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Biotechnological Processes
for Recycling of Rubber
Products

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Introduction

Rubber material as we know it is a material with properties that differ widely from those of the viscous sap of the rubber tree, *Hevea brasiliensis*. Elasticity and extensibility are the features most characteristic for rubber (Blow and Hepburn, 1982; Brydson, 1988; Franta, 1989; Gent, 1992). To gain these desirable rubbery properties—which make it possible to produce tires, hoses, and a wide range of other rubber products—it is necessary to vulcanize the raw rubber. By adding a few percent of sulfur and heating the mixture under pressure, sulfur bridges will be formed between the hydrocarbon chains (Figure 1). This irreversible reaction will produce a material with unique mechanical and thermoelastic properties, which is stable over a wide temperature range. Unfortunately, the material will also be almost impossible to reshape.

The synthetic rubbers differ from natural rubber, and from each other in chemical structure as well as physical and chemical properties. The molecular weight of natural rubber is several millions, while the molecular weight of synthetic rubbers is much lower. Rubber materials can also gain different properties by adding for example accelerators, activators, retarders, and fillers. In this way, a wide range of properties can be obtained. The chemical structures of natural and synthetic rubbers are shown in Figures 2–4.

In 1999, the natural rubber consumption worldwide was 6.7 million tons, while synthetic rubber consumption was 10 million tons.

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**Fig. 1** Sulfur cross-links between rubber molecules. The exact structures of the sulfur bridges are not known, though several different suggestions have been presented (Roberts, 1988). The molecular weights between the cross-links (Mc) vary between 500 and 20,000, depending on the cross-link density.

**Fig. 2** Chemical structure of natural rubber, poly-cis-1,4-isoprene.

**Fig. 3** Chemical structure of butadiene rubber consisting of 1,4-butadiene monomers and 1,2-butadiene monomers.

**Fig. 4** Chemical structure of styrene-butadiene rubber consisting of styrene and butadiene monomers.
tons (IRSG, 1999). The ratio between natural and synthetic rubber consumption has increased by a few percent during the past decade. The major part of the produced rubber is used in the manufacture of tires, but different areas of rubber use are shown in Figure 5.

As a consequence of the difficulties in reusing rubber material and of the widespread use of rubber products (mainly in the form of tires), huge numbers of used tires are stockpiled all over the world, with 2 – 3 billion tires currently estimated to be stockpiled in the US alone (Jang et al., 1998). Those tons of material could, instead of being environmental and health threats, provide a great asset of raw material, if efficient methods for recycling rubber could be developed. The problem with the reuse of rubber is caused by the strong sulfur bridges that occur between the hydrocarbon chains, these making it impossible to melt and reshape the material as can be done with thermoplastic and thermoelastic materials. In general, a priority order for decreasing the amount of waste should be: (1) reduction of consumption; (2) reuse of the product; (3) recycling of materials; (4) energy recovery; and (5) as a last possibility, deposition of the waste. In practice, the most environmentally friendly way to reuse scrap tires is of course dependent upon the costs, energy demands and pollution that such reuse creates. In part, the reduction of consumption and reuse of the product is, in the case of scrap tires, obtained by retreading.

A wide range of different methods for reusing and recycling tires and rubber material in general has been developed over the years (Figure 6). The most common method...
is to burn the tires in cement kilns and power plants as tire-derived fuel, or to use them as land-fill or as artificial reefs, for example. Ground rubber powder is used as filling material in a wide range of applications, together with different matrices such as new rubber material, plastics and cement. Shoe soles, plant pots and swings for children's playgrounds are other possible application areas, though at present these are limited in number.

1.1 Grinding of Rubber Material

Some type of size reduction is a prerequisite for most applications of waste rubber material, such as revulcanization with fresh rubber material, blends with other plastic materials, applications in civil engineering, soil improvements, running tracks and even energy recovery. Several such methods have been described (Astafan, 1995; Klingensmith, 1991; Kohler and O’Neill, 1996; Kohler and Jackson, 1998). In general, several steps are needed in the grinding process. The tires are cut or chopped into large pieces, and these are then ground to particles of millimeter size during the removal of textile, dirt and metals. For special applications, crumbs or particles <1 mm are produced. The requirements of energy increase drastically with decreasing particle size. The energy consumption constitutes the major part of the cost in the rubber grinding process. When using crumb rubber in the manufacture of new rubber products, the price of the ground rubber should be around half the price of raw rubber material or less, in order to make the process cost- efficient.

Cutting and grinding of the rubber material requires the use of special equipment due to its elasticity. Most processes are based on a combination of cutting and tearing. However, a general problem of grinding technology is the heat build-up in the rubber material, which means that cooling has to be applied in all grinding techniques. Cutting with hydraulically agitated knives is used to produce rubber chips of a large size. Shredding equipment is mainly used for rough grinding, the device consisting of low-speed rotating shafts with overlapping knives (Astafan, 1995). Granulators or hammer mills are equipped with rotor knives or rotating hammers, the counterparts being stationary knives and a grate, respectively. These can generate further size reduction. The waste rubber is exposed to large shear forces during grinding, and these – together with the heat build-up – leads to the problem of surface degradation. Ground particles tend to re-agglomerate, which further limits throughput. Water slurries of rubber particles and a flour-grinding mill can be used to produce a wet ground rubber, an advantage of which is its uniformity and cleanliness (Klingensmith and Baranwal, 1998).

Another way to avoid degradation is to cool the rubber under the glass transition temperature and then apply impact forces; this leads to cracking of the brittle material. Liquid nitrogen has to be used as cooling medium as the temperature required is –70 °C to –130 °C. Cryo-grinding (as this procedure is called) generates a powder with particle sizes down to 0.2 mm which can be produced without degradation and oxidation of the surface. Easier fiber and metal liberation is also reported (Astafan, 1995; Klingensmith, 1991; Kohler and O’Neill, 1996; Kohler and Jackson, 1998). The surface structure of ground rubber differs between cryo-grinding and ambient milling. Cryo-ground rubber has a smooth surface with relatively little surface area as compared with the ‘cauliflower’ structure obtained with ambient milling processes (Kohler and Jackson, 1998). Considerations on how to handle spent material and a cryo-grinding process have
been described by Liaskos (1994). Cryo-grinding is a relatively expensive method, due to the cost of the liquid nitrogen. Another approach of interest is solid state shear extrusion (SSSE). Waste rubber chips are fed to a cooled co-rotating twin-screw extruder, which permits pulverized material of controlled particle size (down to 0.05 mm) to be obtained (Khait, 1997).

1.2 Recycling of Rubber Material

One way to recycle rubber material is to shred it, grind it, mix the crumbs with virgin rubber, and then to vulcanize it to new rubber products. Rubber materials for certain applications, e.g. the tread on off-the-road tires, contain a few percent of recycled ground rubber which, in addition to giving a cost-reducing effect, also increases stiffness and tear strength. Furthermore, the ground rubber improves mixing and processing characteristics, facilitates the removal of enclosed air, and is an efficient way to control die swell in extrusion operations (Franta, 1989; Manuel and Dierkes, 1997). However, the material's mechanical properties, such as tensile strength and elongation at break, decline drastically when the concentration of ground rubber is higher than a few percent (Asplund, 1996). The reason for this decline is probably the low cross-linking in the interface between the virgin material and the ground spent material, that is due to a low molecular interaction between the polymer chains in the interface. Only a few new sulfur bonds are then formed during the vulcanization process (Myhre and MacKillop, 1996). Another reason could be that sulfur migrates from the new rubber matrix into the ground rubber particles during vulcanization. This makes the new rubber matrix less cross-linked (Gibala et al., 1999). The fracture areas of test pieces of rubber containing cryo-ground tire rubber (CGTR) have been studied with scanning electron microscopy (SEM). Those pictures clearly show that the rubber crumbs are discrete particles in a surrounding matrix (Figure 7).

Different methods for surface activation of the rubber crumbs have been developed to enhance the interactions between the crumbs and the new rubber matrix, and in this way improve the mechanical properties. Those include mechanical, chemical and a few biotechnological methods.

Other ways to recycle rubber include, for example, biotechnological processes such as microbial degradation of rubber into products that are in one way or another useful. There are generally some specific advantages.

![Fig. 7 Scanning electron micrograph of fracture area of rubber material containing 15% cryo-ground tire rubber (original magnification, x150).](image)
with biotechnological processes compared with chemical and physical processes. Biotechnology does not include any harmful or toxic chemicals, and is normally not energy intensive. Furthermore, the specificity of microorganisms and enzymes results in less unwanted degradation of the material. However, there are also some drawbacks, most notably that microorganisms are sensitive towards many chemical substances, including rubber additives. When manufacturing a tire for example, many different substances are added to the polymer to obtain a product that is stable and functional over a wide temperature range and in different applications. Except for sulfur, a vulcanization system also consists of accelerators, activators (e.g. zinc oxide and stearic acid), and retarders. Antidegradants, processing aids, mineral oil, pigments and fungicides are also added. Most of those additives are toxic towards many microorganisms. Some additives, for example fungicides, are added because of just that property, i.e. to prevent microbial attack of the product during use.

Zyska (1981) suggests that, in the manufacture of vulcanized rubbers, compounding ingredients which have a satisfactory level of microbiological resistance must be selected. Finding ingredients that are resistant to microorganisms implies fewer difficulties than finding an adequate fungicide for rubber. Such compounding ingredients will cause problems when biotechnology is to be used for rubber recycling.

1.3 Biotechnological Processes

Biotechnological processes can be defined very generally as “controlled and deliberate application of simple biological agents – living or dead cells or cell components – in technologically useful operations” (Bu’Lock and Kristiansen, 1987). They have also been described as “the integration of natural science and engineering science in order to achieve the application of organisms, cells, parts thereof and molecular analogues for products and services” (European Federation of Biotechnology, 1995). These kinds of processes include such diverse operations as the production of animal feed, citric acid and antibiotics, waste treatment, water purification and agricultural plant improvement. When designing a biotechnological process, one must consider a variety of different methods and reactor designs, for example whether to use an aerobic or anaerobic procedure; to use whole cells or pure enzymes; to use a continuous reactor or a batch-reactor. These different procedures have their specific advantages and drawbacks depending on the process to be accomplished.

2 Historical Outline

Rubber has been used by man for thousands of years (Blow and Hepburn, 1982). Columbus and his crew were the first Europeans to encounter rubber material when they discovered South America in the 1490s. At that time, the material was already well known and used by the Indians, not only as rubber balls for different games but also to make bottles, shoes and waterproof hats. Despite this early encounter, it took many years before rubber became widespread outside South America, and it was not until the middle of the nineteenth century that scientists first began to experiment with rubber. This led to the development of a variety of different rubber products, including the rubber eraser, which was invented by Joseph Priestly in 1770 and considered at that time to be an expensive luxury. In fact, the name ‘rubber’ was derived from its use as an eraser.
The problem with rubber at this time was that the material was sticky and impervious. This made the use of rubber products relatively limited until Charles Goodyear happened to leave a piece of rubber sprinkled with sulfur on a warm oven in 1839. The result of this was, to his surprise, a stable non-sticky material, which in the next few years became one of the most used materials in the world. Fifty years later, Dunlop invented the pneumatic tire, which is at present the most important rubber product. During World War I, Germany began to produce synthetic rubber, and they developed the technique further during the 1930s. Ten years later, during World War II, the USA was forced to start producing synthetic rubber due to the Japanese occupation of the rubber plantations. Today, about 60% of the manufactured rubber is synthetic.

When it comes to the recycling of polymers, rubber lags significantly behind the much more recently developed thermoplastic materials. This is in spite of the fact that rubber has been widely used, and recycled, for over 150 years (Rader et al., 1995). The use of recycled rubber was more prevalent 30 years ago than it is now. During the 1960s, recycled rubber constituted about 20% of the rubber industry’s raw material. However, due to the more widespread use of synthetic rubber, production liability concerns, and the introduction of the steel-belted radial tires, the use of recycled rubber has fallen to ~2%. In recent years, significant technical innovations have been made in the tire-recycling field, and it was only between 1994 and 1996 that the use of tire-derived fuel increased by 70%. The use of ground tires in the production of new rubber products has increased from 4.5 million tires to 10 million tires, while the number of tires used for civil engineering purposes has been constant over those years (Scheirs, 1998). During the years of expansive use of rubber products, there has always been the problem of microbial deterioration, and extensive studies have been carried out aimed at its prevention. One idea is to use microbial deterioration to dispose of rubber material, and perhaps even to gain a useful end product as a result.  

3 Rubber Products to which Biotechnological Recycling is Applied

The number of biotechnological processes for recycling of rubber material is still very limited. Recycling through microbial desulfurization is today probably the most investigated option in this area, but is yet not in commercial use (see Chapter 10, ‘Biotechnological Desulfurization of Rubber Products’). Biotechnological methods in general present promising prospects for finding solutions to the future demands of increased rubber recycling.

3.1 Microbial Degradation of Rubber

Microbial deterioration of rubber products has attracted much interest, and many studies have been carried out on the degradation of both pure rubber elastomers and vulcanized rubber products. The main purpose of those studies has been to reduce rubber deterioration during use of rubber products, but the degradation of rubber products might represent a possible opening in the search for efficient biotechnological methods to recycle rubber products.

In 1955, Rook wrote a survey of the principal publications on microbial attack on rubber. He concluded that the data concerning degradation of vulcanized rubber in most cases are very vague and should be interpreted with great care (Rook, 1955). The same conclusions were drawn by Heap and...
Morrel (1968) some years later. Several different rubber-degrading microorganisms have been isolated. Heisey and Papadatos (1995) isolated 10 strains belonging to the genera Streptomyces, Amycolatopsis and Nocardia, which reduced the weight of rubber latex gloves by more than 10% in 6 weeks. Jenndrossek and co-workers (1997) used natural rubber latex as sole source of carbon and energy to find 50 isolates of rubber-degrading bacteria. A total of 1220 strains from different culture collections was also screened, and revealed 46 positive strains; both their own isolates and strains from the culture collections were Actinomycetes. Linos and Steinbüchel (1998) isolated a bacterium belonging to the genus Gordona that used rubber as sole carbon source. Tsuchii and coworkers made extensive studies on rubber degradation and studied the degradation products from simple natural rubber materials after treatment with Nocardia 835 A. They also found that an increased amount of carbon black, sulfur and addition of the accelerator cyclohexylbenzothiazole sulfenamide (CBS) increased the resistance towards microbial degradation, and that the shape of the particles is of importance for degradation. With Nocardia strain 835 A, a 51% weight loss of truck tire was obtained when pieces of truck tires were incubated with pieces of rubber gloves as cosubstrate, but the degradation rate was slow (Tsuchii et al., 1985, 1990, 1996, 1997). The common observations reported in the different studies are that the isolates capable of rubber degradation generally belong to Actinomycetes, and that natural rubber is more easily degraded than synthetic rubbers.

Linos and Steinbüchel (1996) studied the growth of adapted isolates on natural and synthetic rubber elastomers. The growth behavior of one isolate indicates production of biosurfactants. Tsuchii and Takeda (1990) reported on extracellular rubber-degrading enzymes from the Gram-negative bacterium Xanthomonas sp. strain 35 Y. The enzymes were shown to degrade natural rubber latex to create the same degradation products as Nocardia strain 835 A. When more complex rubber materials were tested, little success was obtained. Linos and coworkers (2000) isolated the first Gram-negative bacterium exhibiting strong rubber-decomposing properties. Interestingly, the most efficient degradation has been obtained with natural rubber and almost only with low-wear products or rubbers with low complexity. There are probably two explanations for this: (1) that microorganisms find it difficult to degrade complex high-molecular weight compounds; and (2) the addition of toxic compounds to the rubber materials. Cundell and Mulcock (1973) investigated the effect of curing agent concentrations on the microbial deterioration of vulcanized rubber, and concluded that the cross-link densities did not affect the deterioration rate, while the nature of the cross-links did affect the rate of microbial deterioration.

Loomis and coworkers (1991) used controlled microbial chemostats to evaluate the polymer degradation with emphasis on plastics, while Steinbüchel and Linos (1997) used natural and synthetic polyisoprenes as model compounds for studies on microbial action on rubber materials. Keursten and Groenevelt (1996) concluded after a series of experiments with unknown microorganisms in soil-rubber mixtures, that the degradation of rubber particles in soil could be described by first-order kinetics. Williams (1986) has suggested that microorganisms preferentially attack the stearic acid content in vulcanized rubber, which is an interesting idea and must be considered in the efforts to prevent rubber deterioration.

The time scales for microbial deterioration in the reports mentioned above are weeks and longer. Tsuchii and coworkers (1985) reported a 100% rubber weight loss of unvulcanized
natural rubber in 8 weeks, but only 7–17% weight loss of tire tread in the same time. Linos and Steinbüchel (1998) noted a weight loss of 20% after 20 weeks of incubation. This indicates that efficient methods for degradation of rubber products such as tires on a large scale are still far from being applicable on a regular basis.

3.2 Surface Modification

A wide range of different methods for surface modification of ground rubber particles has been suggested over the years. Most of these are chemical or physical methods, but some biotechnological approaches have been proposed. The purpose of surface modification is to increase the interactions between ground rubber particles and a new matrix when rubber crumbs are mixed with a new material. This is done to improve the properties of materials that consist partly of ground rubber material.

3.2.1 Cleavage of the Hydrocarbon Chains

A great number of microorganisms have been studied in the context of degradation of rubber (see above). Most studies were aimed at preventing rubber deterioration, though it might be possible that cleavage of the hydrocarbon chains on the surface of rubber crumbs can enhance the interaction with a surrounding matrix material. Limited cleavage of the hydrocarbon chains on the surface of vulcanized rubber could make the chains more flexible, and a larger number of unsaturated bonds would be available to form new bonds with the surrounding material. This could for example apply to CGTR in a new matrix of unvulcanized rubber material or other polymers. Romine suggested that surface-modified rubber can bind with polar species in asphalt to establish a rubber-asphalt phase (Romine and Snowden-Swan, 1993).

3.2.2 Desulfurization of the Rubber Material

The possibility of enhancing the interactions between old ground rubber crumbs and a new rubber matrix by desulfurization of the vulcanized rubber has been studied by several groups (Torma and Raghavan, 1990; Löffler et al., 1993; Christiansson et al., 1998; Romine and Romine, 1998; Kim and Park, 1999; Bredberg et al., 2001; Bredberg et al., in preparation). The principal effects would be about the same as for cleavage of the hydrocarbon chains, but possibly more efficient. Cleaved sulfur bonds make the hydrocarbon chains more flexible and provide a larger number of active sites available for new bonding, but do not affect the quality of the polymers. This topic is extensively discussed in Chapter 10.

3.3 Microbial Detoxification

The largest single rubber product – tires – normally contain a wide range of different rubber additives such as accelerators, retarders, and antioxidants, and this applies also to many other rubber products. Many of the rubber additives used in different applications have been shown to be toxic to microorganisms (Zyska et al., 1971; Christiansson et al., 2000; Bredberg et al., 2001). It has been shown that most toxic rubber additives can be leached from the rubber with organic solvents, but from an environmental viewpoint this is not the best solution. This situation has also become a problem in other applications of used tires. For example, there are reasons to believe that artificial reefs made from used tires pose a threat to the aquatic environment, while ground tires incorporated into roadways and athletic tracks may leak toxic
substances (Evans, 1997; Galbraith and Burns, 1997). This is of course a major obstacle in the biotechnological processes that include rubber material, but it might be a problem that can be overcome with microbial detoxification. The possibility of using microorganisms capable of degrading for example aromatic substances in order to detoxify used rubber has immense appeal. *Rhodococcus*, for example, is reported to be able to metabolize aromatic compounds and a wide range of other compounds (Warhurst and Fewson, 1994). Extensive studies have been carried out with different species of fungi in the area of soil remediation, but there are no reports about this application in the context of rubber recycling.

Some possible ways to reuse rubber material are shown in Figure 8.

### 4 Current State

At present, a very limited number of biotechnological processes exist for the reuse of waste rubber material. A number of patents exist for the biotechnological desulfurization of rubber material, but to our knowledge none of these processes is currently in commercial

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**Fig. 8** Schedule of possible biotechnological methods for reuse of rubber material.