Silica tread compounds · viscosity · processing properties · vulcanization

Modern generation of passenger tire consists of S-SBR/BR based tread compounds con-taining high surface silica in combination with a sulphur silane as coupling agent. A novel processing plasticizer improves the processing of silica compounds significantly. The product reduces the compound viscosity in combination with longer scorch safety and shorter vulcanisation time. It can be used as replacement of mineral oil based plasticizer or as additive. The use of the product results in lower compound viscosity and steeper vulcanisation behaviour. The use of higher amount silica or higher surface area silica is possible without mixing problems.

Vulkanol P – Ein neues Verarbeitungshilfsmittel für Kieselsäuremischungen

Kieselsäurehaltige Reifenlaufflächenmischungen · Viskosität · Verarbeitungseigenschaften · Vulkanisation

Die moderne Generation von PKW-Reifen basiert auf L-SBR/BR Laufflächenmischungen, die Kieselsäure mit großer Oberfläche in Kombination mit schwefelhaltigen Silanen als Kopplungsagenz enthalten.Ein neues Verarbeitungsplastiziermittel verbessert die Verarbeitung von Kieselsäuremischungen signifikant. Das Produkt reduziert die Mischungsviskosität in Kombination mit längerer Anvulkanisationssicherheit und kürzerer Vulkanisationszeit. Es kann als Ersatzstoff für mineralölbasierende Weichmacher oder als Additiv eingesetzt werden. Der Einsatz des Produktes resultiert in einer niedrigeren Mischungsviskosität und steilerer Vulkanisationskurve.

Figures and Tables:
By a kind approval of the authors.

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Vulkanol P – A new Processing Plasticizer for Silica Compounds

Introduction

The introduction of the so-called „Green Tire Technology" beginning 1990´s was a chal-lenge for the tire industry. This new generation of passenger tires consists of solution-SBR/BR based tread compounds containing high surface silica in combination with a sulphur silane as coupling agent to reduce rolling resistance and improve wet skid behaviour without affecting abrasion resistance. In an European patent from Dec. 6th, 1995 Michelin [1] describes in detail all compound ingredients of the new silica tread compound in combination with solution-SBR and G. Marwede [2] highlighted solution-SBR as the elastomer for the next century. The change from the classical system E-SBR/BR filled with carbon black to the new technology has created a change in the philosophy of rubber mixing. In the past the mixing process consists of plastification of the rubber, dispersion and homogenization of the filler and all rubber chemicals. For the new silica filled tread compounds a chemical reaction between the silica and the sulphur silane takes place in the internal mixer beside plastification and dispersion. An overview about the influence of the silica structure on the rubber properties is given by U. Görl et.al. [3]. To improve dispersion of the silica in rubber the macro pore size distribution of the precipitated silica must be modified. W.H. Waddell et.al. [4] describe that small pore diameter is thought capable to increase reinforcement of elastomers by increasing the physical interactions between the silica and polymer functionalities.

The ever-increasing need in the rubber industry – especially the tire industry – towards more efficient rubber mixing and processing resulted in the need to optimize all the available parameters in the factory and compounds, change to interlocking mixers, optimized micro- and macro-structure of the polymers used, etc. The processing properties of silica compounds are considerably poorer compared to equivalent compounds containing carbon black in mixing, extrusion and mould flow properties. To achieve an optimum production process for silica compounds the processability can be improved by the use of processing promoters. Processing promoters act as lubricant improving the rheological control of the processing process. Used in small quantities they increase output, better profile surface and eliminate pressure fluctuations during extrusion. In terms of their effect on rubber lubricants can be divided into two groups, internal lubricants and external lubricants [5]. For internal lubricants the dispersed molecules of the processing promoter and the polymer lie side by side. External lubricants are insoluble in rubber. They are very finely dispersed in the rubber compound but do not produce any molecular lubricating effect as they do not penetrate the polymer coils. They are effective via a large internal surface of the very finely dispersed material as a low viscosity domain inside the compound.

Widely used processing promoters for silica compounds are so-called zinc soaps from fatty acids. They act as internal lubricant reducing compound viscosity to increase the output, improve profile surface and edges and eliminate pressure fluctuations during extrusion.

A further pressure on the tire industry is coming from the new tire labelling around the world. For passenger car tires the label will show the performance of the tire regarding rolling resistance, wet grip and tire noise. According to the European Tyres & Rubber Manufactures´ Association (ETRMA, former BLIC) in 2004 only 60% of the whole European summer tire market met the minimum rolling resistance threshold. For 2016 an adjusted maximum for rolling resistance will come. To improve the rolling resistance of tires it is expected that all manufactures or importers of passenger car tires are forced to use more and more silica in their compounds further to reduce rolling resistance and improve wet grip.

Results and Discussion

The novel processing plasticizer for silica filled compounds is from the group of polyfunc-tional esters called Vulkanol P. It was specially selected to have a polar structure to show strong interference with the silanol groups of the silica surface. This is in contrast to the typical used

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mineral oil based plasticizer used in the rubber. This chemical can be used in compounds with contact to food, has no hazardous label as mineral oil based plasticizers have and it does not contain Zinc as typical processing additives for silica compounds. For this reasons it is very safe and highly environmentally friendly .

For easier handling the product is available as dry liquid with 50% active content on a silica carrier.

The product has been tested in a typical solution-SBR/BR compound with 80 phr loading of active precipitated silica as described in the Michelin patent [1]. The compounds were mixed in an interlocking mixer (GK 1.5 l E), in the first mixing step the polymers, silica, silane, mineral oil, antidegradants, zinc oxide and the processing plasticizer were added. The mixing time was 5 minutes with a maximum mixing temperature of 150 °C, after storage of 24 h the compounds were mixed again in the internal mixer for 210 sec to improve the silica dispersion. Again after 24 h sulphur and accelerators were added on a two-roll-mill.

Used as replacement for the free amount of mineral oil in the test formulation the new processing plasticizer resulted in a drop of the Mooney Viscosity at 100 °C of about 10 Mooney units.

The rheometer behaviour of the compound with the novel processing plasticizer showed a beneficial shape with longer scorch safety and shorter vulcanisation time in comparison to the reference with the free mineral oil. Beside a slightly higher Shore A hardness the mechanical and dynamic behaviour of the compound is uneffected. Overall only by replacing a small amount of a mineral oil based plasticizer by a more polar one the typical drawback of compounds with high silica loading of poor processing with high compound viscosity can be significantly improved.

The chemical can be also used with benefit by adding it on the top of the reference formulation. Also here the compound viscosity is significantly reduced by about 15 Mooney units . Keeping in mind that this formulation has now a silica content of 88 phr it can be expected that the wet grip of a tire is improved. As seen before the rheometer shows again better scorch safety and shorter vulcanisation time. Mechanical and dynamic properties are the same compared to the reference.

Actual tire compounders are looking for tread compounds with silica dosages of 90 phr and higher to improve the wet traction. This kind of recipies resulted in

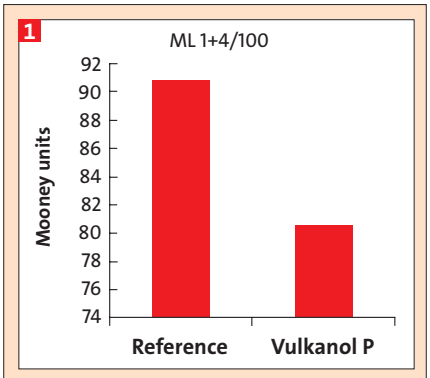

Diagram 1: Mooney Viscosity of reference compound (with TDAE oil) and Vulkanol® P compound (as re-placement of TDAE oil)

mixing problems due to high viscosity. The new processing plasticizer reduce the compound viscosity maintain other properties, as a slight polar synthetic chemical it can be expected that the material as such can improve the wet grip of a tire.

Looking at the Payne effect, the so-called silica-silica network of the compound with the new additive is higher in comparison to the reference or the compound with the zinc soap. This effect can be explained with the high polarity of the additive on the surface of the silica particles in the compound making additional interactions.

Summary

By using processing aids the compound viscosity of full silica compounds can be signifi-cantly reduced. The typical products in the market are so-called zinc soaps. Due to the Zn content this products will give longer scorch safety but show lower hardness, lower modulus and longer elongation at break. This behaviour of Zinc soaps on mechanical properties of the rubber vulcanisate is similar to the effect that mineral oil based plasticizer show very often.

A novel synthetic processing plasticizer for silica compounds is based on polyesters is called Vulkanol® P. Due to the polar structure of this plasticizer it has a tendency to go to the silica surface to make interactions with the silanol groups. As a zinc free additive it is highly environmental friendly with less emission of the heavy metal zinc during the use of tires (street abrasion) compared to tires containing zinc soaps and it has no hazardous label as normal mineral oil based plasticizers has. This chemical can be used as (partly) replacement of standard plasticizers resulting in significant lower compound viscosity and a steeper rheometer behaviour with better scorch safety. The hardness is slightly higher, higher stiffness of a tire can result in better handling performance of the car. Other mechanical or dynamic properties are unaffected using this processing plasticizer.

The novel chemical can also be used on top of a standard formulation. The higher silica content for such a compound will result in improved wet grip but without problems in compound viscosity as normal for such a compound. A new trend in tire industry is working on compounds with very high silica loading to improve wet grip. This novel chemical will overcome the mixing problems for such compounds and is a problem solver for all kind of compounds with high silica loading and can contribute to better wet grip of the tire and though improve their labelling.

Literature

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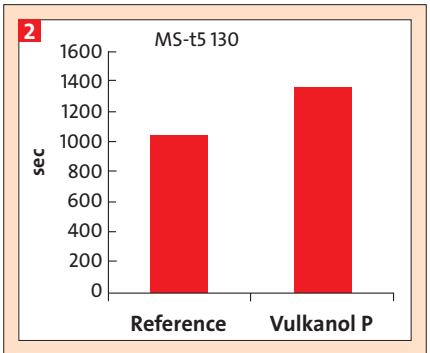

Diagram 2: Scorch time

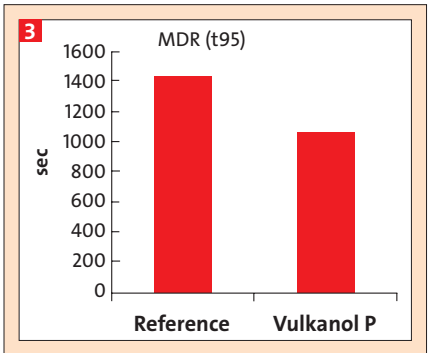

Diagram 3: Curing time (t95)