

Zn-DOPED BOROSILICATE GLASS POWDER AS ZnO SUBSTITUTE IN RUBBER COMPOUNDS

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Introduction

The huge diversity of rubber applications becomes possible both by the variety in the recipe of the rubber mixtures in particular by the vulcanization system and the fillers. Mainly carbon black and silica have been used successfully in technical rubber goods and tires. A novel approach of filling of elastomers was developed as foamed borosilicate glass particles (TP) were inserted into the rubber mixture. Foamed borosilicate glass was generated by extrusion of glass melt using a specific foaming agent and subsequent cooling and milling of the glass foam. Additionally, the procedure allowed a modification of the surface of the glass particles. Currently, the knowledge of the influence of porous glass powder on the processing and vulcanization behavior as well as on the resulting application properties of rubber mixtures is rather small. Therefore, the present research deals with the investigation of the influence of type, chemical composition and morphological performance of the glass powder on the reaction behavior of the crosslinking agents, the processing behavior and final application properties. Unmodified as well as zinc-doped glass powders (ZnTP) were used in SSBR, BR and SSBR/BR blends.

Porous glass powder as filler in rubber mixtures

The application properties of rubber can be influenced in a broad manner by blending, variation of crosslinking system, insertion of several processing aids, plasticizers and stabilizers as well as especially by the addition of fillers. Fillers influence both the processing and vulcanization behavior as well as the final properties of the vulcanized rubber too. In practice of elastomer technology, concerning the fillers, carbon black has still the highest industrial importance, but the market part of silica increases mainly due to the continuous development of the silane technology. It is well known that carbon black and also silica as so called active fillers does not act as reinforcing agents only, but they influence also the viscosity of the mixture and the crosslinking behavior significantly. Consequently, the processing behavior and the final properties are impressed definitively. Generally, the modification of elastomers by means of carbon black or silica bases on the filler-filler as well as filler-polymer interactions, but also the interactions between filler and crosslinking agents as well as other

processing or vulcanizing aids like plasticizers or stabilizers have to be taken into consideration.

The fabrication of the porous glass powder particles was realized via extrusion of glass foam with subsequent cooling and milling of the foam followed by particle classification (Fig. 1) [1].

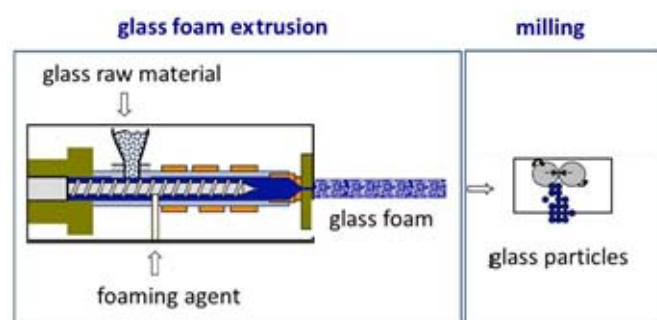


Fig. 1 Scheme of the production of porous glass-foam particles

The glass particles have an irregular shape and surface (Fig. 2a) and an average particle size of some micrometers (2-18 μm) (Fig. 2b). The procedure allowed a modification of the surface of glass particles.

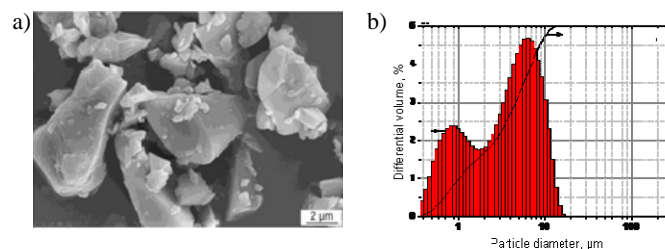


Fig. 2 SEM micrograph (a) and particle distribution (b) of borosilicate glass powder

Unmodified (TP) as well as zinc-doped (ZnTP) glass particles were produced. The application of Zn-doped borosilicate glass opens up the opportunity for a target-oriented manipulation of the vulcanization process. The question has been of specific interest whether zinc oxide (ZnO), which is commonly used as vulcanizing activator, can be substituted by ZnTP, because ZnO was identified to be toxic for organisms in water [2].

Solution styrene-butadiene (SSBR)- and polybutadiene (BR) rubber - glass powder compounds

Vulcanization behavior of SSBR, BR and their blends with ZnTP

Both the unmodified as well as the zinc doped glass powders were used in SSBR, BR and SSBR/BR blends. The recipes of the SSBR and BR single mixtures are displayed in Table 1. The rubber mixtures were produced by means of the Brabender Plasticorder PL 2000 with temperature and time regime adapted to the composition of the rubber mixtures [3].

Table 1. Composition of SSBR and BR based compounds and blends with ZnTP

Component [phr]	incl. activators (standard) [phr]	without activators	“adapted” activator	ZnTP [phr]
a) SSBR			a) 100	
b) BR			b) 100	
c) SSBR/BR			c) 60/40	
S			1.4	
CBS			1.5	
StA	1	0	2.17	0
ZnO	2.5	0	0.29	0
ZnTP	0	0	0	2.5 / 5 / 7 / 10

The influence of ZnTP on the vulcanization behavior of the used rubbers was characterized by means of the vulcameter Scarabaeus SIS-V50 (TA Instruments). The measurements were realized at a frequency of 1.67 Hz in the temperature range of 150-190°C. Torque moment ΔM , incubation time t_i , conversion time t_{90} , activation energy E_A and reaction rate ν were determined from the vulcameter data.

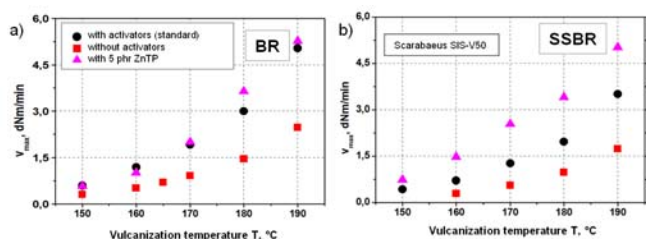


Fig. 3 Vulcanization rate of BR (a) and SSBR (b) in dependence on temperature and type of activator

Fig. 3 shows that the reaction rate depends both on the temperature and the composition of the single rubber systems SSBR and BR. While in case of BR the reaction rate of ZnTP activated BR has nearly the same dependence on temperature like the ZnO activated BR, in case of SSBR the same content of ZnTP accelerated the reaction rate significantly. It is assumed that ZnTP promotes the scission reaction of the vulcanizing agent CBS, hence the incubation time decreases and the reaction rate increases. The torque moment seems to be unchanged, i.e. the glass particles do not have a negative influence on the viscosity of the system [3].

The SSBR/BR blends were produced by means of the laboratory kneader Brabender Plasticorder PL 2000. The AfM image (Fig. 4) shows the heterogeneous character of the blend with island-matrix morphology. Despite of the heterogeneous character, it is assumed that co-vulcanization between the polymer components happens. Fig. 5 demonstrates that the substitution of the activators ZnO and StA by ZnTP results in a significant decrease of the incubation

time as well as in the increase of the reaction rate in comparison to the standard system. That corresponds

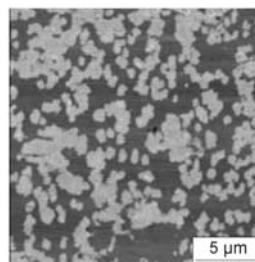


Fig. 4 Phase morphology of unfilled SSBR/BR blend 60/40. AFM, phase image

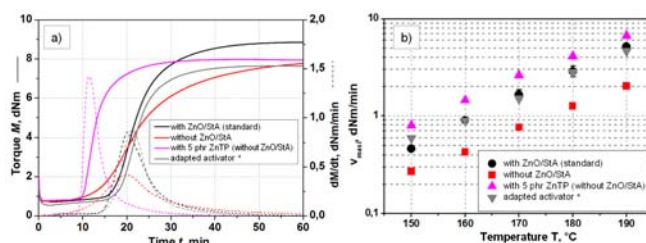


Fig. 5 Crosslinking isothermes at 160°C (a), and reaction rate (b) of SSBR/BR blends 60/40 with and without activators as well as with 5 phr ZnTP

to the behavior of the single rubber systems and confirms the assumption that ZnTP promotes the scission reaction of the vulcanizing agent CBS. The same crosslinking mechanism is running in the co-vulcanizing SSBR/BR blend too.

Mechanical behavior of SSBR/BR blends with ZnTP

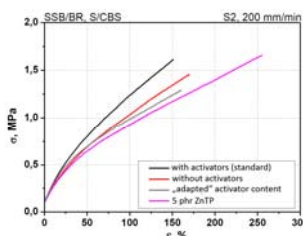


Fig. 6. Stress-strain behavior of SSBR/BR blends with different activators

The stress-strain behavior of the rubber compounds was characterized by means of a Zwick tensile tester Z005 at room temperature and the testing rate 200 mm/min using specimen typ S2. The stress-strain behavior of SSBR/BR blends with different activators and in dependence on ZnTP content is represented in figure 6. The stress-strain curve of the 5 phr ZnTP activated SSBR/BR blend runs below the curve of the standard mixture, but reaches higher ultimate stress and strain values. While the stress values σ_{50} and σ_{100} are only slightly reduced, the ultimate stress gains with increasing ZnTP content. Simultaneously, the elongation at break increases in the same manner.

References

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