Rubber technology: Past, Present, Future

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SOME NOTES IN THE HISTORY OF RUBBER

Rubber technology has a very long history and found fossils from natural rubber residues date back 50 to 60 000 years. Some such old fossils were still elastic when they were found in Germany in deposits of brown coal.

The history of rubber materials and rubber technology has been summarised by Blow and Hepburn[1]. Excellent books in rubber technology can also be found [2-7].

The invention of vulcanization by sulphur by pure chance by Charles Goodyear between 1839 to 1844 was a landmark in rubber technology. Vulcanization was the start of the modern rubber industry in the world. Many improvements have been introduced since Goodyears days. 90% of todays rubber products contain sulphur as the main vulcanization ingredient together with accelerators to obtain reasonable vulcanization times. The spectrum of vulcanization systems used today comprise different peroxides, sulphur donors and specially developed cure systems for the different rubber materials. Ionizing radiation can also be used to crosslink rubber materials.

Dunlop´s invention[1] of the pneumatic tyre was important for the successful development of our car industry. Vulcanization solved problems like reducing the stickiness of the surface of raw rubber. People at that time were not happy about the disturbing mechanical creep of their raincoats hanging in a wardrobe especially during summertime. The observed increased elasticity given to rubber products after vulcanization was a side effect of the vulcanization which was unexpected but positive in many mechanically loaded rubber products like gaskets, O-rings, vibration isolators etc.

Searching for a suitable solvent for raw rubber was an intriguing problem during the 19th century. Turpentine was found to be the early answer. The reinforcement of rubber by carbon black was discovered in January 1904 at Silvertown outside London by Mote and Mathews and others. They were investigating the effects of numerous ingredients on physical properties and found that carbon black had a reinforcing ability when mixed into compounds of natural rubber[1].

RUBBER ELASTICITY

The name rubber was first used by Joseph Priestley in 1770 on account for the usefulness of the material for wiping lead pencil marks from paper. In 1805, long before anything was known about the molecular structure of rubber, its mechanical properties were investigated by Gough, who reported that the length of a rubber sample held under constant stress decreased as its temperature was increased and demonstrated that heat was evolved as a result of adiabatic extension. Thus the study of rubber elasticity was started along thermodynamic lines which were further pursued on the theoretical side by Lord Kelvin and on the experimental lines by the very precise work by of Joule, which appeared in 1859[8]. Lord Kelvin concluded that the tension in a rubber sample arose from the heat motion of the constituent particles in rubber. However attempts to specify the nature of these constituent particles were unsatisfactory and it was not until after 1930, by which time the macromolecular character of the rubber molecules was completely understood and accepted, that the development of a quantitative kinetic theory of the rubberlike elasticity became possible. In a pure rubber sample rubber elasticity is an entropy effect. Descriptions of rubber elasticity along thermodynamic, statistical mechanics and continuum mechanical lines can be found[12].

SOME PROPERTIES OF RUBBER MATERIALS

Rubber materials are incompressible and have a Poisson ratio close to 0.5 and show high elasticity and reversible extension up to 1500%. At the largest extensions effects of crystallisation of the rubber molecules appear. Rubber materials can crystallize when cooled or stretched several hundred percent. Rubber materials also have glass transitions (T_g). A natural rubber has its Tg at -70°C while silicone rubber has its Tg at -120°C. Examples on crystallizing rubber materials are natural rubber, polybutadiene, chloroprene rubber while rubber materials built of copolymers are non-crystallising or amorphous like SBR, NBR, Fluoro-elastomers, EPDM etc. A crystallizing rubber shows much higher resistance to fatigue due to inhibition of crack growth.

UNSOLVED PROBLEMS IN RUBBER ELASTICITY

There are many problems to be solved before we have better knowledge about the phenomenon of rubber elasticity. In the following list is mentioned a few points to be investigated:

- Small chain lengths seem to predominate under large deformations.
- The elasticity of short chains is still not fully evaluated.
- Another point is the influence of type and distribution.
- Influence of loop formation is not at all investigated.
- The mutual interaction between chains is an area to investigate.
- The influence of filler is not understood. In a filled rubber material it is the rubber phase that is responsible for the rubber elastic effect. In highly filled rubber materials the rubber elastic effect is impossible to register because ordinary thermal expansion dominates.

THE RUBBER TIRE AND LONGEVITY

The most important rubber products are related to tires and car technology. The development of rubber technology and transport technology go hand in hand.

In many applications it is important to know the life-time of the used products. Many rubber materials consist of polymers containing double bonds which are known to be sensitive to degradation and estimation of life times of rubber products are sometimes difficult to do.

COMPOUNDING

Rubber compounding is the art and science of selecting various compounding ingredients and their quantities to mix and produce a useful rubber formulation that is processable, meets or exceeds the customers final product requirements, and can be competitively priced. In order to protect rubber products from degradation antidegradants are added. Liners to milk cows present one such demanding problem:

You do not want to drink milk containing antidegradants in the form of antioxidants or antiozonants, because they can be harmful to your health. But at the same time you need a secured product life time in order to secure function and avoid premature failure which may harm the animals. DeLaval AB and KTH have worked on this problem in some studies.

At the department for fibre and rubber technology work is going on to increase our knowledge about the long term performance of cable insulation consisting of mainly PVC and Lipalon. Lifetime assessments are performed based on the experimental data using a failure criterion established from functional electrical experiments simulating a nuclear power plant failure. The work is done by Research Student Maria Ekelund in a contract work in cooperation with Swedish nuclear power plants.

THREAT TO NATURAL RUBBER

The Myrocyclus fungus is a threat to future use of natural rubber. The fungus creates the South American leaf disease and is a serious threat for the world´s natural rubber plantations. Some rubber trees in the Amazona have been resistant to the fungus through plant breeding in cooperation with rubber factories.

RECYCLING OF USED RUBBER PRODUCTS

Discarded vulcanized tires now account for 3% of the weight of all municipal refuse and are the fastest growing forms of refuse. The tonnage is expected to increase annually at 2% as it has for the past 100 years. It is approximated that 67% of disposed rubber is primarily automobile and truck tires. From environmental viewpoint it is necessary to reduce the amount of rubber material since degradation of rubber waste is slow and add a lot of chemicals from the vulcanization and stabilisation systems. Recently S.K. De[11] et al have summarized the situation about rubber recycling in a textbook. Charles Goodyear who invented the sulphur vulcanization was also one of the first to start efforts to recycle cured rubber wastes through a grinding method[(2)]. Many obstacles have to be solved when used rubber materials shall be recycled. One is the contamination by impurities, which make the products unsuitable to recycle.

The abbreviation SKOR (**S**ome **K**ind **O**f **R**ubber) is related to the recycling area and tittle-tattle about the problems with recycling. Recycled material may get a better reputation as an effect of the increased oil prices. The solution to the world´s increasing stockpiles of worn out tires is not by solely one line. Chemical, mechanical, thermal methods may play important roles.

NEWS

At MIT in USA A. Mayes has recently presented news about baroplastics. This group of materials has elastic properties at room temperature and is processable at room temperature and also easy to recycle since the baroplastics are not vulcanized[10]. These materials consist of copolymers of acrylates, polystyrene etc. Nanoparticles mixed with baroplastics can be used to lower the rate of relaxation and be an attractive material in mechanically loaded rubber products?

HAS RUBBER MATERIALS A FUTURE?

A rubber material cannot be replaced by another material having its unique combination of properties. The development since the 1970´s has learnt us that blending of suitable materials may be successful. Techniques like dynamic vulcanization has been introduced. We will probably see increased use of thermoelastomers and reduced use of crosslinked elastomers. Important applications will come in the medical area as well as in the electronic and space areas. For tires natural rubber and SBR will be the logical choice if we want to have good comfort in eg our cars.

By skilful application of rheology demanding processing problems can be handled.

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