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Recent Developments in Rubber Processing, Leading to New Applications such as the "Green Tyre"

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Abstract: Rubber articles derive most of their mechanical properties from the admixture of reinforcing fillers. Most commonly, carbon black is used as reinforcing filler. If silica is used instead, tyres made with such rubber compounds may exhibit a rolling resistance reduction by ca. 30%, which translates in substantial fuel savings of a car. Such silicas are far more difficult to mix with rubber than carbon black. Coupling agents are used as a surface modification of the filler to enhance compatibility with the polymer. Additionally they improve the ease of mixing with the rubber. The development of proper coupling agents combined with improved mixing techniques has contributed to the final break-through of the silica-reinforced "Green Tyre".

INTRODUCTION

Natural and synthetic rubbers (elastomers) are rarely applied in their pure form. Pure products are "too weak" to fulfil practical requirements such as hardness, tensile strength and wear resistance. Tires, for example, must have these characteristics. Rubber articles derive most of their mechanical properties from the admixture of fillers with quantities of 30% up to as much as 1500%.

Originally, fillers such as sand, silica, chalk, mica, etc. were used in order to cut down on compound costs or merely because the (Natural) rubber was polluted with these materials during the harvest in the Amazone region. But very soon it was found that some of these fillers impart special mechanical properties to the processed rubber materials. The range of filler materials has been divided into so-called "non-reinforcing" fillers, such as chalk, also often called whiting, and mica, which are especially added to reduce the price of a rubber compound; and "reinforcing" fillers, such as carbon black and later silicas and silicates, which improve the tensile properties. Even more important, reinforcing fillers contribute to the abrasion resistance and tearing strength of rubber vulcanisates, and hardly influence the outstanding elastic properties which are so important for the hysteresis properties

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and consequently the low rolling resistance of tires.

Carbon black has become well-known as the most versatile reinforcing filler for rubbers. For non-black applications, silicas or silicates can be employed as alternative reinforcing fillers. Because the vast majority of rubber articles are reinforced with carbon black rather than silica or silicates, extensive practical experience is available on carbon black reinforcement. For silica and silicate reinforcement, however, there is far less experience available.

The present paper deals with the renewed interest for silica as a reinforcing agent for elastomers. For tyre applications in particular, generally called "the Green Tyre". But also for non-black or possibly coloured rubber articles, like pigmented automotive door seals, for which carbon black cannot be used.

RUBBER REINFORCEMENT

At present, the use of reinforcing fillers is still mainly based on empirical knowledge. The mechanical action of filler particles in rubbers, which depends on filler loading and the extent of particle dispersion, is not fully understood, despite the fact that there has been considerable research in this area. Medalia, a well-known expert on rubber reinforcement stated in 1980 [1]: "One still may hope that a satisfactory explanation of the problems associated with reinforcement will be available by the year 2000". Coming so close, it is sure that this deadline will not be met.

If reinforcing or active fillers are compared to non-reinforcing or inactive fillers, the former do have a significant positive effect at increasing filler loadings on rubber compound and vulcanisate properties, like viscosity, hardness, abrasion resistance, tensile properties and form-recovery after deformation, usually called the "set"-properties in rubber terminology. Non-reinforcing or inactive fillers have little or sometimes a negative effect on these properties. Their main role can therefore best be defined to reduce the cost-price of a rubber compound.

TYRE PERFORMANCE CRITERIA

A tyre is an extremely complex article, in which many functions are combined. For the purpose of this presentation, a few properties can be highlighted. A tyre producer aims at obtaining the best possible compromise between the following:

- High abrasion resistance of the tyre,
- Low rolling resistance of the tyre,
- Good (wet) skid resistance, high resistance against skidding on wet and icy roads.

As it turns out, a low rolling resistance combined with a high skid resistance is very difficult to obtain. Both are determined by internal hysteretic losses within the tyre rubber. The rolling resistance is commonly related to the phase angle δ in dynamic mechanical testing at 60°C, representing an average operation temperature of a tyre at frequencies of the order of 10 - 30 Hz. The skid resistance is characterized by much higher frequencies involved in the skidding process, and is therefore represented by the hysteretic loss δ at 0°C, where by means of the time-temperature superposition principle the high frequency phenomena are transformed to lower accessible frequencies. The overall aim of the tyre manufacturer is to obtain a high tanδ at 0°C with a low tanδ at 60°C. The tyre producer has two variables at his disposal:

- The particular choice of the rubber polymer,
- The type and amount of reinforcing filler.

THE CHOICE OF RUBBER POLYMER

Figure 1 shows the tanδ of a common synthetic rubber used for tires [2]: SBR1500. This polymer shows indeed a high tanδ at sub-zero temperatures and a low tanδ at 60°C and higher. Figure 2 shows, how by combination (blends) with various other synthetic rubbers - BR and natural rubber NR, each with their own characteristic shape of the curve - the overall curve of the tanδ vs, temperature can be influenced to a limited extent [2].

THE ROLE OF THE REINFORCING FILLER

The reinforcing fillers carbon black and silica are both characterized by a specific spatial structure. Carbon black consists of small spherical primary particles with typical diameters of 20 - 100 nm. These spherical particles form aggregates of several hundreds of primary particles. The aggregates in turn are condensed into so-called agglomerates, which are further condensed into granules in order to ease the handling of the black. Carbon black agglomerates are disintegrated during rubber mixing, more or less to the size of aggregates, so that these latter ones form the actual reinforcing species.

Depending on the production conditions of the carbon blacks, there is a wide variety of spatial arrangements of the primary particles in aggregates. According to the ASTM D3849 classification (N110 - N990), the average diameter of the aggregates increases simultaneously with the diameter of the primary particles, the former ranging between ca. 100 - ca. 800 nm. for N110 to N990. In addition, the concept of "structure" has been introduced for carbon blacks, meaning the tendency of the primary particles to be linked together in either chains or clusters.

With respect to the interaction between carbon black particles and the rubber matrix, various mechanisms have been proposed as functions of the carbon black-rubber combinations and the size and structure of the carbon black particles. These mechanisms are combinations of what are called chemisorption and physisorption.

Although it has been less extensively investigated, silica reinforcement works similarly to that of carbon black. Silicas are characterized by primary particles with

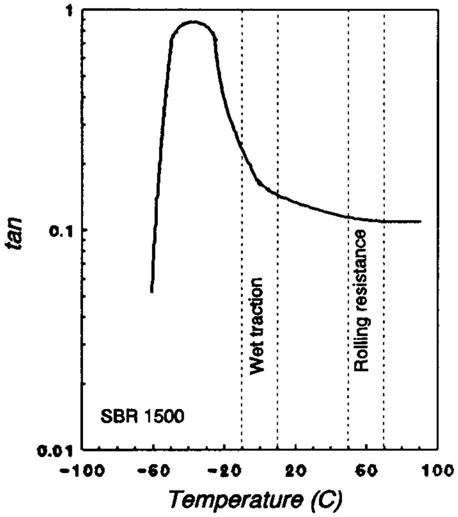


Fig. 1: Dependence of tanδ on temperature for synthetic rubber SBR 1500

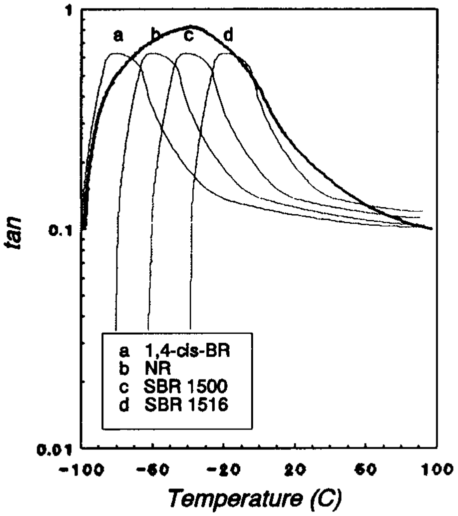


Fig. 2: Damping of an ideal tyre rubber, as composed of contributions from individual synthetic and natural rubbers

typical diameters of 15 - 40 nm, slightly smaller than the primary particles of carbon black. The BET- or N_2-surface of silica, a measure of the surface area activein rubber adhesion, is of the same magnitude as for carbon black. However, silica is more structured than carbon black. The high structure of silica aggregates results from Van der Waals forces between the separate silica particles and hydrogen-bonds and siloxane-bonds, which link the silica particles chemically together.

This higher structure of silica accounts for a greater reinforcing power relative to carbon black. And about 20 years ago already it was discovered by S. Wolff of Degussa [3], that silica has a lower hysteretic loss, as expressed in tanδ, compared to carbon blacks of the same surface area: Figs. 3 and 4.

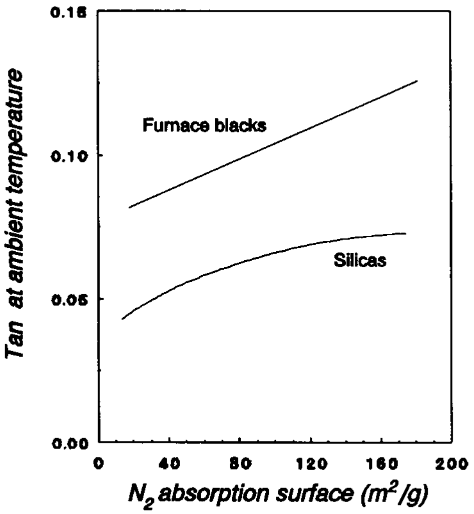


Fig. 3: Dependence of tanδ of vulcanised Natural Rubber on the surface area of Silica; for comparison carbon black

By using silica rather than carbon black reinforcement for tyre tread compounds, tanδ at 60°C can be reduced to such an extent as to reduce the rolling resistance of a tyre by 30%. By a proper choice of the rubber polymers, the other tyre characteristics in particular wear resistance and skid resistance can essentially be kept unaltered [4]. This reduction in rolling resistance results in about 5% fuel savings for an average personal car equipped with such tires: a significant contribution to the environment.

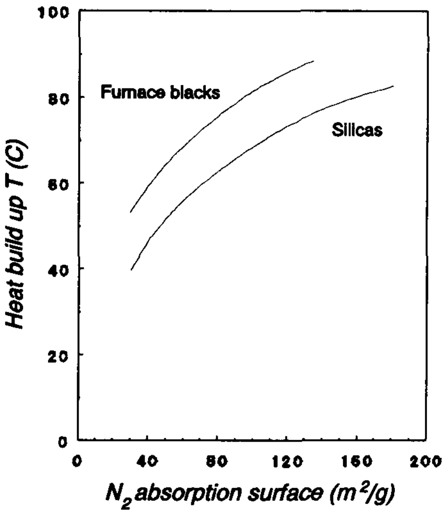


Fig. 4: Dependence of heat build-up of vulcanised Natural Rubber on the surface area of Silica, compared to carbon black

COUPLING AGENTS

Several things make silica on itself a less-effective reinforcer:

- Silica is far more difficult to mix with rubbers,
- Silica tends to deactivate the curing with sulphur.

Silica is difficult to mix with rubbers, because it is hard to break the hydrogen- and siloxane-bonds. It is more difficult to break these bonds than the Van der Waals bonds for carbon black. Furthermore silica lacks the natural compatibility with rubbers that carbon black has. Because of its many silane and siloxane groups, silica behaves in highly polar or hydrophillic ways, while most elastomers are comparatively apolar or hydrophobic.

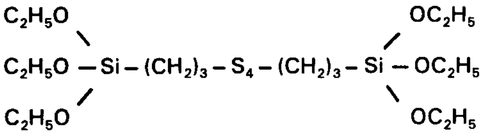
Further, silica tends to deactivate the curing with sulphur due to the acidic nature of the silica particle surface. Sulphur vulcanization, which is by far the most common in rubber technology, takes place in an alkaline environment. The addition of acidic components is commonly applied to retard vulcanisation and as a consequence the level of vulcanisation may also decrease. The siloxane moiety on the silica particle has a similar acidic effect.

Adhesion promoters, also called coupling agents, are often used with silicas as surface modification. They are either applied on the silica particle itself before the mixing, or by addition to the rubber compound. Their role is to shield the acidic groups of the silica particles and possibly form a chemical link between the silica particles and the vulcanized rubber network. In addition, they lower the polarity of the silica particle, which improves the ease with which the silica may be mixed into the rubber matrix.

This type of coupling agent is generally characterized by two functions: one for the adhesion to the hydrophillic silica-surface, the other for adhesion to or enhancement of the compatibility with the hydrophobic polymer matrix.

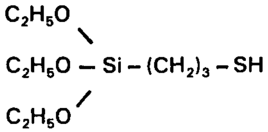
Silanes with appropriate functionality are commonly employed as coupling agents, for example:

- Bis-(Triethoxysilylpropyl)tetrasulfide (TESPT, sold under trade code Si-69 by Degussa GmbH):



$$(C_2H_5O)_3Si-(CH_2)_3-S_4-(CH_2)_3-Si(OC_2H_5)_3$$

- γ-mercaptopropyltriethoxysilane:



$$(C_2H_5O)_3Si-(CH_2)_3-SH$$

The mechanism behind these coupling agents is obvious. The silane moieties of both compounds should react with the silica surface and the mercaptane- or sulphide-groups are supposed to form covalent bonds with the rubber molecules by participation in the sulphur curing. Recent investigations, though, have shown that the validity of this assumption may be questioned [5]. The coupling agents do react covalently with the silica surface, but upon deformation there is pronounced evidence of slippage of "anchored" rubber molecules along the silica surface. In effect, using coupling agents seems only to enhance the hydrophobicity of the silica surface.

THE ROLE OF RUBBER PROCESSING

The process of adhesion of silica fillers to elastomers turns out to be rather irreproducible and subject to variations in mixing and curing conditions, resulting in quality fluctuations of the end products. Many important processes concerning the adhesion of rubber molecules to filler particles are still poorly understood, despite the long history of rubber technology.

As explained before, coupling agents facilitate the mixing of silica in rubber by lowering the hydrophillic nature of the silica surface and by breaking hydrogen and siloxane bonds between the separate primary and aggregate silica particles. If the coupling agent and silica are added as separate components during the rubber/silica mixing, or processing stage, it is considered that the coupling agent then combines in situ with the silica.

One factor which determines the amount of reaction of the coupling agent is the temperature cycle, which the compound experiences during the mixing and later in the vulcanisation stage. In addition, the reaction of the coupling agent (if any) with the rubber is obviously strongly dependent on the temperature conditions during the vulcanisation stage. The often rather irreproducible conditions during mixing and vulcanisation, combined with the different possibilities of adding the coupling agents to the filler/rubber substrate are no doubt major factors in the irreproducibility of silica-reinforced rubber compounds.

Recent developments in rubber mixing technology have certainly contributed to the break-through of the silica reinforcement for tires; in particular the recent change away from internal mixers with tangential rotor designs to mixers with intermeshing rotor designs [6]. The main advantage of intermeshing mixers turns out to be, that due to a greater contact area between the rubber compound and the mixer steel walls and rotors, the temperature rise of the batch due to friction is kept at a lower level than for a tangential mixer. The lower temperature accounts for a higher viscosity of the compound, leading to higher shearing forces to disperse the fillers within the rubber matrix. Particularly for the difficult to mix silica fillers, this is an important factor, leading to better reproducibility of the mixing operation.

CONCLUDING REMARKS

This does not mean that all problems with silica reinforcement of rubber are now solved. There are still many questions left, the answers to which may significantly contribute to a further penetration of silica reinforcement. Such questions are:

- Does Silica form adhesive bonds with NR, BR and SBR of chemical or physical nature, in comparison with Carbon black?

- What is the role of adhesion promoters or coupling agents in the formation of the bonds between silica and rubber? How does this compare with carbon black?

- How does the temperature of mixing and vulcanisation influence the adhesive bonding with and without coupling agents?

- What are the best mixing and vulcanisation conditions to obtain optimal wetting and bonding of the fillers? Can recommendations be made as to the best processing conditions which minimize quality fluctuations of such compounds?

- Are the presently most commonly applied adhesion promoters, e.g. TESPT/Si-69, optimal silica reinforcement materials, or would it be possible to develop even better chemical structures?

Further study into these questions is proceeding these days and will certainly increase the consumption of silica relative to carbon black for reinforcement of rubber, in particular for tyres.

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