Synthetic Layered Silicate as a Carrier for Liquid Ingredients for the Rubber- and Tire Industry

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Summary: We propose the use of novel materials based on synthetic calcium silicate hydrate (C–S–H) for the rubber- and tire industry. We found that the synthetic silicate belongs to the family of layered calcium silicate hydrates. Due to its layered structure and inert surface it easily adsorbs liquid components of rubber compounds, such as bis(triethoxysilylpropyl) tetrasulfide (TESPT) and liquid polysulfide (LP). Then, in processing, the C–S–H can smoothly release these components. The water, trapped in the material's gallery layers, plays the role of a catalyst in the silane coupling on silica's surface. In addition, we used this silicate as a component in promoter systems in order to improve adhesion stability between a brass-coated steel cord and rubber. The application of the calcium silicate hydrate as an inert substrate for the promoter system allowed the development of materials that have comparable adhesion strength with most commercial promoters.

Keywords: adhesion; calcium silicate hydrate; coupling agent; rubber; solid carrier

Introduction

The expansion of industrial and economic activities results in continuous demand for new, low-cost materials, which are able to meet the increasingly stringent requirements. Polymers are commonly admixed with a variety of both natural and synthetic compounds to improve their performances and lower the cost of the material. Different inorganic components have been used in the tire- and rubber industry for this purpose. Application of silica as one of the most commonly used fillers, into rubber forms "filled composite" with good performance. However, addition of only silica into the rubber is mostly insufficient in order to produce materials with desirable properties. Therefore, introduction of other special ingredients into the rubber compounds is required.[1,2]

The compounding process of rubbers containing inorganic fillers is strictly different from the traditional process using carbon black. Due to polar nature of silica particles they are easily agglomerated, and hence hardly dispersed in the rubber matrix.[3–5] Therefore, the surface modification of the filler particles is required. In order to increase the "polymer-filler" interaction the chemical modifiers (so-called coupling agents) are used. Bifunctional silanes such as bis(triethoxysilylpropyl)tetrasulfide (TESPT) are widely used as coupling agents in the tire industry. Bifunctional molecules of TESPT interact with both silanol groups on the silica surface and unsaturated macromolecules of the rubber. Thus they chemically bind the silica particles and the rubber matrix.[6]

It has recently been found that water plays an important role in interaction of alkoxysilane with the silica surface (so-called silanization).[7,8] The presence of water significantly increases silane grafting on the silica surface. It makes the particle's interaction weaker that improves of processability and mechanical properties

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of the rubbers.[9,10] Realization of the silanization reaction in a mixer chamber causes other problems such as a precision batching and the uniform distribution of the liquid coupling agents in the polymer matrix. There are two fundamental approaches for solving these problems. The first method is treatment of filler using various chemical agents.[11–13] However, this approach is quite expensive and the obtained products have relatively short storage time that limit application of these modified fillers. An alternative approach is the use of free-flowing concentrated products. The various powder materials such as carbon black, silica, talc, kaolin, calcium silicate and lignine can be applied as carriers for different ingredients.[14,15]

Because of performance demands, carriers used to develop the concentrated products should have well-defined properties. Therefore, dispersity, surface specific area, specific morphologies in terms of microstructure, porosity and surface chemistry play a key role.

As is well known[16] calcium silicate hydrates (C–S–H) have good sorption properties, and their application as carriers allows the development of light and colored rubbers in contrast to use of carbon black. In addition, the silicate has more inert surface than silica[17] and it does not react with the silane.

The main goal of this study was an investigation of properties and morphology of a new powdered synthetic silicate product in order to apply it as a suitable carrier for the silane coupling agents and other rubber ingredients. In our work we used synthetic Calcium Silicate-Hydrate (C–S–H) as a carrier for TESPT and also for an adhesion promoter system in cushion rubber.

Experimental Part

Materials

In this study, we used synthetic C–S–H provided by OJSC Kaustik, Volgograd, Russia. The composition and properties of C–S–H were supplied by the manufacturer (Table 1).

The solid coupling agent Z-6945™ is a mixture of Z-6940™ and carbon black N330 (50/50 w/w). This agent along with the bis(triethoxysilylpropyl)tetrasulfide, Z-6940 are supplied by Dow Corning, USA. The liquid polysulfide, NVB-2 is supplied by OJSC Kazan Synthetic Rubber plant, Kazan, Russia.

Compounding

The rubber compounds were a Bunbary-mixed masterbatches at 120 °C (Table 2). The preparation procedures of the model compound masterbatch and the wire coat compound masterbatch are shown in Tables 3 and 4 respectively. Sulfur, accelerator and promoter have been added using a laboratory mill at 70 °C.

Study of the Silicate Structure

Powder X-ray diffraction (PXD), simultaneous thermo-gravimetrical analysis (TGA) and differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) were used in order to investigate the structure and water content of the silicate. The PXD measurements were performed at room temperature using a Siemens D5000 diffractometer and CuKα radiation ($\lambda = 1.5418$ Å). The TGA/DSC data were collected on a on a NETZSCH STA 409 PC Luxx instrument at a heating rate of 10 $\mathrm{K min^{-1}}$ under flowing nitrogen. SEM images were obtained using a JEOL JSM-6301F Scanning Electron Microscope at an accelerating voltage of 15 kV, a working distance of 15 mm and a beam current of 10 pA.

Table 1.
Composition and some properties of supplied C–S–H.

CaO, %	36.9
SiO_2, %	39.0
H_2O, %	23.9
Cl^-, %	0.2
pH	11.2
DBP number	154

Table 2.
Rubbers formulation.

Tread model compound		
SBR	100 phr	
Silica, Rosil-175®	60	
Processing oil, PN-6®	4	Aromatic processing oil
Stearic acid	2	
Zinc oxide	2	
Accelerator, Sulfenamid T®	2.2	tert-buthyl-2-benzthiasolyl-sulphenamide
Sulfur	2	
Coupling agent, Z-6940®	5–6	
Wire coat compound		
cis-Polyisoprene	100 phr	
Carbon black, N-330	60	
Processing oil, PN-6®	4	
Stearic acid	1	
Zinc oxide	5	
Accelerator, Sulfenamid T®	0.8	tert-buthyl-2-benzthiasolyl-sulphenamide
Polymeric sulfur, Crystex OT33® a)	7.5	
Antidegradant, Acetonanil N®	2	2,4-trimethyl-1,2-dihydroxyquinoline

a) Crystex OT33 was obtained from Flexsys, and the other rubber ingredients were provided by russian producers.

Table 3.
Preparation procedure of the tread model compound masterbatch.

Procedure step	Time, min
rubber mastication	0.25
introduction of ½ part of filler and a coupling agent	1
introduction of the other half of filler and processing oil	4
Introduction of stearic acid and zinc oxide	4

Mechanical Testing

Mechanical properties of vulcanizates were determined using a dynamometer Instron 1122 (GOST 270-75) with pulling rate of 500 mm/min. The compound was cured for 20 min at 155 °C. The samples were cut to double-sided trowels with thickness of 1 ± 0.2 mm using a notching press.

Adhesion Testing

We used a 3L30 cord (Belarus metal plant) with 65% Cu. Pull-out forces were determined using the H-method (GOST 14311-85) with a pulling rate of 100 mm/min. The compound was cured for 30 min at 155 °C. Humidity aging conditions were 96 hours with humidity of 95% at 90 °C. Thermal aging was performed at 100 °C for 72 hours.

Table 4.
Preparation procedure of the wire coat compound masterbatch.

Procedure step	Time, min
rubber mastication	0.5
introduction filler and processing oil	3
introduction of antidegradant, stearic acid and zinc oxide	4

Results and Discussion

The calcium-silicate-hydrate system is complex with more than 30 stable phases known. In our experiments we used crystalline C–S–H with the ratio of CaO:SiO_2 approximately equal to 1. The X-ray measurement (Figure 1) shows that the structure of the synthetic silicate is very similar to minerals of the tobermorite group. The definition of tobermorite's formula is complicated as it is stable over

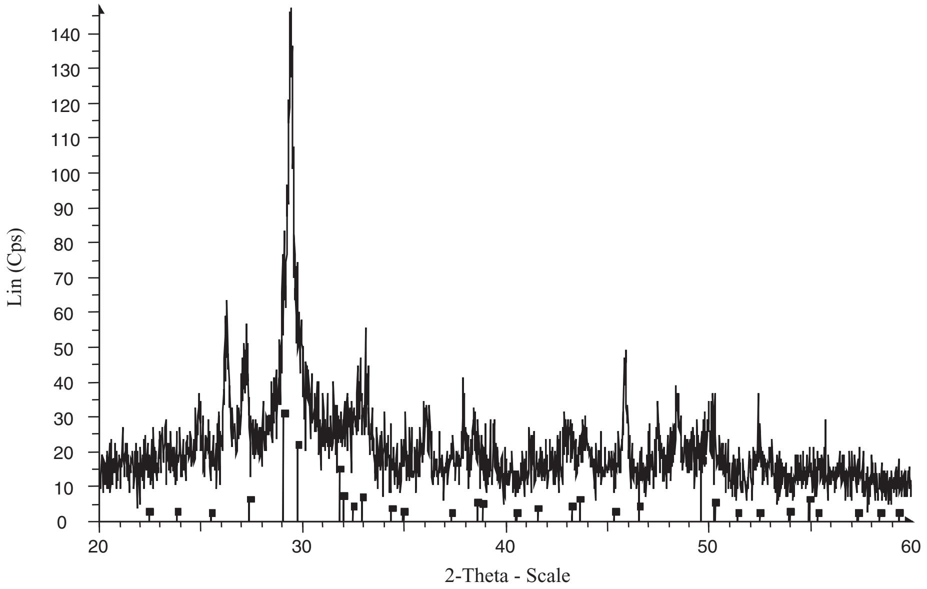

Figure 1.
X-ray diffraction pattern of calcium silicate hydrate at 20 °C; Lines = experimental sample C–S–H, ■ = Plombierite-14 Å - $Ca_5Si_6O_{16}(OH)_2 \cdot 8H_2O$ from the JCPDS database.

a range of compositions from Ca:Si = 0.8 to Ca:Si = 1. This variation is possible due to the nature of tobermorite structure and its intrinsic disorder.[18]

The minerals of the tobermorite group are characterized by wollastonite-type chains connected to sheets of seven-fold coordinated calcium cations. Additional calcium cations as well as water molecules may occupy the structural cavities between adjacent layers. Three polytypes tobermorite exist: tobermorite 14 Å (or plombierite), tobermorite 11 Å, tobermorite 9 Å (or riversideite). They differ from each other by amount of water in the structure. The partial dehydration of tobermorite 14 Å at 80 °C to 100 °C results in the formation of tobermorite 11 Å, subsequent dehydration at 300 °C for few hours gives rise to tobermorite 9 Å.[19]

The structure of tobermorite minerals consists of a central layer of calcium octahedrons, which have silicate sheets on each side. The composite layers, consisting of one calcium and two silicate layers, are bound together by an interlayer (gallery) containing calcium ions and water molecules. The interlayer can contain variable amount of calcium and this causes an accompanying charge alteration. This variation in occupancy is compensated by a change of the number of hydrogen atoms bonded to the silicate chains. Therefore, the variable occupancy of calcium in this layer allows the Ca:Si ratio to vary in tobermorite.[20]

The difference between our obtained X-ray pattern and the one from database is probably caused by a presence of some impurity substances (for instance, the precursors, NaOH, $CaCl_2$, etc). Furthermore, at temperature below 80 °C there may be other closely related calcium silicate hydrates present, which contain more crystal water and this can also affect the X-ray pattern.

TGA- analysis showed that the sample looses mass through the whole temperature range but two distinct steps are clear (Figure 2). In the first temperature range about 50–200 °C evaporation of molecular water and release of adsorbed water from

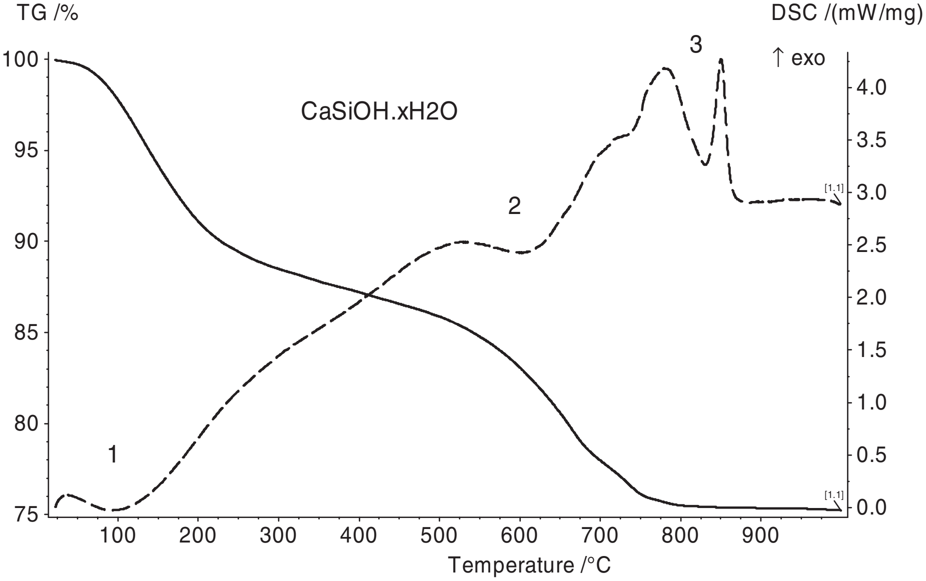

Figure 2.
Thermo-gravimetric (solid line) and differential scanning calorimetry (dashed line) curves of C–S–H.

crystal pores take place. Dehydration of the surface –OH groups starts at temperatures just above 500 °C. Subsequently, release of water molecules occurs due to the formation of Si-O-Si bonds between two different particles. This process can lead to a reduction of specific surface area of the silicate. At approximately 800 °C the sample stops to lose mass. The isotherm at 1000 °C and the cooling cycle showed no significant mass change. Probably the sample becomes $CaSiO_3$ at this stage without any water or –OH groups. The DSC trace shows negative peaks (1 and 2) indicative of endothermic reactions at the start of both of the mass loss processes, so energy is needed for those processes which is consistent with the removal of H_2O (Figure 2). The endotherm at $T \approx 820\,°C$ (peak 3) is not linked to a big change in mass and therefore is most likely a sign of a structural transition.

As shown by the SEM images the calcium silicate particles have the layered structure belonging to the family of layered silicates also known as phyllosilicate (Figure 3). Tobermorite is represented as a sequence of stacked nanometer thick layers that are two-dimensional. As a result of its unique structure, tobermorite possesses the ability to absorb large amount of water and other liquids. The liquid is either sorbed onto a surface of tobermorite or hydrates or forms layers at the interlayer cation site causing swelling.

We developed a solid coupling agent based on the synthetic C–S–H and Z-6940 (50:50). Generally, the coupling agent can be attached to clay fines by various mechanisms including chemical bonding, adsorption, or coating to form a monomolecular layer or oligomer film on the clay minerals surface.[21] The SEM images C–S–H hybrids demonstrate that TESPT coats a C–S–H particle and is adsorb on its surface (Figure 4). The efficiency of solid coupling agent is estimated from mechanical properties of filled rubber vulcanizates (Figure 5). The vulcanizates based on styrene-butadiene rubber containing the silicate carrier have mechanical properties comparable with those of rubbers containing liquid coupling agent. This is a result of effective hydrophobization of the filler

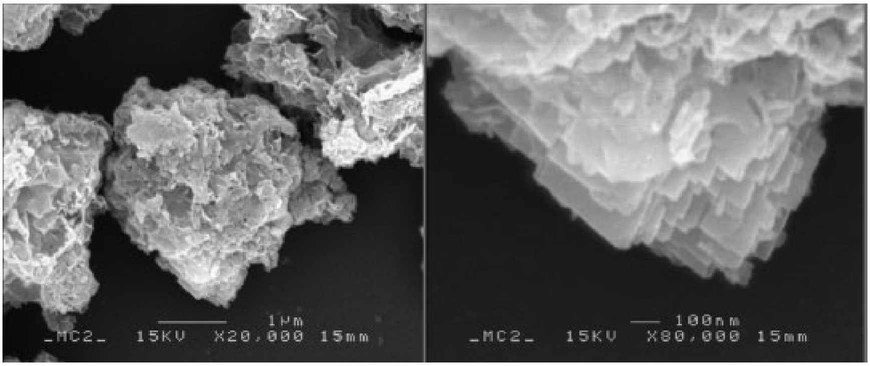

Figure 3.
SEM-images of calcium silicate hydrate.

particles by coupling agent at compounding process. Interaction between TESPT and silica occurs at 120–150 °C, i.e. during the first stage of the compounding process. In this temperature range we consider that C–S–H can release water according to the reaction:

$$Ca_5Si_6O_{16}(OH)_2 \cdot 8H_2O \underset{-4H_2O}{\longrightarrow} Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$$

This water accelerates hydrolysis of the alkoxy group in the TESPT. Then the hydrolyzed –OH group forms a hydrogen bond with a hydroxyl group on the silica surface. Water promotes silanization reactions. As a result of this, increased numbers of siloxane bonds are formed between the silica surface and TESPT. Slight deterioration of rubber mechanical properties containing the C–S–H:Z-6940 system is caused by presence of the surface hydroxyl groups, which could react with silane at a preparation stage. Better mechanical properties of filled rubbers containing coupling agent based on C–S–H indirectly confirm that the surface of C–S–H is sufficiently inert in comparison with silica. Silica carrier probably reacts with the most part of TESPT whereas C–S–H carrier mainly adsorbs it. Hence, when silica is used as a carrier the improvement of mechanical properties of filled rubber may not be achieved.

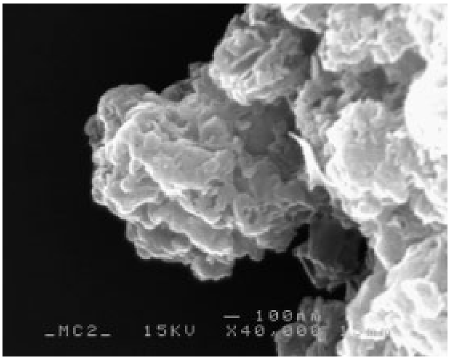

Figure 4.
SEM-images of TESPT deposited on the C–S–H particle.

The reinforcement index of vulcanizates with different solid carriers is shown in Table 5. The rubber containing C–S–H as a carrier for TESPT has better reinforcement properties than the commercial product Z-6945. Hence, the use of C–S–H as a carrier allows us to obtain uncolored rubbers with good technical performance.

In our previous work[22] we developed novel promoter systems for improvement of adhesion between rubber and tire brass-steel cord. These promoters are mixtures comprising an organic salt of metal and LP, while the latter is deposited on an inorganic carrier such as silica. However, because of large specific surface area of the silica particles they constitute highly reactive siliceous materials. The silica is not an inert substrate and interacts

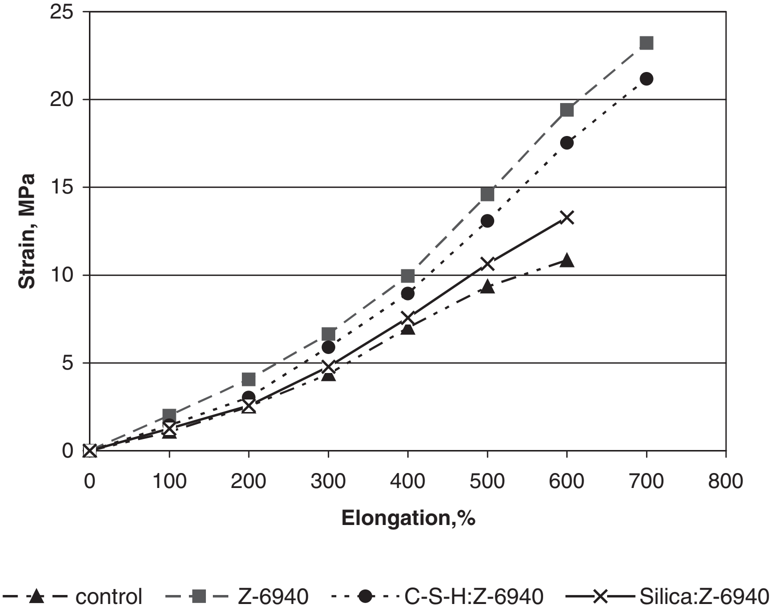

Figure 5.
Strain stress curves of silica filled SBR rubbers containing different coupling agent. All compounds contain an equal amount of Z-6940 (liquid coupling agent is 5 phr, solid coupling agent is 10 phr). The control compound does not contain a coupling agent.

with liquid polysulfide and lowers the efficiency of the promoter system as a whole. This fact is corresponded to our LP crosslinking analysis[22] which shows that contain of a gel in a LP and silica mixture is 27% at room temperature. Contrary, LP macromolecules are mainly adsorbed on the C–S–H surface (Figure 6). Contains of the gel in a C–S–H and LP mixture is less than 7% at room temperature which confirms relatively weak combination between the C–S–H particles and LP. Therefore, in processing of rubber compound C–S–H can desorb more amount of LP.

Replacement of the silica carriers with the synthetic C–S–H allowed us to improve adhesion stability of a brass-coated steel

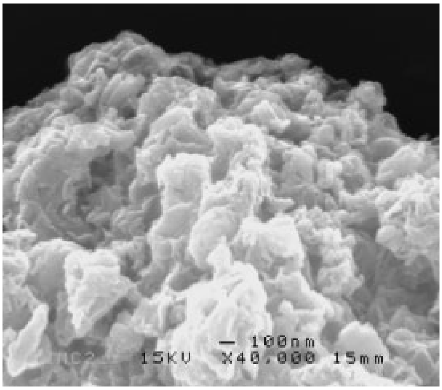

Figure 6.
SEM-images of TESPT deposited on the C–S–H particle.

Table 5.
Reinforcement index of silica filled SBR vulcanizates filled with different carriers (liquid coupling agent is 6 phr, solid coupling agent is 12 phr).

Sample	Z-6940	C–S–H:Z-6940	Z-6945	Silica:Z-6940
Carrier	None	Tobermorite	N-330	Rosil-175
F_{300}/F_{100}	5.89	5.14	4.94	3.35

Table 6.
Adhesion properties of the wire coat rubber containing different promoters. Experimental systems contain equal amounts of Co-stearate and LP.

Promoter	Experimental system	Experimental system	Co-stearate	Manobond 680 c
Carrier	C–S–H	Rosil-175	None	None
Co amount in rubber, %	0.06	0.06	0.09	0.1
Adhesion strength between rubber and brass coated steel cord, N				
20 °C	379	374	327	374
100 °C	294	254	235	298
Thermally aged	274	211	252	276
Humidity aged	216	205	212	233

cord to rubber at humidity aging without deterioration of initial adhesion performance. The adhesion strength of the rubber containing C–S–H as a carrier for promoter system is comparable with most commercial promoters though the content of the metal ions is less (Table 6).

A decade ago W. J. Van Ooij[23] showed that organic metal salts deposited on a substrate are much more active than if they were used without any support. In the case with a substrate, the salts work as slow-release systems. The interesting data were published by Japanese researchers.[24] It appears that widely used promoter systems are less efficient or even ineffective if they have no moisture, and the addition of some water to the promoters is required in a number of cases. The water that is contained in C–S–H structure could act as a transport agent for metal ions, so it would be released slowly along with the metal ions during a vulcanization process. This would result in a better control over amount of metal ions actually supplied to the cord surface.

Conclusions

We demonstrated successful application of synthetic C–S–H as a carrier for various ingredients. Structural investigation showed that the synthetic calcium-silicate-hydrate is related to the tobermorite minerals, and as shown by our TGA measurements its layered structure contains some water that is trapped in gallery between neighbor layers. The good adsorption ability of C–S–H is determined by high dispersity, its layered structure and the chemically inactive surface. In contrast to silica the C–S–H carrier contains smaller amounts of the surface hydroxyl groups, which could react with functional groups TESPT and LP. Liquid ingredients are mainly adsorbed on the C–S–H surface forming a hydrophobic layer on the particles surface. This improves material distribution in the polymer matrix. Then, at processing of the rubbers these ingredients are easily desorbed and participate in formation of a polymer composite.

Recent investigations demonstrate that water plays an important role in the various chemical processes in rubber during compounding and vulcanization. Moisture catalyzes coupling of the bifunctional silane on the silica surface and is also involved in the formation of the interfacial sulfide layer between rubber and a brass-coated steel tire cord. Therefore, the use of materials containing a certain amount of water in their structure allows better control over the aforesaid processes and results in rubbers with good performances.

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