Flokkulation in Kieselsäure-verstärkten Gummimischungen: Studie zum Einfluss der Füllstoff-Polymer Wechselwirkung und Morphologie
Silica Flocculation: Study of Filler-Polymer Morphology and Interaction

W. K. Dierkes (Sp), R. N. Datta, J. W. M. Noordermeer, University of Twente, Enschede (NL);
S. Mihara, N. Amino, Y. Ishikawa, The Yokohama Rubber Company, Ltd., Kanagawa (Japan);
S. Nishitsuji, M. Takenaka, Kyoto University (Japan)

ABSTRACT

Filler-filler and filler-polymer interaction play a crucial role for the reinforcement of rubber. Strong filler-polymer interactions result in high bound rubber contents and facilitate dispersion, both improving the material properties. However, in silica-reinforced compounds, the filler tends to flocculate or demix during the heating period of the vulcanization process, which negatively influences the properties. This flocculation can studied by ultra-small-angle X-ray scattering (USAXS).

The radius of the aggregates R_a and their mass-fractal dimension D_m, which indicate the degree of aggregation and agglomeration, were estimated for a highly-dispersible (HD) and a conventional (CV) silica in a 80 phr reinforced tire tread compound. The aggregate radius of CV silica is relatively high and increases faster as the radius of HD silica during vulcanization. This translates into a flocculation rate of CV silica which is relatively fast compared to the rate of HD silica. For the CV-type silica, the mass-fractal dimension D_m is low, but increases fast during vulcanization, whereas the HD silica shows no significant change.

Bound rubber measurements show that the thickness of the polymer layer decreases with increasing CTAB surface. The reinforcement index M_{300}/M_{100} shows a positive correlation with chemically bound rubber, which is independent of the type of silica. The bonding ability of butadiene to the filler is about half of the ability of styrene-butadiene rubber.

Introduction

It is generally known that the hierarchical structure of fillers such as the primary particles, aggregates and agglomerates can still be recognized in a filled rubber. The presence of remaining agglomerates negatively affects the reinforcing properties of the fillers in rubber, while the aggregates are the real reinforcing species. The reinforcing properties strongly depend on the following factors:

- the degree of physically linked aggregates in the filler network, as often quantified by the Payne effect, and
- the polymer-filler interaction, for example described as bound rubber.

It is well known that silica tends to agglomerate / flocculate to some extent during the early stages of vulcanization, causing an extra hub in the curemeter-curve.[1] Small-angle X-ray scattering is a useful technique for 3-dimensional characterization in order to understand the morphological properties of fillers in a rubber matrix and to trace the kinetics of filler flocculation.[2,3] It can be used to characterize the changing filler morphology in a silica-filled rubber compound.

The tendency of a polymer to get adsorbed onto the filler surface can be measured by pyrolysis gas chromatography. The measurement of physically and chemically bound rubber allows determining the thickness of the bound rubber layer using the Tokita-Pliskin equation, which gives the correlation between the volume fraction of bound rubber V_b, the thickness of the bound rubber layer b, the fraction of the filler surface exposed to the polymer sol S, the volume fraction of silica Φ, the density of silica ρ and the gel fraction Γ:[4]

$$V_b = b \cdot f \cdot \left(\frac{\phi \cdot \rho \cdot S}{1-\phi} \right) + \Gamma$$

Experimental

Component	phr
S-SBR, OE	103.0
BR	25.0
Silica	80.0
TESPT	Var.
Aromatic oil	4.4
Zinc oxide	2.5
Stearic acid	2.5
Sulfur	Var.
CBS	1.7
DPG	2.0

Tab. 1: Compound formulation

Sample preparation: The compound formulations are based on a typical tire tread compound according to the fuel-saving green tire technology as shown in Table 1. Two types of silica, highly dispersible (HD) silica (Zeosil 1165MP, Rhodia Silices) and conventional (CV) silica (Ultrasil VN3, Evonik) are used. The amount of TESPT was adjusted according to the CTAB surface area. The total amount of active sulfur was adjusted to 2.1 phr, being the sum of the sulfur contained in the silane and in the curatives. The compounds were mixed in 2 steps in a tangen-

1

tial mixer. The temperature setting of the mixer was 60 °C, and the dump temperature was kept below 160 °C. The curatives were mixed in on a two roll mill in the third step.

Ultra small-angle X-ray scattering (USAXS) measurements: The USAXS measurements were done at ambient pressure at the Spring-8 at the Japan Atomic Energy Research Institute. The X-ray scattering was detected using the pixel detector covering a q-range of 0.01-0.4 nm^{-1} at a wave length of 0.5 Å. The distance between the sample and the detector was approximately 40 m. The time division method was applied in the present investigation. Data correction was done for sample transmission and for background scattering arising from air and fused quartz in the thermostatic chamber.

The unified approach developed by Beacauge was applied for curve fitting for estimation of the structural parameters such as R_{ss}, corresponding to the aggregate size. At low scattering angles, two Guinier regions corresponding to the two levels of aggregate and agglomerate sizes, can be seen. The power-law decay in this region indicates the mass-fractal dimension D_m.

Bound rubber was determined by immersing the sample in toluene for 72 hours. Chemically bound rubber was measured after treatment in ammonia atmosphere for 72 hours.

Bonding ability was estimated from the ratio of bound BR and SBR. This ratio was determined by pyrolysis gas chromatography on the ammonia-treated sample.
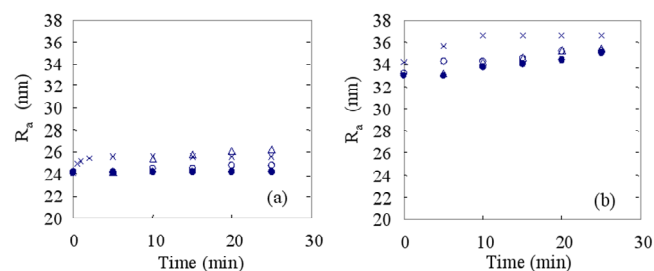
Results

Fig. 1: Radius of aggregates R_a as a function of vulcanization time at specified temperatures
(a): HD silica; (b): CV silica
(●): 90 °C; (o): 100 °C; (Δ): 120 °C; (x): 160 °C

The radius of the aggregate R_a, under the assumption that they are spherical, is increasing during vulcanization as shown in Fig. 1. This radius is linked to R_{ss}, the lower cut-off length of the mass-fractal structure, and hence the aggregate size increases during vulcanization: a proof of flocculation when the material is heated up and before it is sufficiently vulcanized. Both silica types have a primary particle diameter of approximately 14 nm; the aggregate

radii Ra of HD silica and CV silica are approximately 24-26 nm and 33-37 nm respectively before start of the vulcanization: aggregates are rather small.

For CV silica, the increase of aggregate radius R_a during vulcanization is relatively fast compared to HD silica. This corresponds to the flocculation rate of the two silica types estimated by vulcanization speed measurements.[5] In these measurements, an increase of storage modulus G' due to silica flocculation during the heating process is also observed: the increase of G' can be related to an increase of the aggregate size.
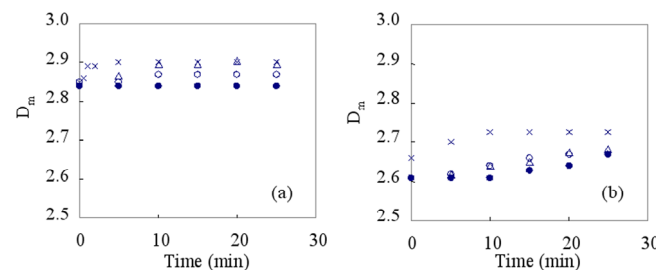

Fig. 2: Mass-fractal dimension D_m as a function of vulcanization time at specified temperatures
(a) HD silica; (b) CV silica
(●): 90 °C; (o): 100 °C; (Δ): 120 °C; (x): 160 °C

As a consequence of the large aggregate radius of CV silica, the hydrodynamic radius is also higher than the one of HD silica. The Stokes-Einstein equation allows estimating the mobility of particles in terms of diffusion based on their hydrodynamic radius: the mobility of CV aggregates is expected to be rather low due to their large radius, and this leads to a lower degree of agglomeration D_m, as seen in Fig. 2.
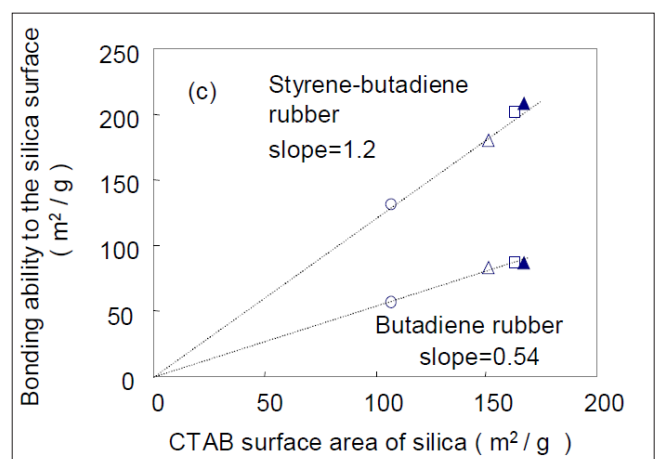

Fig. 3: Bonding ability of BR and SBR as function of CTAB surface

The filler-polymer interaction has been studied by measuring the bound rubber in this SBR/BR blend. It shows that the thickness of the polymer layer decreases with increasing CTAB surface, as the filler-filler interactions are more pronounced with increasing surface area. The re-

inforcement index M_{300}/M_{100} shows a positive correlation with chemically bound rubber, which is independent of the type of silica: the interfacial area available for chemical bonding of the polymer is the dominant factor for reinforcement. The bonding ability to silica is lower by a factor of 2 for BR compared to SBR, see Fig. 3. Pyrolysis gas chromatography measurements of the chemically bound rubber layer on the filler surface show that the bonding ability of butadiene is about half of the ability of styrene-butadiene rubber.

Conclusions

The USAXS technique is useful for real time analysis of silica flocculation. This study showed that the aggregate size of CV silica is relatively high compared to the size of HD silica. The aggregate radii R_a for HD silica and CV silica were estimated as 24-26 nm and 33-37 nm, respectively. The aggregate radius of CV silica increases faster during vulcanization compared to HD silica. This result corresponds to the flocculation rate of silica as estimated from vulcanization kinetic measurements. However, the tendency to agglomerate is lower for CV silica than for HD silica, resulting from the lower mobility of the larger aggregates.

Chemically bound rubber shows a correlation with the reinforcement index M_{300}/M_{100}, and this correlation is independent of the silica type. The bonding ability of the two polymers in this blend differs: the bonding ability of BR is about half of the ability of styrene-butadiene rubber.

Acknowledgement

References

[1] Reuvekamp, L.A.E.M., Debnath, S.C., ten Brinke, J.W., van Swaaij, P.J., Noordermeer, J.W.M.; Rubber Chem. Technol. 77, 34 (2004)

[2] Klüppel, M., Heinrich, G.; Rubber Chem. Technol. 68, 623 (1995)

[3] Göritz, D., Schneider, G.J., Kautschuk Herbstkolloquium of the DIK, Hanover, Germany, 10.-13. Nov. 2004

[4] Pliskin, I., Tokita, N., J. Appl. Polym. Sci. 16, 473 (1972)

[5] Mihara, S.; Datta, R.N.; Noordermeer, J.W.M.; Rubber Chem. Technol. 82, 524 (2009)

10-2330 DKG 5-P-1630 K2.pdf Juni 6, 2012 11:40:46