the additive dispersed evenly, shorten the mixing time, reduce energy consumption, and can reduce the heat generated during the mixing process;

(3) to increase the plasticity, fluidity, adhesion of rubber, can reduce the heat generated during the mixing process;

(4) to improve some physical and mechanical properties of the vulcanizate, such as reducing the hardness of vulcanized rubber and give vulcanized rubber higher flexibility, improve its cold resistance;

(5) Since processing oil prices are relatively low, it can be filled a lot in rubber, so it can be used as a ‘’compatibilizer’’ to reduce the cost of rubber.

3.3.2 - Plasticizers

Plasticizer is widely used in industrial polymer additives. In the processing of rubber products, the addition of this substance can make it soft and elastic, easy to bend, fold, and to shape and easy to process. From the chemical structure classification, plasticizers include: aliphatic dibasic organic acid esters, phthalates, benzoates, polyol esters, chlorinated hydrocarbons, epoxy, citric acid esters, polyesters and so on. Among them, phthalates is the most commonly used plasticizer, is a kind of esters which formed by the dicarboxylic acid phthalic acid and alcohols, it has good water and oil resistance. The molecular weight of dioctyl phthalate (DOP) is high and it has low volatility, so, it is suitable for harder products

3.3.3 – Peptizing agents

The peptizing effect is to chemically disperse the insoluble matter into a colloidal system. Usually by adding the appropriate electrolyte in the clean precipitation, this electrolyte is called plastic solvent. Different materials require different peptizers, which are closely related to the ions that can be adsorbed on the surface of the material. The peptizer is also a colloid stabilizer. The reason why the dispersion is stable is due to the formation of double layers around the colloidal particles. There are some species of peptizers: pentachlorothiophenol, phenylhydrazine, certain diphenylsulfides, and xylyl mercaptan.

3.3.4 - Colorant

The colorant is a substance that makes the rubber product colored. There are two kinds of colorant: inorganic colorant and organic colorant. Inorganic colorant is inorganic pigments, titanium dioxide for white, iron oxide for red, chromium oxide for green, and so on. Organic colorants are organic pigments and certain category of dyes. Most of these colorants are organic salt compounds such as barium or calcium salts.

3.4 - Foam rubber

3.4.1 - Introduction

Foam rubber (also known as cellular, sponge, or expanded rubber) refers to a rubber filled with an airborne matrix structure made of a blowing agent. Commercial foam rubber is mainly made of polyurethane or natural latex. The main idea is that solid rubber foam to produce rubber sponge. The principle is to add the foaming agent (or a co-foaming agent) to the selected rubber materials and to decompose the forming agent to release gas in the curing temperature. The gas remains enclosed in the rubber material forming cells, so that the compound expands and shapes as a sponge. Foaming agent can be divided into three categories: chemical foaming agents and physical foaming agents and surfactants.

Chemical foaming agents are those compounds which, after being decomposed by heating, can release gases such as carbon dioxide and nitrogen and form pores in the polymer. Typical are compounds containing azo, sulfonyl hydrazide, nitroso, and carbonate substituents, seldom called blowing agents.

The physical foaming agent is that the foam pores are formed by the physical form of a substance, that is, by the expansion of the compressed gas, the volatilization of a liquid, or the dissolution of a solid. Commonly used physical foaming agents are low boiling point alkanes and fluorocarbons.

The surfactant has high surface activity, can effectively reduce the surface tension of the liquid and in the liquid film surface to form a double charged layer arrangement and surrounded by air, thus forming bubbles, and then by a number of bubbles to form foam.

The main factors that determine and influence the structure of the foam are the amount of the foaming agent, the rate of diffusion of the gas in the compound, the viscosity of the compound, and the rate of vulcanization. The most critical of which is the amount of the foaming agent, the rate at which the gas is generated and the vulcanization rate of the compound.

Figure 3. 5 - Appearance of commercial foam rubber

3.4.2 - The foaming capacity and decomposition rate of foaming agent

The foaming capacity refers to the volume of gas that released by the unit foaming agent decomposed in standard state; the unit is mL/g. The decomposition rate of foaming agent means the amount of gas released of unit mass in unit time and in certain temperature. Since the polymer itself does not change the decomposition mechanism of the foaming agent, it is not possible to measure the gas content of the foaming agent in the polymer. Usually, the method is that place the foaming agent into an inert dispersant (such as DOP or mineral oil) at a certain temperature for a period of time to collect the emitted gas, draw the gas volume curve with the heating time. The decomposition rate of foaming agent can be obtained by the slope of the curve under the temperature, the quality of decomposition gas after completely divided by the total volume of the foaming agent to get foaming capacity. Different foaming agents have different particle sizes and their decomposition rates are also different. Generally, the decomposition temperature of the foaming agent is low and the decomposition rate of the foaming agent is fast; for one foaming agent, the particle size is small, and the temperature is high, and the decomposition rate of the agent is fast.

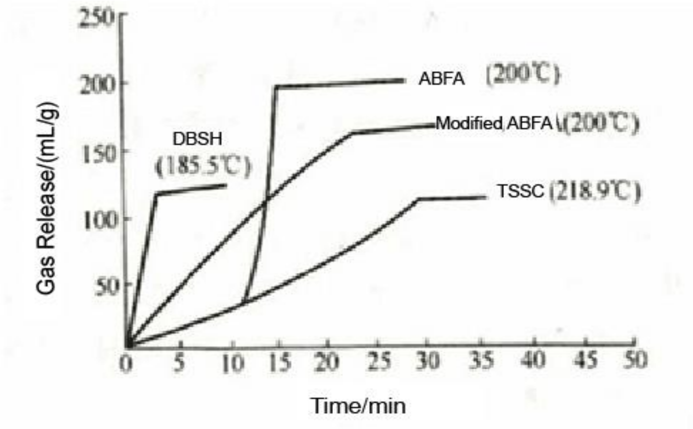


Figure 3. 6 - Typical time dependence of gas release by foaming agent in rubber

The matching of between decomposition rate of foaming agent and vulcanization speed of rubber influences the formation and structure of the foams. If there are a big difference between the decomposition rate of foaming agent and the rate of vulcanization of the rubber material, they cannot be matched and the rubber cannot be foamed.

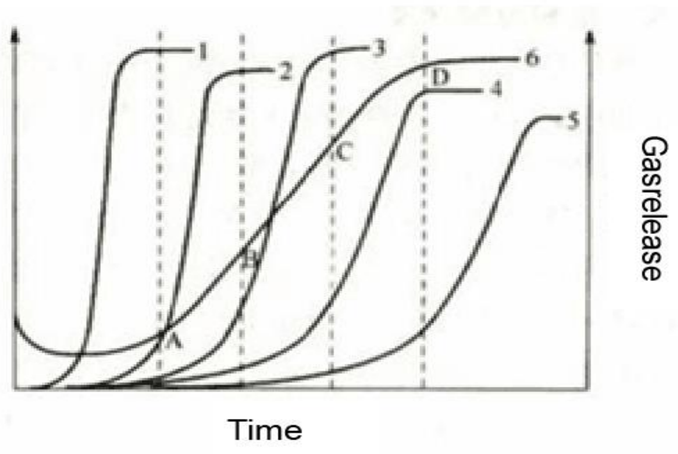


Figure 3. 7 - Decomposition curve of the foaming agent with the vulcanization curve of the rubber

The diagram of **Error! Reference source not found.** shows the decomposition curve of the foaming agent matches with the vulcanization curve of the rubber. In this **Error! Reference source not found.**, curve n.6 is the vulcanization curve, A is the scorch point, and D is the positive sulfuration point. Before A, there is no crosslinked rubber, if foaming agent decompose (curve n.1), gas release can easily escape from the very low viscosity rubber; if foaming start In the D or after D points (curve n.5), the rubber has been fully cross-linked, viscosity is too high, it also cannot induce foaming.

In order to realize the matching of foaming agent and vulcanization, to make better rubber products, the key is to select the right foaming agents and curing system. There are two kinds of methods: one is to choose the foaming agent based on decomposition temperature, such as the use of delayed action accelerator, so that it can be used to adjust the amount of accelerant to adjust the curing rate; the second method is to select suitable foaming agent and particle size. The particle size of foaming agent is also one of the most important factors which determine the decomposition rate. If the foaming agent particle size decreases, the specific surface area of particles increases and the efficiency of heat conduction improve along with the decomposition rate. Therefore, must be selected a suitable grain size of the foaming agent to adjust the balance between decomposition rate and curing speed. The average particle size of foaming agent is commonly between 2 and 15 μm (Table 3.1).

Table 3. 1 - Selection of dimension of foaming agent particle size on vulcanization and foaming conditions

Particle size/µm	Foaming conditions
2	The fastest decomposition rate. Pre-cure at 132-143°C. Expanded foam at 157-166 °C.
3	Decomposition rate is fast, Wide range of applications
5	The vulcanization rate of the compound is slow, suitable for EPDM.
10-15	Pre-cure at 172-182 °C, Expanded foam at 204-220 °C, suitable for SBR blends of automobile parts.

CHAPTER 4

RUBBER MOLD TECHNOLOGY

4.1 - Introduction

The rubber molding process is used to place the mixture blank in the model and the press process of the flat vulcanizing machine under the specified time, pressure and temperature is adopted. Its products are called molded rubber products, which are referred to as molded products. The so-called mold forming is to fill the rubber mixture into the mold cavity of the metal mold. When the mold is closed, two plates put pressure on the elastomer, which then fills the cavity. The elastomer is maintained under pressure and heated until the rubber is cured, allowing the part to maintain the shape of the designed final rubber product.

The entire rubber mold process is divided into several parts, which includes raw rubber cutting, raw rubber mastication, compound mixing, calendaring into sheet, cut-sheet forming, mold pressure vulcanization, finishing.

4.2 - Main processes of rubber mold technology

Although there are many different types of rubber for different uses, for shoes rubber the mold technology is almost the same. The process of rubber mold technology is complex, from raw rubber to finished products; there are many steps that should be followed, mainly including the following steps.

4.2.1 - Preparation of raw materials

The main material of rubber soles is raw rubber and the agent. During the preparation of the raw material, the ingredients must be accurately weighed according to the formula. In order to make the raw rubber and the compounding agent can be mixed with each other; some materials need to be processed.

Raw rubber cut includes commonly the following steps:

a) As raw rubber, raw materials are large and heavy, therefore, before starting the raw rubber mastication process, it must be cut into small pieces and make it suitable for raw rubber mastication. In order to facilitate the cutting and raw rubber mastication process, the heating and softening treatment is needed for large pieces of raw rubber. The conditions for heating and softening treatment include commonly a temperature between 60 to 70 °C and a time ofmore than 24 hours;
b) A block agent such as paraffin, stearic acid, rosin, etc. to be crushed;
c) Powder agent containing impurities or coarse particles need to be removed;
d) A liquid agent (pine tar, ancient malon) need to heat, melt, evaporate moisture, filter impurities;

All agent have to be dry, otherwise they will agglomerate easily, cannot be dispersed evenly, produce bubbles when vulcanization start, thus affecting product quality.

4.2.2 - Raw rubber mastication

The purpose of raw rubber masticate is to improve its plasticity to meet the mixing and dispersing requirements of the various compounding agents in the compound mixing process，so that it is easy to calendaring and forming, and to improve the fluidity of the compound during high pressure molding. The equipment used in this process is open mill. During this process, there is a pair of smooth and hard roller at different speeds relative rotation, when the rubber pieces are put into the rollers, they are involved into the spacing between the two rollers by the extrusion, stretching and the mechanical force of the shear, and the heating and friction generated by the chemical effect, the elasticity of raw rubber is rapidly reduced, plasticity increases so as to achieve the purpose of raw rubber mastication. The diameter and length of the two rollers determine the weight of loaded. This process can also be carried out in closed mills.

4.2.3 - Compound mixing

Compound mixing is a refining process that evenly mixed a variety of compounding agents according to the provisions of the formula into the rubber compound. The quality of the compound determines the quality of the molded outsole. The facility used for compound mixing is an open mill; the feeding order should be strictly in accordance with the requirements of the formula to prevent the occurrence of uneven dispersion and scorching. Mixing process should not be too long, to prevent the occurrence of over refining phenomenon.

In order to adapt to a variety of different conditions of use, to obtain a variety of different properties, but also to improve the performance of rubber outsoles and reduce costs, different kinds of agents must be added to the raw rubber. Compound mixing is a process that mixes masticated raw rubber and agents, placed into the mixing machine, through the mechanical mixing effect, so that the agent completely and evenly dispersed in the raw rubber compound. Compound mixing is an important stage of the production process. If the mixing is not uniform, the full function rubber and agent cannot be reached, affecting the performance of the final product. The material obtained after mixing is known as compound, a semi-finished material, usually sold as a commodity, for the manufacture of various rubber products. The purchaser can use the compound to be directly processed and vulcanized to produce their final rubber products. According to the different formulations, the compound has a range of different grades and varieties of different properties.

4.2.4 - Calendaring into sheet

Before filling the compound into the mold cavity, it needs to be calendered into pieces, which are in accordance with the provisions of the sheet form into mold vulcanization. Forming outsole parts are required to be rolled into pieces and cutting. Calendering is a process where rubber compound is formed to a continuous sheet or coated on a fabric. This is done by feeding the rubber compound to one or several on each other following roll gaps (calendar). The thickness, size accuracy, pattern and shape of the adhesive used in different shoes are different. There are no stringent requirements for the thickness of the film used in the outsole. Perfect sheets up to 2 mm thickness can be produced without air inclusions. For thicker sheets a combination of an extruder and a calendar is used, so called roller head calendar.

4.2.5 - Cut-sheet forming

The film used for pressing the outsole should be cut into pieces before forming in the mold, so that the shape of the film is basically the same as that of the bottom mold shape, so as to enter the mold easily and conducive to vulcanization. The equipment used for the forming is a gantry cutting machine or a flat cutting machine.

4.2.6 - Mold pressure vulcanization

The shoe outsole is produced in the mold cavity, and the equipment used is flat vulcanizing machine. In the molding process, the mold is arranged on the heating plate of this machine, so that the temperature of the mold can reach the curing temperature, then put the rubber film into the mold cavity and the mold is closed. Under the condition of high temperature and high pressure, the mold cavity is fully filled by the rubber compound, thus eliminating gas bubbles, increasing the compactness of the outsole. There are many different kinds of pressure for the vulcanizing press used in shoes, and the curing temperature is related to the formula of the rubber. Under the condition of high temperature and high pressure, the vulcanized molded outsole has the advantages of beautiful appearance, clear pattern, wear resistance, good flexibility, high strength, heat resistance, waterproof, and so on.

Compression and injection molding happen to be just two of the many ways to produce midsoles. Although, as far as running shoes are concerned, these two methods (or a combination of) will account for over 95% of the models produced. Compression molding is the process of compressing a block of rubber compound inside a metal mold. The sides of these molds have a design etched into them. When heat and pressure are applied to the mold, the material expands and fills the inside of the mold. Under pressure, the rubber takes on the shape of the mold cavity, including the design etched on its sides. In the injection molding process a super-heated liquid mass of rubber compound is injected into a mold which is less than half the size of the actual midsole. It is left in there for some time to cure, and when the mold is opened, a midsole suddenly jumps out of the mold. After the midsole expand to a larger size, it also contracts or shrinks on cooling down. So the process of managing the expansion-contraction is more complex than the simple compression molding.

4.2.7 - Finishing

The main contents of Finishing are removal the excess compound at the edge of outsole, spray color, polishing and so on. The equipment that removes the excess compound is the outsole trimmer. In injection molding this stage is prevented because this technology leads to zero wastage as the midsole uses the exact amount of rubber required.

4.3 - Main equipment used in rubber industry

At present, the rubber mold process has achieved industrial production. A series of machines are available for use in the vulcanization mold process of rubber.

4.3.1 - Open mill

Open mill is also called double roller plasticizing machine. It mixes the material or makes the material conform to the specified state by means of two rotating rollers. After initial mixing the rubber and additives through the mixing machine and then mixing and plasticizing by open mill, a masterbatch can be obtained as semi-finished product. The open mill is one of the earliest mixing equipment. In about 1935, steam heating two roll variable speed open mills appeared. In the last 100 years, the structure and control of the open mill have been improved. Because of its inherent shortcomings, part of its work has been replaced by banbury mixer, but it is still widely used in recent years. A representative example of an open mill is reported in **Error! Reference source not found.**.

Figure 4. 1 - Open mill

Principle of open mill

When the mixer works, the two rollers rotate opposite to each other, and the speed is unequal. The material stack on the roller is drawn into the nip due to the friction and adhesion of the roll surface and the adhesion between the materials, and the material is strongly squeezed and sheared in the nip. The shear causes the material to be deformed, thereby pulling back the interface between the components, resulting in a distributional mix. The shearing also causes the material to be subjected to large stresses, and when the stress is greater than the allowable stress of the material, the material is dispersed. Through the nip, the material layer is thinned and wrapped on the roller increasing the temperature, and the heat generated by the shear gradually melt or softthe material. The process is repeated until the desired melting, plasticizing and mixing states are achieved, and the plasticization is completed and the granulation can be achieved immediately. Factors affecting the melt plasticization and mixing quality of the mill are the control and adjustment of the roller temperature, the size and regulation of the roll distance, the roll speed, the amount of material in the roll above the stacking and the direction of the material along the roller line distribution and transposition and so on.

Features:

1. When open mill work, the sample can be directly observed in the mixing process, which can adjust the operation process to achieve the intended purpose, especially for those who are not yet fully aware of its physical properties of materials, with the open mill are easier to explore the most suitable process operating conditions than banbury mixer.
2. Open mill structure is simple, strong mixing strength and low prices.
3. The main drawback of the mill is poor labor conditions, labor intensity, energy use is not reasonable; the material is easy to oxidize and so on.

4.3.2 - Calendar

Calendar is relatively sophisticated general rubber machinery, mainly used in the rubber industry for rolling film. It is composed of two or more rollers, arranged in a certain form, at a certain temperature, the rubber pressed into a certain thickness and surface shape of the film. According to the number of rollers, it can be divided into two rollers calendar, three rollers calendar, four rollers calendar and five roller calendar; According to the arrangement of the roller, it can be divided into "L" type, "T" type, "F" type, "Z" type and "S" type.

Ordinary calendar mainly composed by the roller, rack, roller distance adjustment device, roller temperature adjustment device, gearing, lubrication system and control system. Compared to ordinary calendar, precision calendar requires a device to ensure the accuracy of rolling.

The basic structure of the calendar includes：

a) Roller:

   Roller is the main working parts of calendar, which directly affects the quality and output of the rolled products. Therefore, it must have high working surface hardness, wear resistance, sufficient rigidity and hardness, good thermal conductivity, large heat transfer area and high processing precision.

b) Roller bearings

   There are two kinds of roller bearings: sliding bearings and rolling bearings. Due to the simple structure, easy manufacturing, easy to obtain materials, sliding bearings have been widely used.

c) Rack

   The structure of the rack varies depending on the number of rollers and the type of arrangement. Rack materials are generally used high strength, good seismic performance gray cast iron, occasionally cast steel or ductile iron.

d) Roll distance adjustment device

   Depending on the application, the roll distance adjustment range is generally between 0.1 and 10 mm, and the special purpose calendar can reach 30 mm. The distance device is installed in the left and right of racks and connected to the roller bearing, which adjust the operation to be flexible, convenient, accurate and reliable.

One example of a three roller calendar is reported in **Error! Reference source not found.**.

Figure 4. 2 - three rollers calendar

Principle of Calendar：

The working principle of the calendar is roughly the same as that of the open mill. When the rubber material reaches a certain temperature and plasticity, it is fed between two oppositely rotating rollers, the rubber material is pulled into the rollers under the action of the frictional force, and as the roll cross section becomes smaller. Strong extrusion makes the rubber material molding to film[13]. Usually many calendaring processes require the mating rollers to work at a certain speed ratio, to further mixing and increase the plasticity, and finally through the minimum roll distance, rubber material was rolled into a certain thickness and width of the film. In addition to pressing the rubber into the film, some of the processes also need press material into a certain pattern and shape, and the need for multi-layer film together.

4.3.3 - Cutting machine

In industrial production, the cutting machine is very versatile. Its function is mainly the use of forming mold knife, with the help of the movement of the machine pressure in the mold knife, through the punching action to get the sheet or semi-finished products. It is suitable for foam, textiles, leather, rubber and other non-metallic materials. Hydraulic cutting machine is the most common one.

Figure 4. 3 - hydraulic cutting machine

4.3.4 - Flat vulcanizing machine

Flat vulcanizing machine is mainly used for vulcanized flat type rubber compound, belonging to hydraulic machinery; the main function of flat vulcanizing machine is to provide the required pressure and temperature for vulcanization. The pressure is generated by the hydraulic system through the hydraulic cylinder and the temperature is provided by the heating medium.

Figure 4. 4 - Flat vulcanizing machine

Working principle:

During the flat vulcanizing machine work, the hot plate causes the rubber to heat up and crosslink the rubber molecules, the structure from the linear structure into a reticular structure, which is available with a certain physical and mechanical properties of the product, while the rubber is heated and begins to become soft, and the moisture and volatile substances in the compound are gasified. The hydraulic cylinder is given sufficient pressure to fill the mold and limit the formation of the bubbles. In addition, to give enough pressure to prevent the mold from the seam surface overflow, pattern missing plastic, pores and other sponge phenomenon.

Work process:

After the semi-finished product without vulcanization is loaded into the model, the model is placed in the gap between the two hot plates. And then adding hydraulic medium (oil or water) to the hydraulic cylinder, the plunger will push the active platform and hot plate up or down movement, and promote the movable plate compression mold or products. During this process, heating is applied to the plate so that the mold (or product) obtains the pressure and the temperature required for the vulcanization process. After a period of time (vulcanization period), the product is ended, the hydraulic medium is removed, and the plunger can be removed due to its own weight (or the hydraulic pressure of the double acting cylinder), so that to get the suitable cross-linked product.

4.4 - Advantages and drawbacks

At present, rubber molding process technology has been developed more mature, and widely used in the industrial production of soles. Its advantage is very obvious, by using a series of machinery, formed a complete production line, greatly improving the production efficiency of the footwear industry, and to improve the accuracy of mechanized production, so as to ensure the quality of products, and reduce the defect elimination rate, it will help to reduce production costs. In addition, large-scale mechanized production also reduced the labor force.

However, the current rubber molding process also has many problems, such as the material added entirely rely on manual, a little bit wrong proportion can lead to quality unqualified products. In addition, the control of time and temperature also needs experience accumulation; otherwise it is easy to fail. Moreover, some issues arise from the large variety of chemicals used in these processes, some of which are known to cause toxicological and eco-toxicological concern.

CHAPTER 5

SEPARATION OF RECYCLED RUBBER FROM FOOTWEAR

5.1 - End-of-life scenarios for footwear

For shoes at end-of-life, four approaches are currently considered which include: landfill, incineration, reuse and recycling. The alternatives are schematically summarized in **Error! Reference source not found.**.Different approaches have different requirements for resource utilization, environmental impact, and economic input that have to be considered.

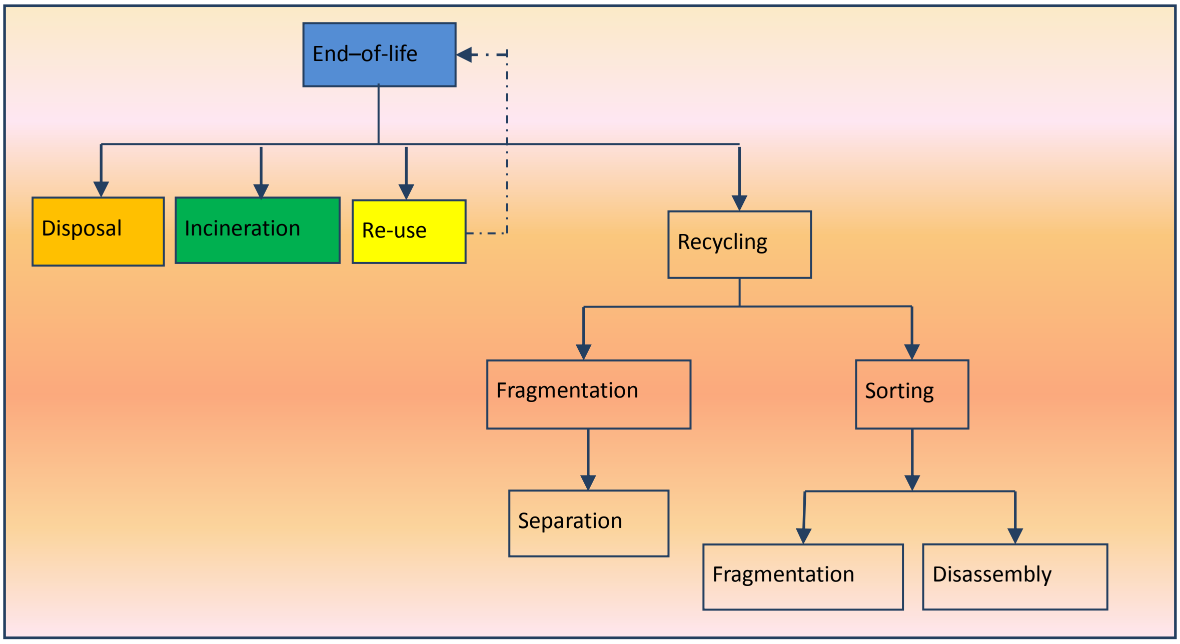


Figure 5. 1 - End-of-life scenarios for footwear

Disposal means that the end-of-life shoes will be sent to landfill. Until 20 years ago, landfill has been the main approach to deal with the end-of-life shoes. However, it has obvious drawbacks, such as pollutions, waste of resources, increases landfill area and so on. So, in last years, incineration is considered as an effective approach to deal with the drawbacks of landfill, but it still releases polluting emissions. Reuse means that end-of-life shoes can be used again, for instance in developing countries. This approach is significant because not only deals with the end-of-life shoes but also because it improves poor people's life conditions. Many organisations support this scheme such as Salvation Army Trading Company Ltd. and Oxfam in the UK. However, there are also some problems for it; some of the shoes cannot be reused again due to their poor conditions and with the economic development of nations, the demand for second hand shoes may decreases[14].

According to those problems, recycling seems to be the best option for end-of-life shoes. About the reuse of waste shoes, the famous footwear manufacturer Nike, play a very important role around all over the world. In the early 90s of last century, Nike carry out the end-of-life shoe recycling program, they encourage consumers to bring the unwanted shoes back to the store, these shoes were recovery, and then broken and processed in one of two central recycling plants – in USA or in Belgium. After the recovery of Nike shoes, each pair of shoes was wrecked into three pieces - rubber outsole, foam insole and upper fiber. These slices were sent to a machine for grinding, and then the triturate was purified; alternatively, the whole shoes were grinded into powder and then separated in streams of products to be processed into materials for many uses. After the dismantling process, these shoes are typically converted into three categories of high-quality wear-resistant materials. One is rubber particles, called Nike Grind (rubber), made of shoes outsole which can be used for plastic runway, gymnasium ground and other sports ground or even new Nike products; the second is the plastic foam, called Nike Foam made of shoes insole, which can be used as a carpet of outdoor basketball and tennis courts; the last one is the textile, called Nike Fluff, which is made of wear-resistant fibers, useful for Cushion, in indoor plastic stadium and wood floor[15]. However, this program just aims at sport shoes. Therefore, a more generic recycle approach is needed to deal with various types of end-of-life shoes.

5.2 - Separation process of footwear rubber

The structure of shoes is quite complex owing to the various components assembled, including vamp, sock liner, insole, outsole and so on. Different materials are used in different parts and different construction techniques are adopted. So, recycling process must separate those materials as efficiently as possible and various technological machines were designed for this scope. Generally, the separation process of end-of-life shoes involves shredding or granulation, which means reduce the material size to get fragments and prepare for the next processes. Then, the fragments are sent to the separation machines to separate into different materials, based on the different physical properties, such as density, shape, and size of materials. However, this process is just effective for plastic and metal, since they have obvious different properties. For rubber and other materials the separation is more difficult because they usually have similar properties. Therefore, other technological processes were designed and commercially proposed. For end-of-life footwear products, the main recycling technologies fall into these categories: shredding and granulation technology; air-based separation devices; magnetic and eddy current separations, electrostatic separation devices, advanced sensors, etc..

During the process, there are three main steps, these are: (i) sorting, (ii) metal removal, and (iii) material separation. The figure summarise the main stages involved in the recycling of end-of-life shoes.

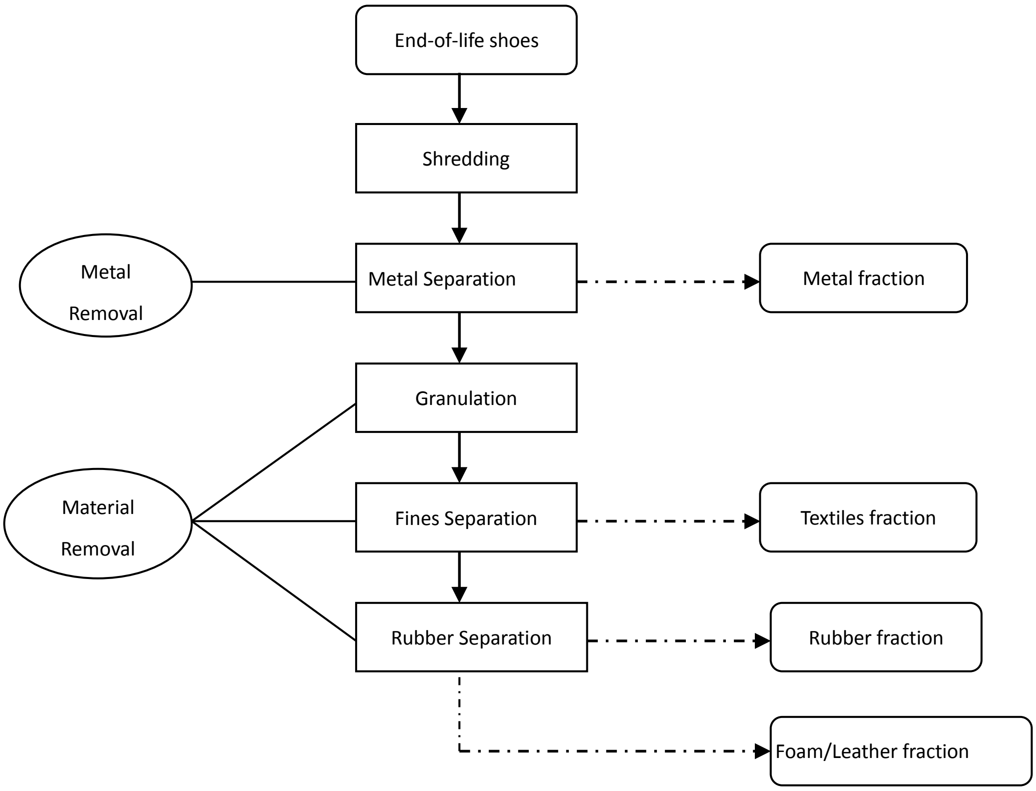


Figure 5. 2 - Scheme for recycling end-of-life shoes.

5.2.1 - Sorting

Sorting refers to the classification of end-of-life shoes according to different types, such as sports shoes, leather shoes, casual shoes and so on. Different types of shoes have the different types of materials, so they are based on different recovery methods. For example, sports shoes have high content of foam; leather shoes have high content of leather, so that different types of shoes should be recycled separately.

5.2.2 - Metal removal

At present, metal fittings are used in footwear products. So, metal removal is an important process for material recovery. There are some different options for the removal of the metallic parts in end-of-life shoes. The first one is manual recovery. Shoes need to be pre-shredded and remove the metal parts by manual sorting. However, manual sorting means consuming a lot of workforce and increase the labor cost. So, it is not an economical sustainable way for industrial recycling. The second option is mechanical separation. It separates the metal parts by using specialist metallic separation equipment, such as magnetic and eddy current. The end-of-life shoes are pre-shredded into small pieces so that the metal parts are exposed and metallic separation equipment can remove it easily. In this way, not only increased metal recovery efficiency, but also reduce labor costs.

Usually, the end-of-life shoes are shredded to 20-30mm so that it is easier to recover the metal parts. Shoes contain not only ferrous metals but also non-ferrous metals. So, after magnetic separation, there are still some non-ferrous metals left. Therefore, a subsequent separation stage is needed to remove the non-magnetic metal parts. In this case, the eddy current separator is used. Eddy current separator uses a powerful magnetic field to separate non-ferrous metals after all ferrous metals have been removed previously by some arrangement of magnets. The device makes use of eddy currents to effect the separation. However, since non-ferrous metals are present in small quantities in end-of-life shoes, eddy current separators are not the most economically way. In order to solve this problem, there are also some technologies that can remove the metal parts without using magnetic separators. Hydrocyclone is a new idea to remove the metallic parts from shredded end-of-life shoes. It is a dense media separator which using a simple sink-float liquid based density separation process which can separate metals form other materials[16]. For example, magnetite powder is dissolved in water to produce a liquid medium having a density of 2.00 g/ml. Metals with density higher than 2.00 g/mlwill sink. All other end-of-life shoes materials have density < 2.00 g/ml and thus they will float.

However, Due to the metal contamination in the recovery process will significantly reduce the recovery of other materials, and there is currently no obvious solution to this problem. Therefore, reducing or eliminating the use of metallic materials in the design stage of footwear production can solve more easily this problem.

5.2.3 - Material separation

Once the metal parts have been removed by the metallic separation equipment, an additional grinding is required to further reduce the size of the materials to meet the requirements of air separation stages. In the actual recycling industry of end-of-life shoes, the size range of end-of-life shoes materials is grinding into 3-6mm. Since in this size range, there are fewer materials particles will interconnect each other, so that can improve recovery purity. There are many different types of granulator, which can provide different particle sizes, so as to adapt to different industrial uses.

After materials are grinded into smaller particles, different materials need to be separated into district fractions. The main technology that is used in this process is the air-based separator. These equipments rely mainly on the difference in terminal velocity of particles between different materials. Usually, the terminal velocity of the particle depends on its size and weight. So, both those two parameters will affect the separation of particles from end-of-life shoes. Firstly, the size of different materials tends to be different. For example, textiles need to be grinded into fine particles which have a low terminal velocity so that they can be separated from other materials. Secondly, different materials have a different density, so that they have different terminal velocities of particles. For example, rubber has a higher density than foam and it can be separated easily.

According to those principles, the air-based separators can recover four kinds of materials which are the most common used in shoes products. It includes: leather, rubber, foam and textiles. The separation process of air-based separator has two stages. First, remove the textiles fine particles by using air-cascade separator due to the different size. Then, a vibrating air-table is used to provide final separation of rubber from other materials.

Stage 1: textile fines separation

The grinded footwear material particles are fed into the air-cascade separator from the top and the particles falls down through a number of shelves. Air is blown into the machine during this process creating small air vortices in the separator. Since the textile fines have a low terminal velocity, they are blown free of the other material particles. After the mixed material particles have passed all the shelves, they can be gathered at the bottom of the separator. In the mixture, the textiles basically have been removed, leaving only leather, foam, and rubber.

Stage 2: rubber separation

The second stage of separation process is to recover rubber particles from the leather and foam. The machine that it is used a vibrating air-table; the air table uses air and vibration to separate rubber particles from other material due to different density. The heavier rubber particles will stay on the table and moves up to the collector and the lighter materials will stratify on top and slides down the table due to the vibration.

5.3 - Main equipment used in separation process

At present, the footwear separation process has achieved industrial production. A series of machines are available for use in the separation process of footwear rubber.

5.3.1 - Preliminary shredder

Before removing the metal, it is necessary to reduce the size of the footwear to modify different material diameters to homogenize the material. The primary shredder is equipped with a series of circular blades, fixed on two opposite horizontal axes of rotation, rotating at a speed of about 50-200 rounds per minute and cutting materials across the entire blade **(Figure 5.3)**. The size of the processed materials can vary from 3 to 30 centimeters depending on the distance between the shaft and the cutter.

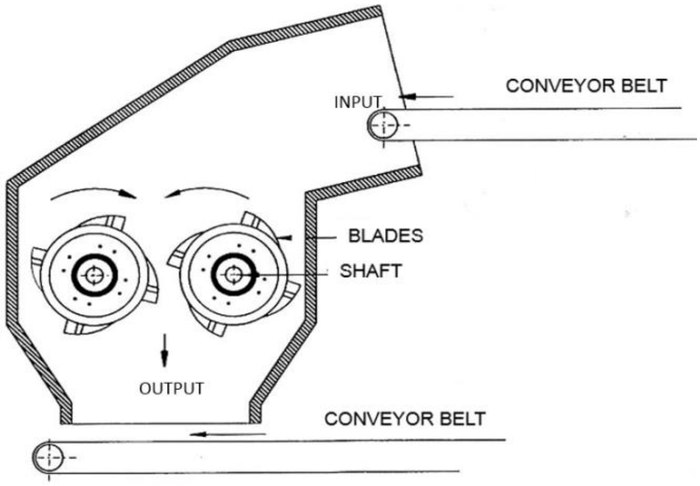


Figure 5. 3 - Preliminary shredder

5.3.2 - Drum separator

Magnetic separation is the most common technique for separating the ferrous material from untreated or previously shredded materials. The separation efficiency can exceed 95%. The most commonly used magnetic separation equipment is the drum separator.

It consists of a cogged conveyor belt and a magnetic pulley that traps the ferrous material until a non-magnetized part. In order to achieve a higher purity of the ferrous material, a double drum magnetic separator can be used **(Figure 5.4)**: the first drum holds the scrap ferrous material and moves them into the middle downflow conveyor belt, where the smaller and closer drum is located, the rotate in the opposite direction to the material flow to avoid dragging.

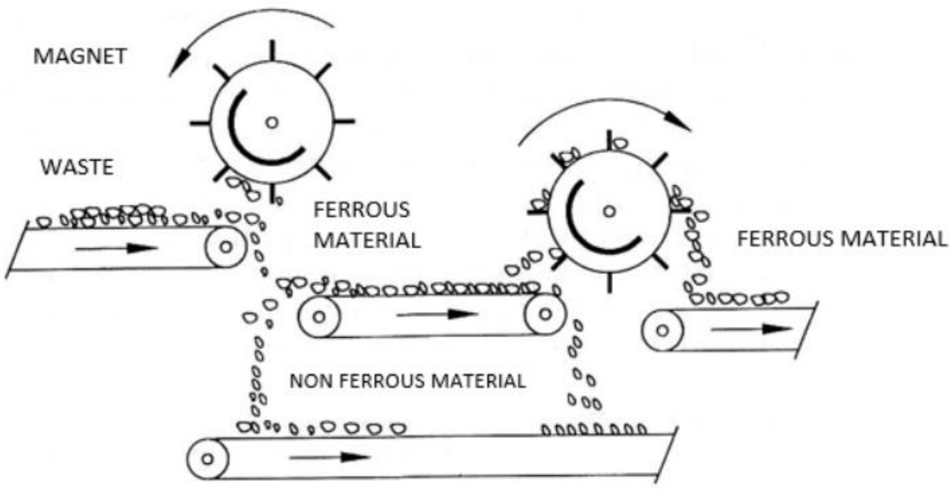


Figure 5. 4 - Durm separator

5.3.3 - Air classifier

Gravity separation is based on waste density and aerodynamic drag. The previous scrap was subdivided into two parts: the light part consisted mainly of textile, leather, foam, and the heavy part only left rubber. The most commonly used system is the air classifier.

It consists of a pipe in which the materials are exposed to the action of a reverse flow of air to lift the light particles upward while heavy material falls on the bottom of the pipe.

To create turbulence in the air, an internal baffle can be installed to force the particles into the shell and break it into smaller pieces. In order to improve the separation of particles characterized by similar settling velocities, a serrated pipe sorter was introduced to change the air velocity in the pipe. The efficiency of the process is related to the speed of the air stream, the size and shape of the pipe cross-section, and the input materials flow rate. Downstream of the pipe, a cyclone is usually placed to separate light-weight solids from the gas stream **(Figure 5.5).**

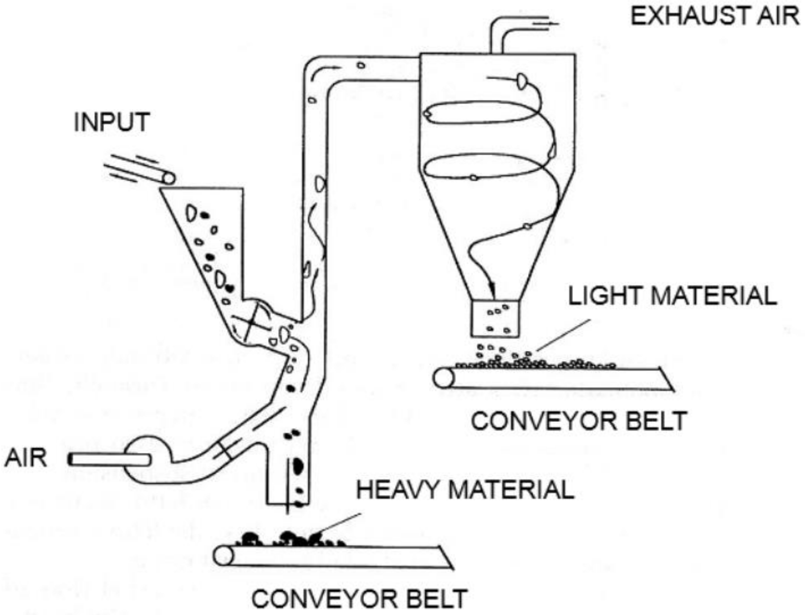


Figure 5. 5 - Air classifier

5.4 - Summary

Through the introduction of various treatment methods for end-of-life shoes, it is found that recycling is the most environmentally friendly and economical way to deal with. In the recycling process of end-of-life shoes, through a series of processing we can attain recycled rubber particles and other recycled materials. These recycled materials can be re-applied to the production of other products which help to reduce production costs and save resources.

CHAPTER 6

GRINDING AND RECLAIMING OF RECYCLED RUBBER

6.1 - Grinding

The recycled rubber from end-of-life shoes has already cut into small particles through the separation process. Granulated rubber and chemical additives are often passed through a smooth roll mill multiple times at a specific temperature and friction ratio to get the size of the powder needed. Grinding is roughly divided into three methods: chemical method, cryogenic method and ambient method. The cost of chemical method is high and it is difficult to apply to large-scale production. Therefore, cryogenic method and ambient method are used more in industrial production. Cryogenic is a method to prepare grinding powder by freezing the rubber to below the glass transition temperature and then grinding it. The cost of cryogenic method is high, so it is used mainly for high performance products. Ambient method generally refers to the crushing of recycled rubber by mechanical action at normal temperature or slightly higher than ambient temperature, so as to make the grinding powder. The grinding powder prepared by ambient method has a large surface area, which is beneficial in activating modifications and further improve its utilization value[17].

Table 6. 1 - Rubber powder classification and use

Classification	size/mm	mesh	Main application	
			Rubber industry	Non-rubber industry
Rubber blocks	30-10			Pavement
Rubber particles	5-2	4-10		Stadium tracks
Coarse powder	1.5-0.5	12-30	Reclaimed rubber	Carpet
Fine powder	0.5-0.0.075	30-200	Rubber products	Modified asphalt
Superfine powder	below 0.075	over 200	Military products	Coatings

Representative classification in term of particle size and use of recycled rubber powder obtained by these methods are summarized in

.

The grinding powder is widely used. It can be surface-activated to replace part of the raw rubber used in the manufacture of tires, shoes and other rubber products, can also be widely used in highway construction and housing construction. Fine grinding powder can also be used for anti-corrosion coatings, ground for commercial and industrial buildings, stadiums or stadium tracks, cushions and so on. For example, grinding powder contains antioxidants, so modified asphalt pavement made of grinding powder can significantly slow down the aging of the road and make the road flexible and reduce the noise. The wear resistance, water resistance and abrasion resistance of this kind of pavement are 2-3 times as much as that of the ordinary pavement, which also reduce the road maintenance costs[18].

6.2 - Reclaiming

Reclaimed rubber refers to the renewable rubber that after crushing, heating, mechanical processing and other physical and chemical processes, which can be blended, processed, and vulcanized again. The so-called devulcanization, is the process that use of physical, chemical and biological means to break the sulfur-to-sulfur bonds and some sulfur-carbon bonds while importantly leaving intact the molecular carbon-carbon backbone created by the vulcanization process. This transforms the rubber particles back into a reactive polymer that when properly mixed with virgin material can replace large quantities of virgin stock while producing comparable physical properties[19].

There are three typical reclaiming technologies and principles of the recycled rubber: physical, chemical, and biological technology. Physical technology is the use of external energy, such as microwave, ultrasonic, far-infrared ray, and so on, so that the three-dimensional network of cross-linked rubber broken to form a liquidity of reclaimed rubber. Chemical technology is the use of chemical additives, such as organic disulfides, mercaptans, alkali metals, etc., at a certain temperature by means of mechanical directional catalytic cracking of rubber cross-linking to achieve the purpose of reclaiming. Biological technology aims to break the sulfur crosslinking bond of rubber broken or to remove sulfur atoms under the action of microorganisms, so that the waste rubber can be re-processed.

Table 6. 2 - Characteristics of different technologies of devulcanization

Technology	***Basis of Processing***
Physical	Microwaves
Physical	Ultrasonic waves
Physical	far-infrared
Chemical	Dynamic de-vulcanization
Biological	Microorganisms

6.3 - Physical Treatment

6.3.1 - Microwawes

Microwave is the method that delivers the recycled rubber powder to the glass or ceramic pipe, by controlling the microwave electromagnetic energy, rapidly warming to 260-350°C, in order to selectively break the S-S bond, C-S bond, while retaining the main chain C-C bond, in order to achieve the purpose of reclaiming[20]. However, the premise of the ideal temperature is that the waste rubber must be enough polar.

Microwave has a strong penetrating power for not too thick materials, and a nearly homogeneous electromagnetic field con be originated by appropriate microwave waveguides so that the selectivity in breaking the chemical S-S bonds should be better.

Moreover, this method does not involve any solvents or chemicals. However, because rubber material is a poor heat conductor, internal hot spots may cause excessive degradation of rubber in not well designed ovens, resulting in decreased performance of reclaimed rubber.

6.3.2 - Ultrasonic wawes

The ultrasonic method is to establish the high frequency stretching vibration of the ultrasonic emission field to generate high energy to selectively break the C-S bond and the S-S bond, so as to achieve the purpose of reclaiming. In 1973, Pelofsky was the first to use ultrasound for rubber recycling[21]. He invented a device that uses ultrasound to degrade rubber in organic solvents. The reactor consists of a single-screw rubber extruder and ultrasonic die attachment. A small piece of vulcanized rubber was devulcanized using 50 kHz ultrasonic waves after treatment for 20 min. Ultrasounds determine elongation efforts and high-frequency compression on the molecules, thus causing the breaking of cross-links.

Ultrasound penetration is very strong. However, due to the viscoelastic characteristics of the rubber material, a part of the sound waves will be transmitted, and part of the sound waves will be dissipated in the internal friction due to the excited vibrations between macromolecules and the remaining part will be used for breaking the chemical bonds. Therefore, how to utilize the ultrasonic energy more efficiently and improve the selectivity of ultrasonic desulfurization needs further research.

6.3.3 - Far infrared ray

Far infrared is the method to reclaim waste rubber by the thermal effect which comes from the absorption and reflection of the far-infrared light of rubber. The whole process generally includes the following steps: 1) mix rubber powder, the regenerative agent and softener; 2) feed the mixed material into the desulfurization zone by conveyor belt; 3) the material is heated under the combined action of far infrared and screw, and the desulfurization is finished at high temperature of 240~250°C; 4) after the desulfurization is finished, the cooling screw is used to cool down the materials;5) this is transferred to the post-process, such as finishing and packaging.

In view of the rubber absorption spectrum and the far-infrared wavelengths are closer, the efficiency of far infrared conversion into heat is high. The use of far-infrared desulfurization technology can make the rubber inside and outside at the same temperature, so that neither temperature difference nor thermal hysteresis can be observed. This technology has the advantages of convenient operation, significant energy saving and no pollution.

6.4 - Chemical treatment

Chemical treatment is carried out mainly by adding chemical compounds; the compounds and S-S bond interact with each other, reduce the energy of cross-linking bonds formed in the vulcanization process, and therefore activate the cross-linking bond to breaking. The key of the chemical treatment lies in the selection of chemical compounds, and how the compounds infiltrate into the interior of the particles. The traditional method uses water vapor, oil and other media, through the principle of simultaneous reaction and permeation, to achieve the dissociation of the crosslink. This method has good desulfurization effect and low cost, so it is widely used in the industry, but suffers from toxicological problems associated to the exposure to toxic chemicals in vapor and solid forms.

6.4.1 - Oil method

Oil method, also known as disk method, was invented by Muraoka Nobuhito in Japan in 1940s. The method comprises the following steps: loading the rubber particles mixed with the compounds into an iron plate, then placing the iron plate on an iron frame equipped with a pulley, pushing into a horizontal desulfurization tank for heating; the desulfurizing temperature is generally controlled at 158-170 °C, the pressure is 0.5 ~ 0.7 MPa, usually in about 10 hours.

As the oil method is static desulfurization, rubber material desulfurization is uneven, and the temperature and pressure cannot reach the condition of desulfurization, so the quality of reclaimed rubber is poor. This process has been practically eliminated.

6.4.2 - Water -oil method

Researchers in the former Soviet Union invented the oil-water method in 1942, also known as neutral method. The desulfurization stage of this method is carried out in a vertical agitated desulfurization tank. The tank is heated by steam through the interlayer. Temperature control at 180 ~ 190 °C, the ratio of rubber particles and water is 1: 2; desulfurization time is about 4 h. The quality of reclaimed rubber produced by the water-oil method is better than that of the oil method, but due to the large amount of wastewater produced by this process, this process has been eliminated.

6.4.3 - Dynamic method

Dynamic desulfurization tank method appeared in 1970s, which can be regarded as a comprehensive improvement of the oil method and water-oil method, in essence, is the fundamentally improvement of oil method, the temperature and pressure is higher than the oil method, but also in the dynamic desulfurization. Dynamic method with high temperature, fast heating, uniform mixing of material, high product quality, no waste water pollution, which is the most widely used method at present.

However, dynamic method can cause serious flue gas pollution when the desulfurization rubber particles are released from the tank. In order to solve this problem, recently, people have changed the tank into a continuous pipeline and carried out continuous desulfurization reaction and cooling by double screw propulsion. However, because of the severe thermal oxidative degradation of rubber particles, the quality of the reclaimed rubber is affected.

6.5 - Biological treatment

In recent years, some scholars have proposed the reclaiming of waste rubber by the mechanism of the conversion of combined sulfur during microbial metabolism. In this method, the waste rubber is crushed to a certain degree of fineness and then placed in a solution containing microorganisms to make biochemical reactions in the air. Under the action of microorganisms, the sulfur bonds on the surface of the rubber particles are broken to show reclaimed rubber properties, the thickness of the surface layer is about a few microns, but the inside of the colloid is still in a cross-linked rubber state[22].

One of the obstacles to the microbial treatment is that some rubber additives are toxic to microorganisms and cause the microorganisms die within a short period of time so that the rubber cannot be effectively desulfurized. Therefore, the key point of this method is to cultivate bacteria with antibiotic resistance or to eliminate the toxicity of waste rubber. On the other hand, the period of the movement and diffusion cycle of microorganisms to the interior of the particle is pretty long, so improve the efficiency of this method is also very important.

6.6 - New technologies

6.6.1 - Supercritical CO_2

Supercritical fluid is a kind of fluid which is formed when the substance is above its critical temperature and critical pressure. In this state, the physical and chemical properties are between gas and liquid, and have the advantages of both. Supercritical CO2 technology is the use of excellent solubility and mass transfer ability of supercritical fluid, in a certain temperature and pressure range (Error! Reference source not found.), to swell vulcanized rubber, while the desulfurizer penetrates and evenly dispersed in the cross-linked network[23]. The desulfurization agent dispersed between the cross-linked networks participates in the desulfurization reaction to reclaim the waste rubber.

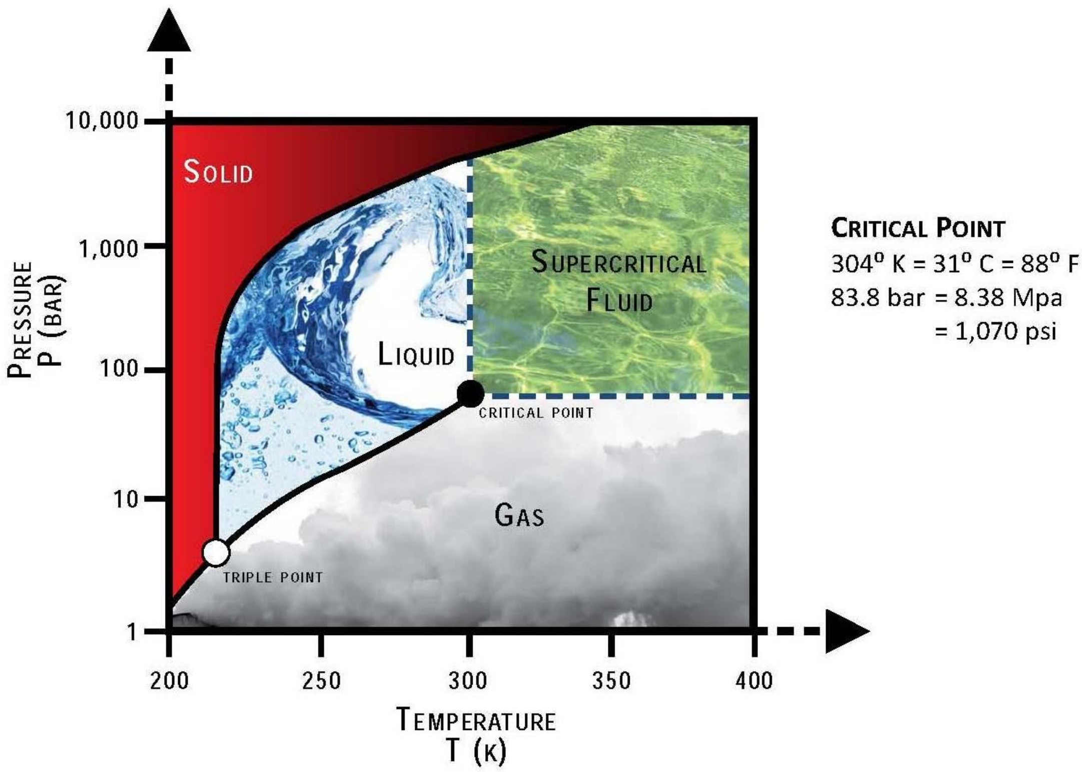


Figure 6. 1 - Phase diagram of carbon dioxide (CO_2)

Supercritical CO_2 has low critical temperature (31.1°C) and critical pressure(8.38MPa). In addition to its general characteristics of supercritical fluid, it also has the advantages to be non-toxic, flame retardant, chemically inert, mild critical point, cheap and easy to dissolve, along with a strong dissolving ability. Besides, it is cheap and can have high purity. The SC process is simple, and the operation process is easy to realize under automatic control. Therefore, supercritical CO_2 is one of the most used supercritical fluids and have found special attention in the field of wasted rubber reclaiming.

6.6.2 - Mechano-chemistry method

Mechano-chemical method refers to the mechanical stress-induced chemical reaction and material structure changes, the active radicals produced by the reaction with the presence of chemical regeneration agent in the matrix to achieve the purpose of reclaiming.

The mechanical stress must reach or exceed the bond energy of S-S bond and C-S bond to generate free radicals. At present, the desulfurization technology developed by the principle of mechano-chemical has attracted extensive attention.

Jana and Da[24] use the principle of mechano-chemical, mixing the waste rubber in a two-roll mill at 110°C in 10 minutes, then add the desulfurization agent diphenyl disulfide and the operating oil to achieve the effect, the reclaiming products have good performance and mechanical properties. The performance of reclaiming rubber can reach up to 87% of the raw rubber.

CHAPTER 7

SHOES FROM A SIMPLIFIED LIFE CYCLE PERSPECTIVE

The life cycle analysis carried out in this thesis is limited to some specific objectives, mainly centered on the following three aspects:

a) evaluate the impact of raw materials with special emphasis on rubber components,
b) obtain an approximate value of the impact of shoes production with specific attention on rubber components
c) evaluate the impact of different end-of-life treatments of the rubber component in comparison with the other raw materials

The analysis was mainly restricted to rubber, and in particular to natural rubber, because this compound is used in large amount in several models of shoes and the recycling of this material has been significantly investigated, so that alternative are present on the market, therefore allowing to be compared in term of sustainability.

However, it is important to notice the production stage is only a part of the whole supply chains of shoe companies and this involve “a network of suppliers, distributors and consumers and includes the transport that occurs in the group”. Therefore, a more deep evaluation would be necessary at the level of shoe industry, taking into account that globalization has resulted in a supply chain in which processes might be spread all over the world.[25] That means a shoe bought in a nation might have been designed in one country and produced in another, while all materials have been imported from a third. Therefore, since the life cycle of shoes will affect the environment on both a local, national and global scale, it will be necessary to understand the processes involved and the origin of all the components used in the production. All these data are sensitive inside industries and not available to public, therefore, we have decide to focus our attention on the available data on raw material, process technology and end-of-life treatments for which data are in part available.

This section will describe the life cycle of shoes based on three different models of Italian shoes whose raw material composition was established by specific chemical analyses.

7.1 - Shoe composition and environmental impact of raw materials

Even though several attempts has been made in the shoes industry to improve efficiency regarding energy and material use, along with to reduce any harmful substances, the raised consumption of shoes is counteracting these improvements.[26] So far, the focus was set on reducing chemicals used in shoes and preventing emissions from the production phase, but, more recently, the sustainability of resources and the waste generated from use of shoes has been acknowledged as a significant problem. This means to not only consider waste from raw material extraction and shoe production, but also final waste in form of used shoes. Therefore, a full or partial life cycle analysis (LCA) can provide to shoe industries important information on the identification of environmental concerns in raw material, energy use and production processes to devise environmental management strategies to make more sustainable products.[27]

Shoes are often complex products with many materials and parts involved.[28] This means that appropriate design and material selection can have big influence on the impact of the final product. Also the amount of energy and the type of energy source (renewable or not renewable) can generate different environmental impact,[29] so that a full analysis must contain at best this information.

Moreover, as concern the raw materials, some shoe companies have their own production facilities, and they can control the environmental standards to a greater extent.[30] More commonly, however, the material is coming from the free market and real origin of materials used and related environmental impact is often unclear, in particular, as concern the generated wastes and their treatment processes.[31] In some countries, landfill might be dominating whereas in others incineration is more common,[32] and very uncommon are the recycling approaches. Some countries with lack of proper waste management strategies might have production facilities which release waste straight into water ecosystems without any treatment.[33]

Owing to these uncertainty, our analysis was started from the composition of three representative shoes (named as SHA, SHB and SHC, respectively) to evaluate the relative importance of the main components used, and we have considered as a mean representative composition of the wide variety of shoes available.

In **Error! Reference source not found.** the results of these analyses are collected in terms of percentage of different materials found.

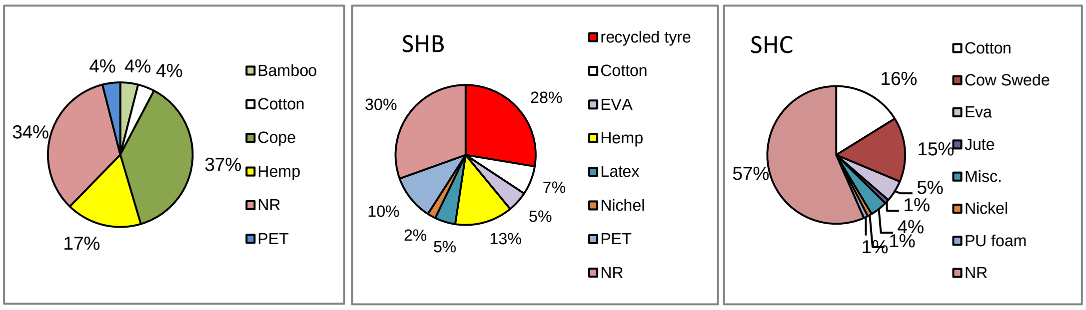


Figure 7. 1 – Distribution of raw materials found in the shoes SHA, SHB and SHC.

It can be observed from **Error! Reference source not found.** that rubber materials range from 40% to 70%, constituting the more relevant raw material component. In one case (shoe SHB) a significant amount of recycled rubber from tire (in red) was present, along with some virgin rubber (NR) and PET. Significant were also the content of natural fibers (hemp, jute, and cotton) and leather (as cope or cow Swede).

The distribution of typical components can be found with reference to **Error! Reference source not found.**, were a representative schematic figure of shoe is reported.

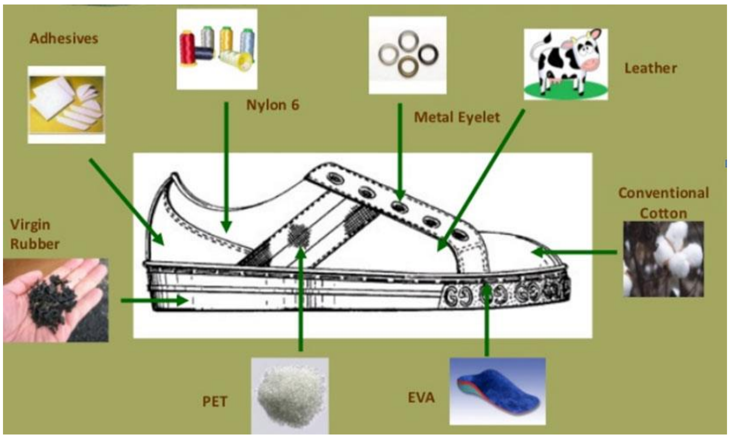


Figure 7. 2 – Main component materials of a shoe

From literature date the impact of the main components were estimated as GWP in terms of kilogram of carbon dioxide produced for le production of 1 kg of single pure material. The results are summarized in **Error! Reference source not found.**.

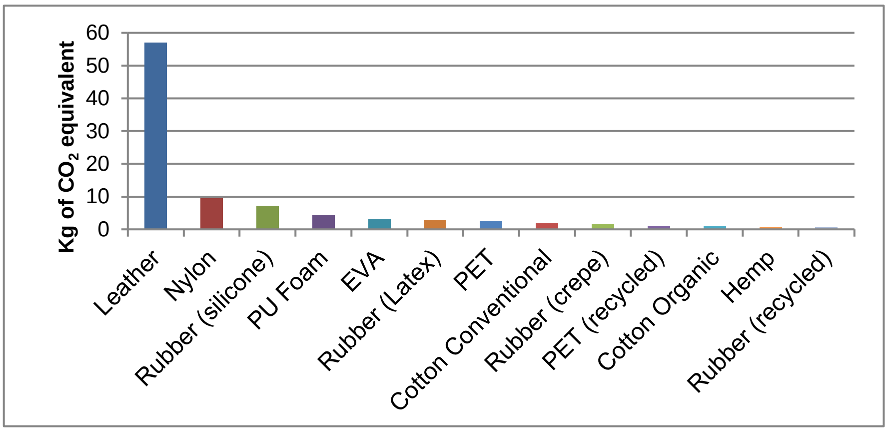


Figure 7. 3 – GWP of the different materials present in examined shoes

These data indicate the relevant impact of leather and in minor amount of some synthetic materials (i.e. nylon, PU foams, silicone rubber, and EVA), whereas natural rubber and recycled polymers (i.e. recycled PET and recycled rubber) have the minimum impact. The GWP is, however, only one of the impact category for which is useful to take information, therefore we decide to extend the analysis to 9 other selected environmental impact categories. These were: Acidification Potential (as kg of SO_2 eq.); Eutrophication Potential (as kg PO_4^{3-} eq.); Freshwater Toxicity Potential, Terrestrial Toxicity Potential, Marine

Aquatic Toxicity Potential, Human Toxicity Potential (all evaluated as kg DCB eq.); Ozone Layer Depletion Potential (as kg R-11 eq.); Photochemical Ozone Creation <Potential (as kg C_2H_6 eq.); and Radioactive Radiation (as DALY) For these evaluation the 2008 peer reviewed data were adopted, following the CML 2001 Methodology using the Simapro program.

In **Error! Reference source not found.** are collected as a bar graph the normalized results of the ten environmental impact categories examined, compared for the tree different shoes taken in consideration.

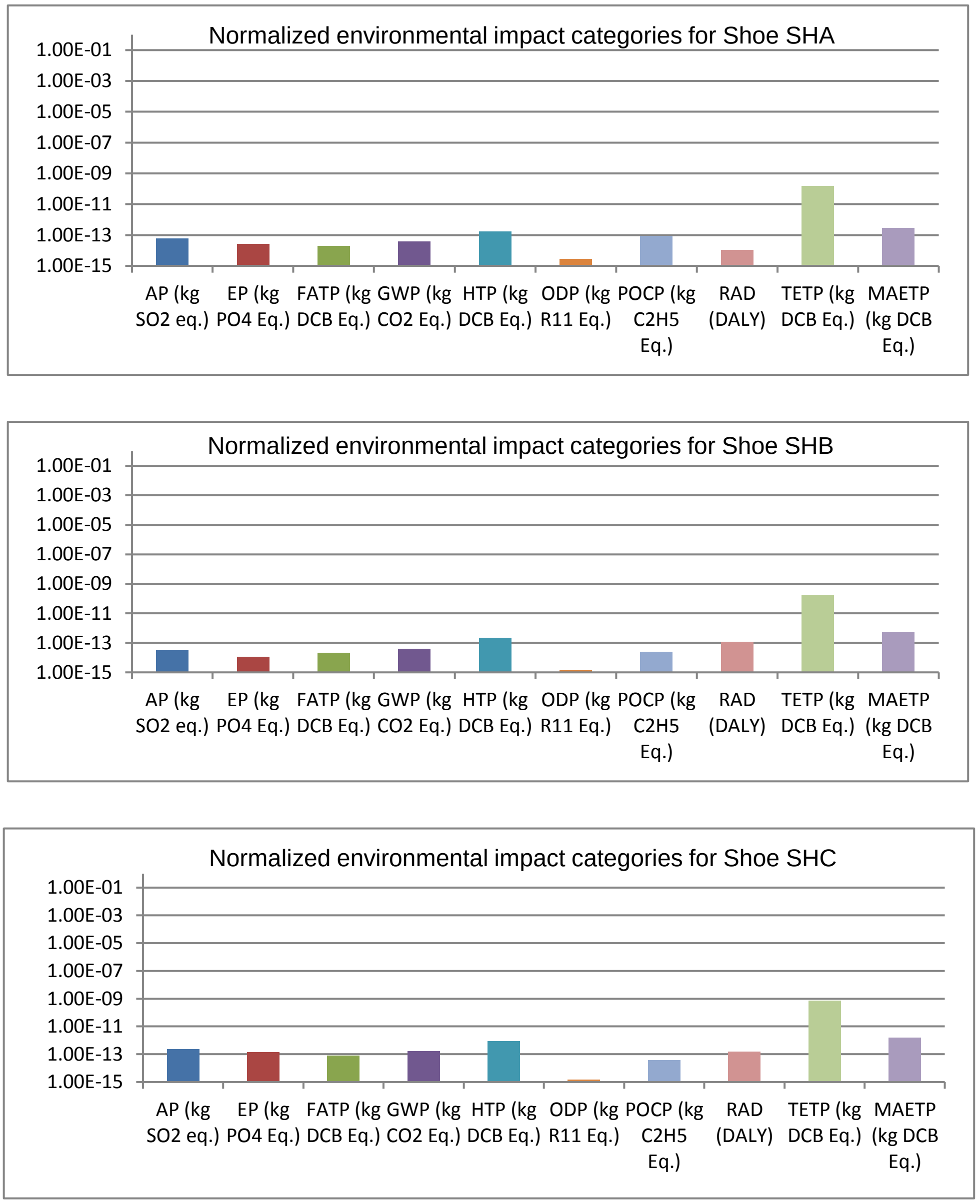


Figure 7. 4 – Normalized environmental impact categories for shoes SHA, SHB, SHC

The data are reported in logarithmic form, so that even limited differences indicate significant impact change. So, for instance, shoe SHC has all categories of impact higher than shoe SHA and SHB with TETP and MAETP impacts 5 times higher.

It is evident that the main impacts are related in all case the categories GWP, HTP, TETP and MAETP, with the last two more relevant. The main difference between shoes SHC and SHA is the abundance of leather in the first and of vegetable fibers in the second.

In order to evaluate the relative contribution of raw material to the final specific category of impact, the shoe production/manufacturing process and other system process (i.e. transportation, packaging and end-of-life) were determined. The relative importance was found to be more than 80% for raw materials, around 15% for the production and other system processes and less than 5%for the end-of life by incineration. Only for AP and EP the system processes was found to have a relevant contribution (up to 50%); EP and GWP are less affected and POCP and MAETP show minimal contribution, whereas the contribution to other impact categories is irrelevant.

For this part of our analysis the standard used in a medium factory in the north of Italy were adopted; therefore, the data cannot be extended to other situations, where the control of production and end-of life treatment are less organized. This explains why the impact of the production and system processes appears so limited for all three types of shoes investigated.

Even if the conclusion cannot be considered fully general, these combined results evidence the importance of the selection of raw materials in reducing the environmental impact of shoes. In particular, natural materials play a relevant role in the reduction as can be seen from the difference between shoes SHC compared with SHB and SHA. But there is big difference in contribution between vegetable and animal components and the first must be strongly preferred. Also synthetic polymers play a significant role in reduction of the impact if associated to the possibility to reuse the end-of-life recycled materials (i.e. comparing shoe SHC with SHB, where a ¼ of recycled matter is present).

This further confirms that our selection to focus the attention on rubber processing and end-of-life can be a significant part of the reduction of environmental impact of these goods, owing the possibility to recover materials and not use new natural resources.

7.2 - Impact of Shoe manufacturing

The production of shoes involves many different steps. In the process, shoe parts are often produced separately to be assembled together in a later production stage.[34] When the materials and shoe parts have been ordered, the manufacturing involves processes such as cutting, sewing and lasting (see chapter 4).[35] Finally, the shoes will be packed and prepared for transport to retailers.

As previously mentioned, the dominating part of shoes sold in Italy is produced in Italy and Asia countries. These last countries often have a lack of environmental legislation and even if some regulations exist they are seldom complied. This has become a problem since many chemicals and adhesives used in shoe production may have toxic effects on humans and the environment.[36]

In shoe manufacturing, the waste treatment follows the same principles as for material production since it depends on factories and systems of the area in question. The environmental conditions in shoe factories are often examined by inspectors sent by the shoe companies, which might evaluate the treatment of wastewater as well as use of chemicals and resources.[37]

In order to overcome these uncontrollable data, we decide, as above indicated, to take as reference a medium factory in the north of Italy in order to have consistent data. This choice can explain why the production and system processes appear to have such a limited importance, as above reported.

7.3 - Impact of End-of-life treatment

Even if in our analysis the end-of-life appears to have a limited role compared to raw materials, the relevance of the possibility of reuse or recycle of the material into new shoes is evident from the reduced used of raw materials. Moreover, taken into consideration that some biological component are always present, the alternative to compost the entire or a selected part of the shoes cannot be excluded, as the alternative more simple to simple reuse the shoes again in relative good conditions. The last approach was adopted on large scale by Nike and the results obtained cannot be considered marginal if, as indicated by this company, until 2010 were reused 16 millions of pair of shoes.

A recently proposed detailed waste management option for shoes is reported in **Error! Reference source not found..**[38] Along with waste minimization by design and material improvements, the main alternatives are reuse, recycling, energy recovery, and disposal.

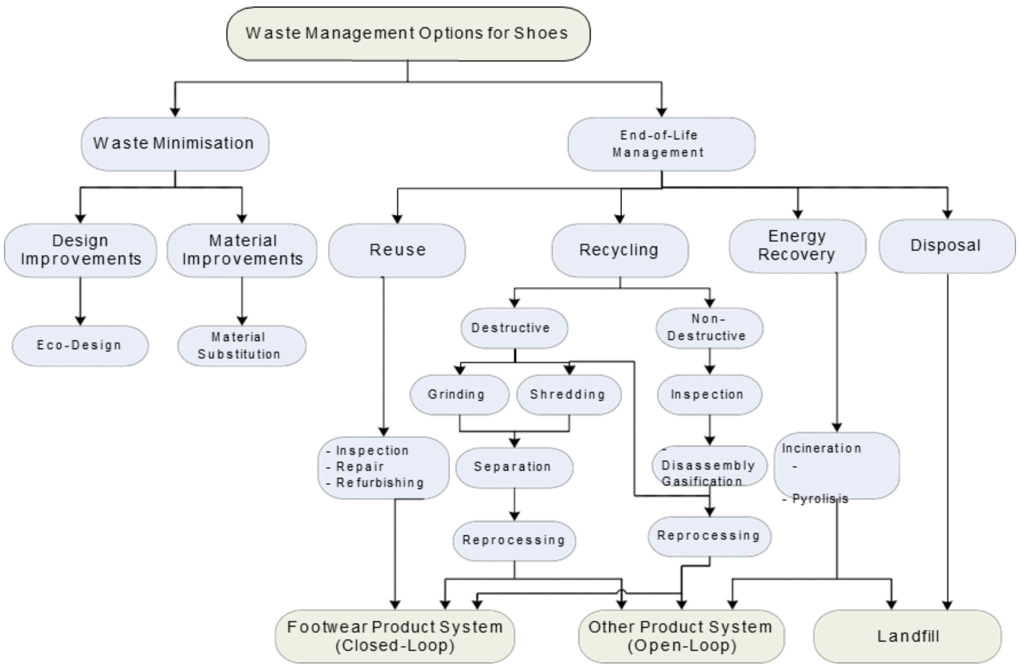


Figure 7. 5 – Waste management options for shoes

For our analysis we decide to compare only four different alternative options of possible end-of-life treatments and to compare them with the landfill impact of shoes. The evaluation of this last impact has been determined independently by some authors and the data are fairly in agreement. The impact category selected was GWP and two other parameters were introduced, the feasibility and the potential. The results of this comparison, in order of reduction of GWP, are reported in **Error! Reference source not found.**.

Table 7. 1 – Impact of four End-of-life options for shoes compared to landfill

	Net GWP (kg CO_2 Eq. pair of shoes)	Feasibility	Potential
Grinding	-1.5	5	1.5
Composting	-0.30	3	2
Reuse	0.17	2	1
Recycling	0.90	1	5

The feasibility to apply the option was estimated from 1 to 5 based on the number and complexity of supply chains, the possibility to take back and the amount of shoes for an economic application. The potential to improve the option was in turn estimated (again from 1 to 5) on the prospect to introduce new value-added technologies or to simplify the supply chain.

It is clear that at present the grinding option appear the more feasible and sustainable approach. It applies easily to the elastomeric part of the shoes using the presently available technology of grinding shoes and separation of rubber and metal components (see chapter 6 for details). The main impact in this technology arises from the energy requirements and the mechanical approach to grinding is at present the most efficient compared with the other available alternatives. The direct use of the material represent the best gain in GWP, but it must be considered that, in order to be introduced as a component into a new shoe, the grinded rubber must be chemically or physically or biologically treated. Therefore, in this direction the net GWP decreases to a value of about

-0.7 to -1.0, again well negative, which evidencing a net gain in GWP if this option is adopted. The grinding technology is somewhat mature and future significant improvements are unpredicted.

Also composting has some potentiality to reduce GWP along with a good feasibility. However, it applies to natural components present in the shoe and contamination of the resulting compost can limit the possible use if the shoes design is not correctly selected. For the future it is expected that improving the natural fraction of the shoe will favor further this option. Moreover, potentially this approach can be combined with an improved desulfurization of the rubber component, making available a better recycled material for new uses, comprising the shoes manufacture.

The reuse of end-of-life shoes has some potentiality for its high feasibility but involve limited but positive GWP impact than landfill. After the reuse, however, the shoes can be again submitted to grinding or composing, so an overall gain can be finally reached by a combination of options.

Surprisingly, by applying the present technology, the recycling of all materials appears the more demanding option as concern the GWP. This arises because non-destructive recycling methods involve the dismantling of shoes to isolate materials for further recycling in order to obtain high grade of quality of recycled materials which can be used in a wider range of applications. Non-destructive methods generally include sorting, inspection, disassembly, and then shredding of separated materials. However, disassembly of shoes is not an easy task due to the large amount of adhesive typically used to join shoe parts together along with stitching techniques. The complex operation to be carried out and the relevant energy to apply is the main reason of this high GWP impact, but this option has great potentiality for the future because better design and more appropriate materials can significantly reduce this negative effect. On the other hand, recycling and product recovery activities for footwear products need to be identified to ensure that landfilling is reduced and hazardous substances do not enter the environment or impact on human health while the economic value of the end-of-life materials, components and products is recovered. Proactive waste management activities such as material substitution will not, in the short term, be able to solve the issues connected to current End-of-Life waste generation. Therefore, only two strategic directions remain potential for the future: a) increase the use of natural fibers and rubber to favor composting, and b) improve the shoes design to favor disassembling in order to recover the maximum amount of materials to be recycled.

CHAPTER 8

SUMMARY

Life-cycle refers to the general theory and engineering related to the life-span of the entire product from the aspects of product design, manufacture, assembly, packaging, transportation, use, disassembly and recovery. The goal is to maximize the comprehensive utilization of resources and the least negative impact on the environment.

Lack of resources, environmental pollution, which are the common problems facing the world today. Sustainable development is an inevitable choice for the development of the world, which requires people to use the basic idea of life cycle to explore how to make rational use of resources and recovery of waste.

For the earth with a population of more than 6 billion, the number of footwear products cannot be ignored. Among them, the rubber as sole material is of particular concern. Direct landfill or incineration of rubber can cause huge pollution and damage to the environment and also it result in waste of resources. In order to meet the requirements of the sustainable development of human society and the greening of the footwear industry, it is necessary to study the recovery of footwear rubber so as to reduce the waste of this natural resource.

The study is focus on rubber, from the extraction of raw materials, production before use to the separation, reclaiming after use, to identify the complete life cycle of rubber products. At present, the recycling process of waste shoes is still in its infancy. We found that the current viable rubber recycling process is: waste shoes - sorting - cutting - dismantling removal (metal attachments, etc.) – material separation - recovery. With this step, at least 87% of the rubber can be recovered.

For reclaiming of rubber, there are many different treatment methods that can be used, such as physical treatment, chemical treatment, and biological treatment. Select suitable method to better recovery of rubber, improve processing efficiency and improve the quality of recycled rubber, reduce the industrial cost. Some new reclaiming methods have made breakthrough progress; can better solve the feasibility of the process conditions and environmental friendliness and other issues.

The research on the life cycle of footwear rubber cannot only guide the formation of a new bright spot in shoe recycling, but can also provide a theoretical basis for the recycling of footwear rubber, and promote the efficient recycling and reuse of waste footwear products. Moreover, the development of these technologies will create a further base for circular economy, controlling and reducing the generation of waste and improving a coordinated development of economy, society and environment. It is a new industrial project with low cost, high benefit and sufficient resources, which is of great economic and social significance and broad prospects for development.

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