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FACTORS REDUCING THE MARCHING MODULUS OF SILICA FILLED TIRE TREAD COMPOUNDS

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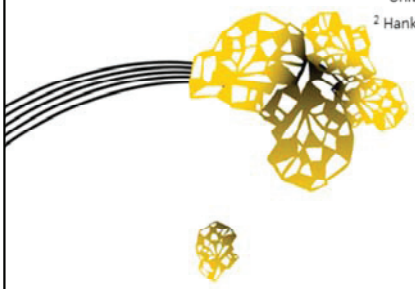

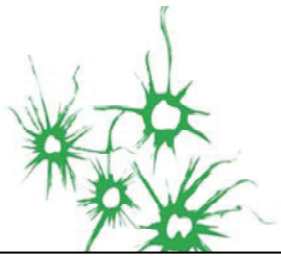

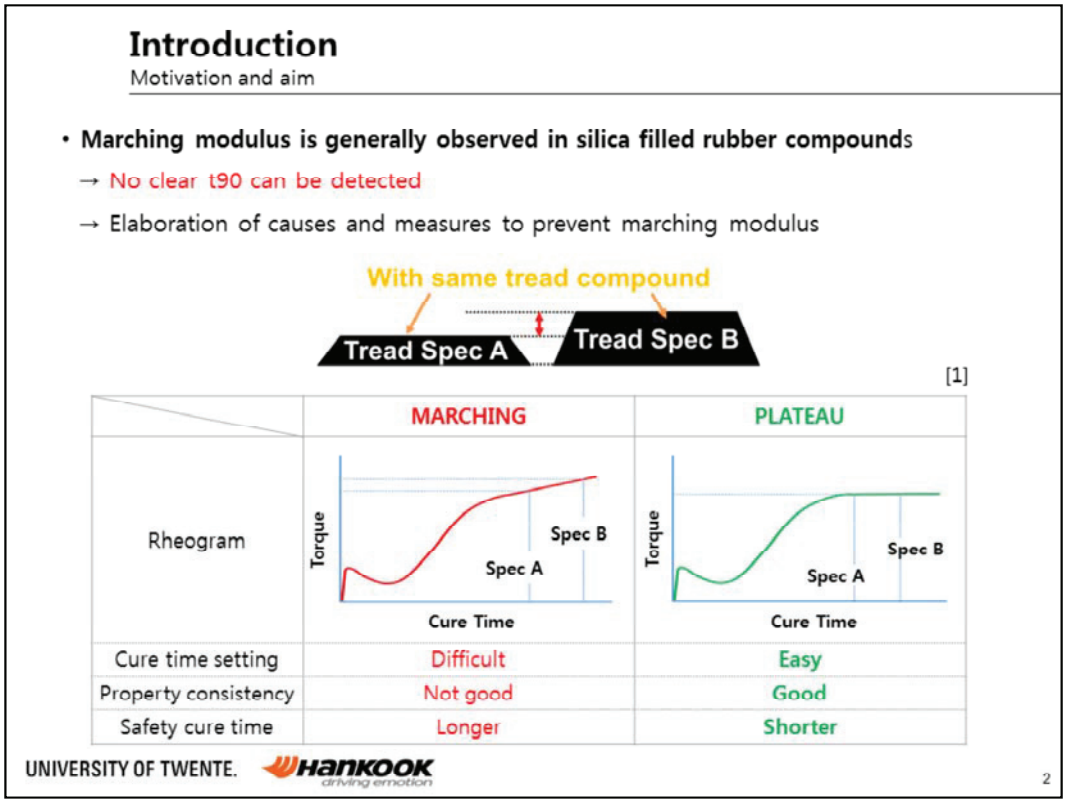

Marching modulus - a crosslinking reaction ongoing for a long period - is often observed in silica filled S-SBR/BR tire tread compounds. This phenomenon makes it difficult to evaluate the correct curing time [1], and as a consequence, the physical properties will vary.

Experimental

Compound formulation

Ingredient	Product name	Supplier	phr
S-SBR※	Buna VSL5025-2HM	Lanxess	110
BR	Buna CB24	Lanxess	20
HD Silica	ULTRASIL7005 (CTAB: 164m^2/g)	Evonik	90
Silane (TESPT)	Si69	Evonik	8.05
TDAE Oil	VIVATEC 500	Hansen & Rosenthal	5
Stearic acid	Stearic acid	Merck	1
Zinc Oxide	ZnO	Merck	2
DPG	Perkacit DPG	Flexsys	1.5
Sulfur	S	J. T Baker	0.7
ZBEC	Vulkacit ZBEC	Lanxess	0.2
CBS	Santocure CBS	Flexsys	2.2

※27,3 wt% oil extended

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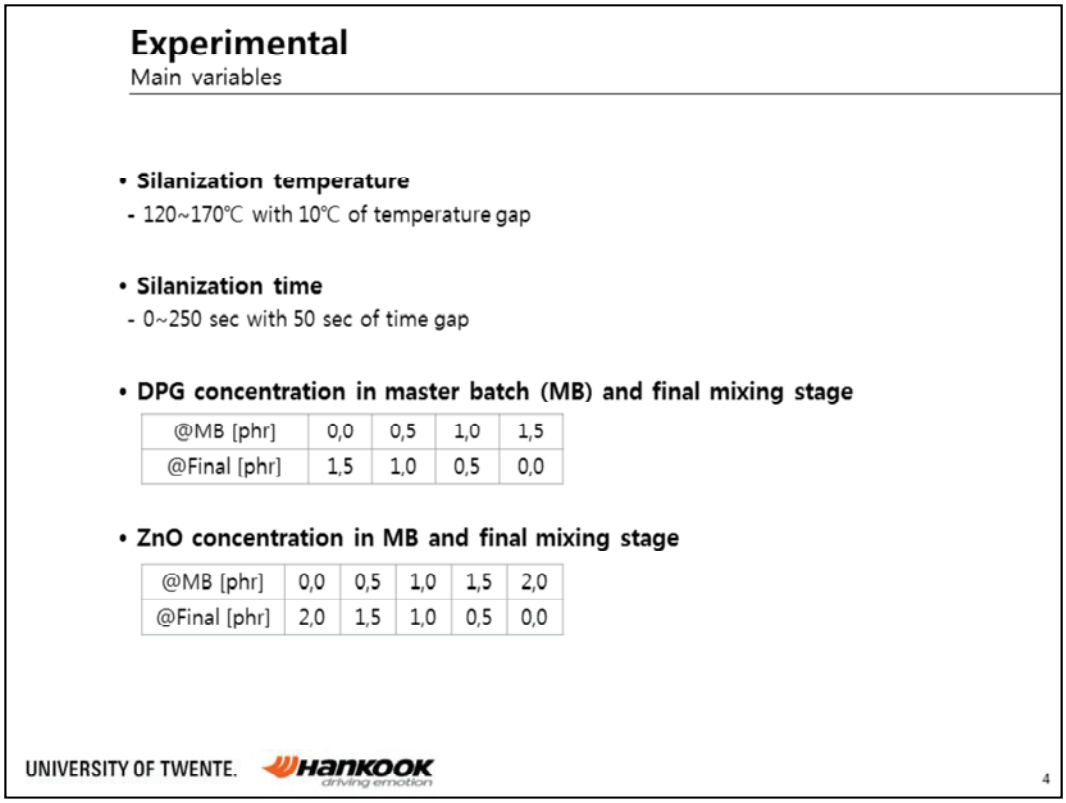

In this work, four main variables, which are well known as influencing factors for the degree of silanization, are taken into account. The variation gap and the range of DPG and ZnO concentrations in the MB and final mixing stage were determined according to the model compound formulation which is shown in previous page.

Experimental

Mixing procedure: master batch mixing stage

Silanization temperature		Silanization time		DPG concentration @ MB stage		ZnO concentration @ MB stage	
Action	Action time [sec]	Action	Action time [sec]	Action	Action time [sec]	Action	Action time [sec]
Add polymer	20	Add polymer	20	Add polymer	20	Add polymer	20
Mastication	60	Mastication	60	Mastication	60	Mastication	60
Add ½ Silica, Silane	30	Add ½ Silica, Silane	30	Add ½ Silica, Silane	30	Add ½ Silica, Silane	30
Mixing	60	Mixing	60	Mixing	60	Mixing	60
Add ½ Silica, other remains	20	Add ½ Silica, other remains	20	Add ½ Silica, Oil, ZnO, St.Acid, (DPG)	20	Add ½ Silica, Oil, DPG, St.Acid, (ZnO)	20
Mixing (Up to 120~170℃)	60	Mixing (Up to 150℃)	60	Mixing (Up to 150℃)	60	Mixing (Up to 150℃)	60
Ram sweep	4	Ram sweep	4	Ram sweep	4	Ram sweep	4
Mixing (at target temp.)	150	Mixing (at 150℃)	0~250	Mixing (at 150℃)	150	Mixing (at 150℃)	150
Discharge	-	Discharge	-	Discharge	-	Discharge	-

- Fill Factor: 63%
- TCU setting: 50℃ / 70℃ (for the silanization temperature test at 170℃)
- Starting Temp.: 55℃ (After B0 mixing)
- Starting rotor speed: 100RPM

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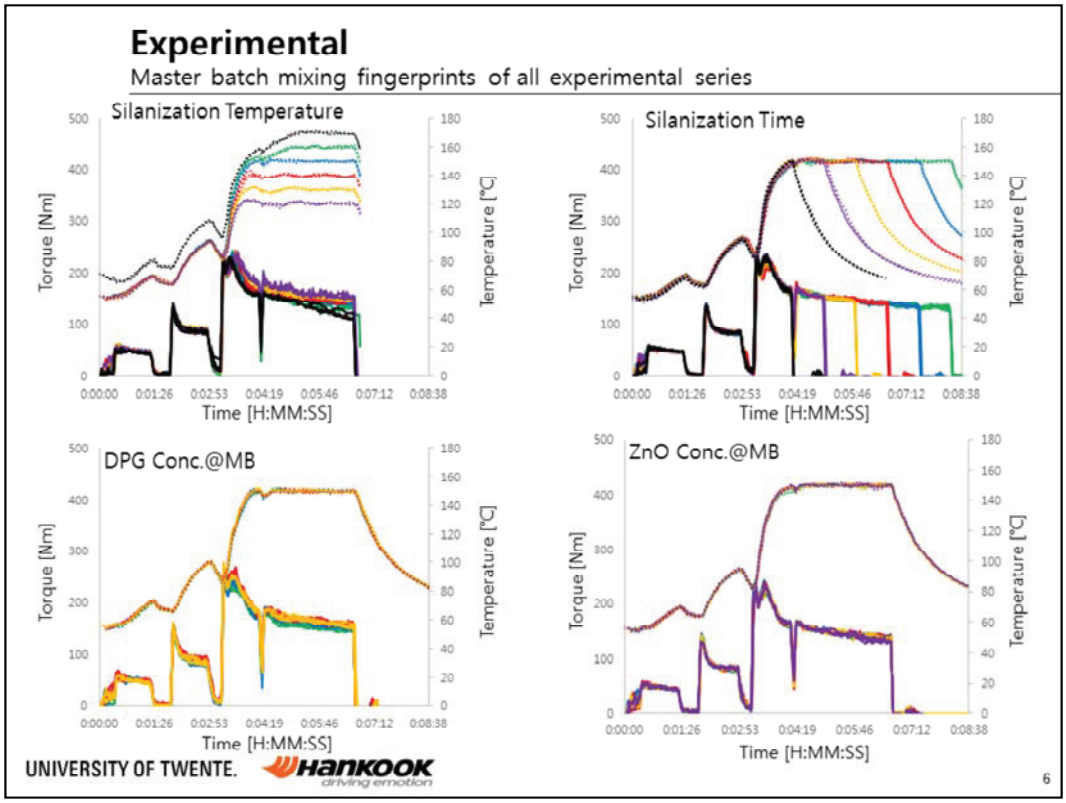
The compounds were mixed in 2 stages. The master batch stage was done using a lab scale internal mixer (Brabender Plasticorder) with a 390 ml chamber. The fill factor of the mixer was fixed at 63%: the mechanical load of the mixer was taken into account when determining the fill factor. The mixer temperature control unit (TCU) was set at 50ºC except for the silanization temperature test at 170ºC: 70ºC of TCU temperature was applied for this test. In order to avoid the first batch effect, one initial batch (B0) was mixed before the regular mixing started. After B0, the regular mixing was started when the mixing chamber reached 55ºC. After the first mixing step, the compounds were sheeted out immediately on a lab scale two-roll mill (Polymix 80T) in order to cool down the compound and prevent further reaction. Three batches were mixed for each set of conditions in order to check the reproducibility.



All batches were mixed with good reproducibility.

Experimental

Mixing procedure: final mixing stage on two roll mill

Silanization temperature		Silanization time		DPG concentration @ MB stage		ZnO concentration @ MB stage	
Action	Action time [sec]	Action	Action time [sec]	Action	Action time [sec]	Action	Action time [sec]
Add master batch	-	Add master batch	-	Add master batch	-	Add master batch	-
Milling	120	Milling	120	Milling	120	Milling	120
Curatives	30	Curatives	30	Curatives, (DPG)	30	Curatives, (ZnO)	30
Milling	350	Milling	350	Milling	350	Milling	350
Discharge	-	Discharge	-	Discharge	-	Discharge	-

- Roll TCU setting: 40°C

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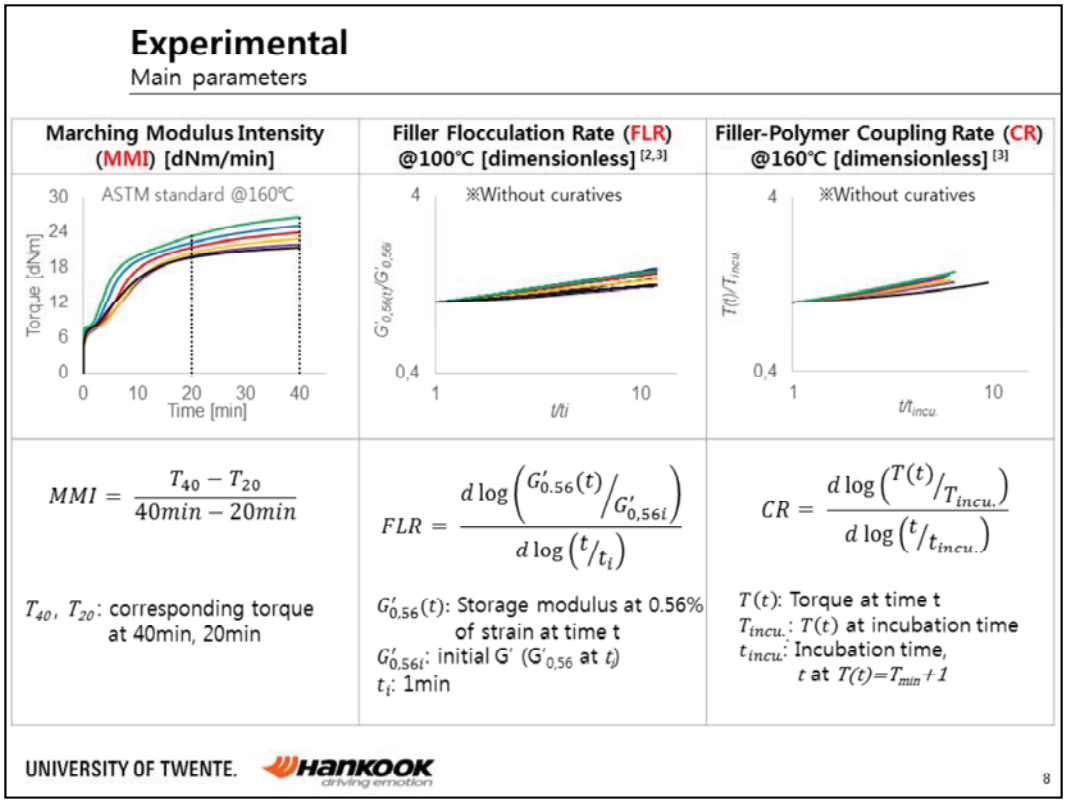
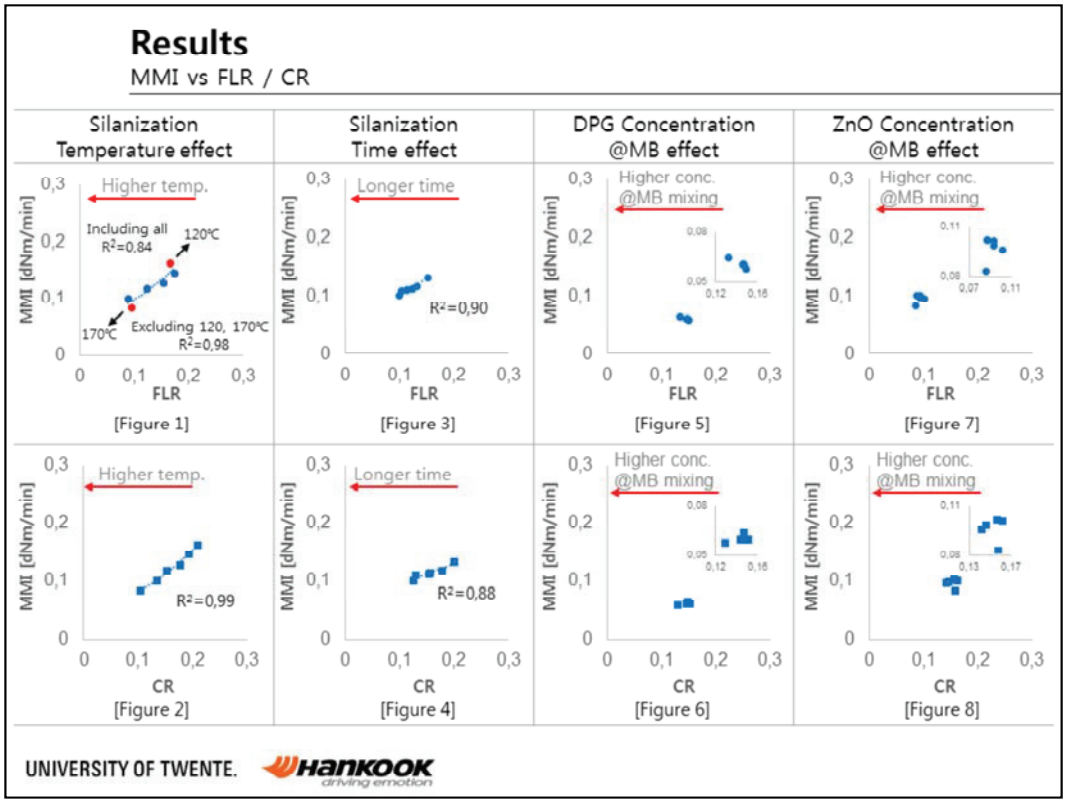
Curatives were mixed in on the two roll mill in the final stage.



Mathematical expressions were made for the main parameters: marching modulus intensity (MMI), filler flocculation rate (FLR) and filler-polymer coupling rate (CR). The MMI, FLR and CR were monitored using a Rubber Process Analyzer (RPA).

The MMI is easily calculated from the vulcanization rheogram which was measured under ASTM conditions. The measuring conditions and method for FLR are described in Mihara's [2] work. The CR was measured under the following conditions: 160˚C, 1.677 Hz and 3 degree (≒40%) of strain for 40 minutes. A large strain was applied for the CR measurement in order to break the filler-filler interaction. Therefore, only filler-polymer interaction is taken into account in CR.

In a previous study, Mihara [2] assumed silica flocculation as a first order reaction; however, the silica flocculation rate measured here was best described using a power law or logarithm plot. The kinetics of the coupling reaction followed a power law from the incubation time on. In order to transform those rates into a linear correlation, ASTM D1646-04 [3] was used.



FLR and CR are strongly affected by silanization temperature and time (Figure 1-4). Higher silanization temperatures and longer silanization time result in low FLR and CR as expected. A higher degree of silanization leads to low filler-filler interaction. Dierkes [4] reported that a higher silanization temperature and longer times result in low filler-filler interaction. As a consequence, this leads to a low degree filler flocculation after mixing (Figure 1, 3). However, at 120ºC and 170ºC of silanization temperature, the flocculation rate is out of trend (Figure 1). This means that the silica flocculation has an upper and a lower limit: when the filler-filler interaction gets off limit, the FLR level off. Mihara [2] reported that polymer-filler coupling via the silane coupling agent can occur during mixing. Thus, it is possible that a higher degree of polymer-filler coupling can be established during mixing under the condition of a higher temperature and a longer reaction time. As a result, a lower CR is observed with increasing silanization temperature and time (Figure 2, 4).

DPG and ZnO concentration in the MB mixing stage had just a small effect on MMI, FLR and CR (Figure 5-8). Except for those experiments, MMI showed a moderate to good correlation with both, the flocculation rate and the coupling rate: R^2 was higher than 0,8. This indicates that the curing behavior of the silica compound can be affected by not only the filler-polymer coupling reaction, but also silica flocculation during curing. However, if the silica compound is poorly mixed, then the silica can still flocculate even though it undergoes a vulcanization process. Additionally, a higher amount of remaining free silane is capable to form filler-polymer crosslinks during the vulcanization process, which will lead to higher MMI.

Conclusions

MMI vs FLR / CR

- **Silanization temperature, time ↑ → FLR, CR, MMI ↓**
  - However, FLR has lower and upper limit
- **DPG and ZnO concentration at MB mixing had not much effect on MMI, FLR and CR**
- **Controlling the silanization reaction during mixing is crucial for FLR, CR and the curing behavior**
  - MMI of the silica compound influenced by silica flocculation and the degree of filler-polymer coupling after mixing

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ACKNOWLEDGEMENT

The authors gratefully acknowledge financial and materials support from HANKOOKTIRE CO., LTD. (Daejeon, Korea).

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