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Abstract. Silica-silane technology for low rolling resistance tire compounds requires efficient bridging between the silica surface and rubber molecules through silanization and coupling reactions. The presence of diphenylguanidine (DPG) as secondary vulcanization accelerator is also needed to catalyze the silanization reaction between the alkoxy groups of silane coupling agents and the silanol groups on the silica surface. However, DPG can liberate toxic aniline under high mixing temperatures and therefore safer alternatives are required. This study investigates the influence of amines with different structures, i.e. hexylamine (HEX), octadecylamine (OCT), cyclohexylamine (CYC) and dicyclohexylamine (DIC) on the primary silanization reaction rate constant in a model system, and on interfacial compatibility of practical silica-reinforced NR compounds. Compared to the system without, the amines clearly increase the reaction rate constant for which linear aliphatic amines work better than cyclic ones. This is due to better accessibility of the amines towards the silica surface, in agreement with the values of Payne effect as observed in the rubber compounds, except for the OCT case. The lowest Payne effect of the OCT-containing rubber compound is attributed to the additional shielding effect obtained from the long alkyl-chain that leads to more hydrophobicity, resulting in good physical interaction between silica and rubber. The presence of all amines improves the cure properties in which the linear aliphatic amines give shorter cure times than the cyclic aliphatic ones. As a result of good interfacial compatibility, the OCT-containing compound which shows lowest filler-filler interaction gives good mechanical properties that are closest to the reference compound with DPG.

1. Introduction

Natural rubber (NR) is a renewable resource that is used for several applications in which tires take up a large portion of NR consumption. NR is used in many parts of the tires, especially for truck tire tread compounds while it provides low heat build-up and excellent mechanical properties derived from its ability to form crystals upon being stretched, i.e. strain-induced crystallization. Reinforcing fillers are a crucial ingredient in tire compounds, added to improve tire performances. After the emergence of the "Green Tire" introduced by Michelin for low rolling resistance tire treads, i.e. energy saving tires based on a silica/silane reinforcement system that can reduce about 25% rolling resistance compared to conventional carbon black-filled tire tread compounds [1], the silica technology was widely implemented. However, the mixing of silica into rubber compounds encounters the incompatibility problem, that can be overcome by using a silane coupling agent. Interfacial interaction of the silica/silane-reinforced rubber compounds is

obtained via chemical bonding between the silica surface and rubber matrix by silane bridge formation. The reaction between silanol groups on the silica surface and alkoxy groups in the silane molecules, the so-called silanization reaction [2-4], occurs via a condensation reaction during mixing of the rubber compounds. Thereafter, the sulfur moiety in the silane molecule reacts with the rubber chains during the vulcanization reaction [4].

Diphenyl guanidine (DPG) is widely used as secondary accelerator in rubber compounds to provide a synergistic effect with the primary accelerators such as sulfenamides and thiazoles. For the silica/silane system DPG is found to also act as a silanization catalyst [5]. Further, the DPG provides a positive effect on deactivation of free silanol groups that are left over after the silanization reaction. However, the DPG can liberate toxic aniline during high temperature mixing, i.e. compounding and vulcanization [6]. Aniline has been classified as a probable carcinogenic substance [7]. Several amines have been investigated to find an alternative for DPG. The effect of different amine types with varying acid dissociation constant (pKa) values on the rate constant of the silanization reaction was studied by Mihara [8] using model compounds. It was found that the rate constant of the silanization reaction increases while the activation energy decreases with increasing pKa values from 6.5 to 11.5.

The present study covers the effect of different amine types having similar pKa values but different structures. Linear aliphatic amines, i.e. hexylamine (HEX) and octadecylamine (OCT), and cyclic aliphatic amines, i.e. cyclohexylamine (CYC) and dicyclohexylamine (DIC), are compared in both a model system and practical silica-reinforced natural rubber compounds. The silanization efficiency of the silica/silane systems having different amines is evaluated by their rate constant of the primary silanization reaction. Then, the properties of rubber compounds with these different amine types are tested.

2. Materials and methods
2.1. Materials
The chemicals used in the model compound study were ULTRASIL7005 silica and bis-(3-triethoxysilyl-propyl)tetrasulfide (TESPT) (both from Evonik, Germany), anhydrous-grade decane and diethyleneglycolmonobutylether (both from Sigma-Aldrich Chemie, Germany). Diphenyl guanidine (DPG) was obtained from Flexys, Belgium. Amines used in this study as alternatives for DPG were hexylamine (HEX), octadecylamine (OCT), cyclohexylamine (CYC) and dicyclohexylamine (DIC) (all from Sigma-Aldrich Chemie, Germany). The chemical structures of all amines used in this study are shown in Fig. 1. The ingredients used in rubber compound study were Ribbed Smoked Sheet (RSS#3)-grade Natural Rubber (NR) (locally produced in Thailand), Treated Distillate Aromatic Extract (TDAE) oil (Vivatec 500, Hansen & Rosenthal, Germany), 2,2,4-Trimethyl-1,2-dihydroquinoline (TMQ) (Flexys, Belgium), zinc oxide, stearic acid and sulfur (all from Sigma-Aldrich Chemie, Germany).

2.2. Model compound study
Mixtures containing 0.5 g of silica, 0.94 mmol of TESPT, 0.30 mmol of the respective amines and 4 ml of decane in ampoules were immersed into an oil bath at 135 ± 2°C for different reaction times. Then, the reactions were quenched by cooling in an ice bath. All physical interactions were removed by adding 2 ml of diethyleneglycolmonobutylether. The resulting mixtures were filtered by using filter paper. The concentration of ethanol (EtOH) was determined by gas chromatography (GC) using a GC-2010 plus (Shimadzu, Kyoto, Japan). The rate constant of the primary silanization reaction was calculated by plotting $ln\ [TESPT]_t - ln\ [TESPT]_0$ against time t; where $[TESPT]_t$ is the TESPT concentration at time t and $[TESPT]_0$ is the initial TESPT concentration. The rate constant of the primary silanization reaction is obtained from the slope of the plot [2].
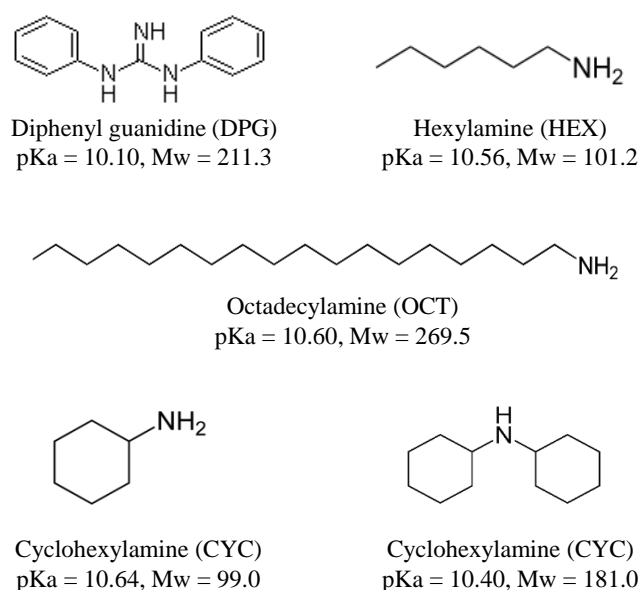
Fig. 1. Chemical structures of amines used in this study.

2.3. Rubber compound study

Rubber compounds were prepared in an internal mixer (BrabenderPlasticorder 350S) with mixing conditions of fill factor 0.7, initial mixer temperature setting of 100°C, and rotor speed of 60 rpm. The rubber formulation and mixing procedure are shown in Tables 1 and 2, respectively. The discharge temperature after the first mixing step of all mixes containing the respective amine types were in the range of 131-135°C. The rubber compounds obtained from the first mixing step were tested for the property that can be related to filler-filler interactions, i.e. the Payne effect.

Table 1. Compound formulations.

Ingredient	Quantity (phr)
NR	100
Silica	55
TESPT	5
ZnO	3
Stearic acid	1
TMQ	1
TDAE oil	8
DPG*	1.1
CBS	1.5
Sulfur	1.5

* Other types of amines were used based on molar equivalents to 1.1 phr of DPG.

Table 2. Compound mixing procedures.

Cumulative mixing time (min)	Step of mixing
1st step: Internal mixer	
0	NR
2	½ Silica + ½ TESPT + ¼ amine
7	½ Silica + ½ TESPT + ¼ amine + TDAE oil
12	ZnO + Stearic acid + TMQ
15	**Discharge**
2nd step: Two-roll mill	
0	CBS + ½ amine
2	S
5	**Mixing completed**

2.4. Testing and characterization

2.4.1 Payne effect

The storage shear moduli (G') of the rubber compounds without curatives were evaluated by using a Rubber Process Analyzer (RPA) (Alpha Technologies, Akron, USA) at a temperature of 100°C, frequency 0.5 Hz and varying strains in the range of 0.28-100%. The Payne effect was calculated from the difference in storage shear moduli at low strain (0.56%) and high strain (100%), i.e. G'(0.56%)-G'(100%).

2.4.2 Cure characteristics

The cure behaviors (i.e., scorch time and optimum cure time [$t_{c,90}$]) of the rubber compounds were tested using the RPA at 150°C, frequency 0.833 Hz, and 2.79% strain.

2.4.3 Tensile tests

Type 2 dumbbell test specimens were prepared, and the tensile properties (i.e., modulus at different strains, tensile strength, and elongation at break) were tested with a Zwick tensile tester model Z1.0/TH1S (Zwick Roell Group, Ulm, Germany) at a cross-head speed of 500 mm/min according to ASTM D412.

3. Results and discussion

3.1. Rate constant of silanization reaction

The silanization or condensation reaction takes place between silanol groups on the silica surface and alkoxy groups on the silane molecules in which the silanization efficiency depends on the adsorption of silane onto the silica surface. The amines play a role as basic catalyst for the silanization reaction promoting more nucleophilicity on the silica surface via hydrogen bonding between the amino group in the amines with silanol groups on the silica surface. Thereafter, the silica surface can easily interact with the silicon atom in the silane molecules through a

pentacoordinate intermediate prior to the condensation reaction, resulting in enhancement of the silanization reaction [9-11]. Rate constants of the primary silanization reaction of the model silica/silane systems with different amine types are shown in Fig. 2, in comparison with the system without amine. Due to the enhanced silanization reaction by amines, the mixtures with amines show much higher rate constants of the primary silanization reaction than the one without amine. Compared to the one without amine, the use of DPG, HEX, OCT, CYC and DIC increases the rate constants of the primary silanization reaction by 256, 266, 194, 192 and 79%, respectively. The linear aliphatic amines enhance the reaction better than the cyclic aliphatic amines. The increase of carbon atoms in the linear aliphatic amines from 6 to 18 carbon atoms reduces the rate constant of the primary silanization reaction by 72% due to less mobility of the larger molecule and less accessibility to the silica surface. In case of cyclic aliphatic amines, a reduction by 113% of the rate constant of the primary silanization reaction is observed when the number of aliphatic rings is increased from one to two, causing steric hindrance. It is clear that the structure affects the adsorption efficiency of the amines on the silica surface. The straight alkyl-chains can adsorb easier on the silica surface than the cyclic structures. With regard to DPG that contains two bulky groups of aromatic rings in the structure but still displays a high rate constant of the primary silanization reaction, its three polar –NH groups help to enhance the adsorption efficiency onto the silica surface.
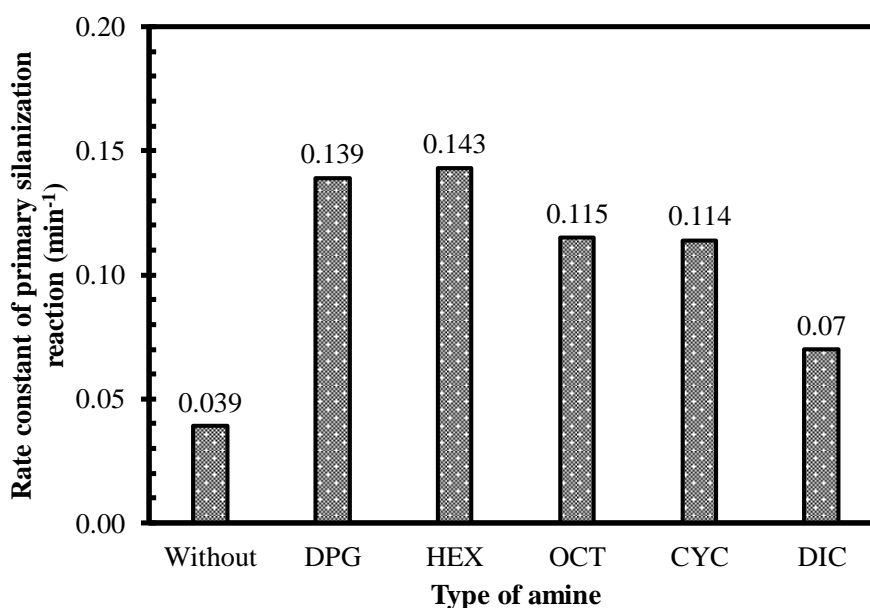

Fig. 2. Rate constant of primary silanization reaction of silica/silane system with different amine types.

3.2. Payne effect

The storage modulus as a function of strain of the silica-reinforced NR compounds with different amine types is shown in Fig. 3. The storage modulus of filled rubber compounds is influenced by four main factors, i.e. the hydrodynamic effect, the rubber network, filler-rubber interaction and filler-filler interaction. The storage modulus decreases under strain deformation due to reduction of the filler-filler interaction causing a breakdown of the filler network, which is well-known as the "Payne effect" [12]. The rubber compounds with amines show a lower filler-filler interaction than the mix without amine. As discussed earlier for the model system, all amines can promote the silanization reaction of the silica/silane system. The reaction between silane and alkoxy

groups on the silica surface reduces the reactive silanol groups, resulting in weaker filler-filler interaction within the rubber matrix and a reduction in accelerator adsorption. The linear aliphatic amines that show a higher primary silanization reaction rate constant display lower filler-filler interaction in the rubber compounds compared to the cyclic amines. The CYC with one cyclic ring in the structure gives a lower filler-filler interaction than the bi-cyclic ring DIC. The Payne effect results agree well with the model study. The linear aliphatic amines that have better accessibility towards the silica surface not only enhance the silanization but also shield the free silanol groups that are left over after the silanization reaction. This shielding effect by long alkyl-chains results in more hydrophobicity of the silica surface. Therefore, the use of OCT gives the lowest filler-filler interaction in the silica-filled rubber compound.
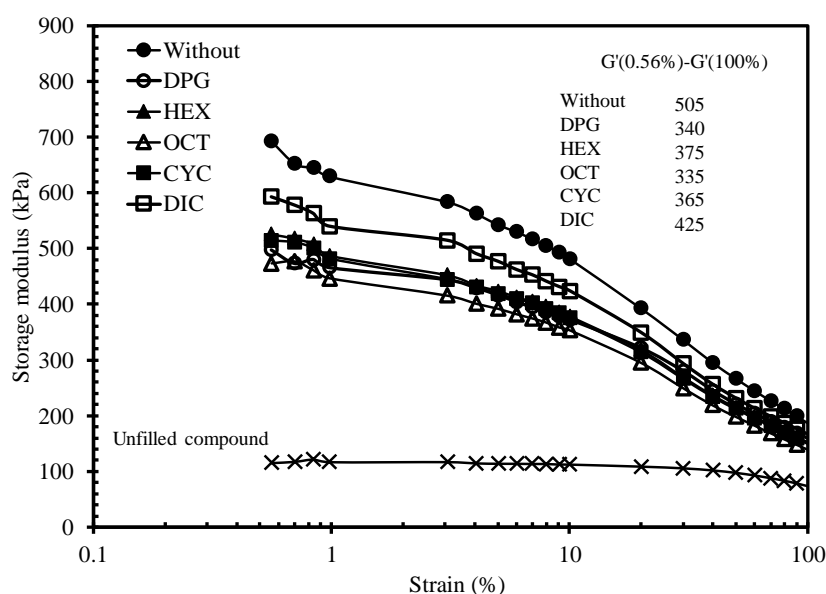

Fig. 3. Payne effect of silica-reinforced rubber compounds with different amine types.

3.3. Cure characteristics

Cure curves, scorch times and optimum cure times ($t_{c,90}$) of the rubber compounds with different amine types are shown in Fig. 4. The presence of all amine types clearly enhances the cure properties of the rubber compounds, as observed in the reduction of scorch and cure times. The amine-containing rubber compounds show reversion behavior whereas the one without amine shows a marching curve. The amines with linear aliphatic chains give shorter cure times than the cyclic structures, as the result of the higher silanization efficiency and better mobility of the secondary accelerators. Among the amines studied, the use of DPG as conventional secondary accelerator gives the fastest cure, i.e. shortest scorch and cure times. Further, the torques of the rubber compounds are affected by the different amine types. The rubber compounds with cyclic aliphatic amines show higher maximum cure torques than the mixes with linear alkyl-chains. The level of torque difference of the rubber compounds is influenced by both chemical and physical crosslinks/interactions. The OCT- and DPG-containing rubber compounds with similar Payne effect show similar cure torques, indicating similar crosslink density. The compounds with higher filler-filler interaction show higher maximum cure torque.

3.4. Tensile properties

The mechanical properties, i.e. moduli at different strains, tensile strength and elongation at break of the rubber compounds are shown in Fig. 5. The use of all amines improves the mechanical

properties due to enhancement of the silanization reaction, interfacial compatibility by the shielding effect, and the vulcanization reaction. Comparing the different amine types applied as alternative for DPG, the moduli of the rubber compounds with cyclic aliphatic amines, i.e. CYC and DIC, are higher than the mixes with linear structures, i.e. HEX and OCT, corresponding to the Payne effect and crosslink density within the rubber matrix. However, the interfacial compatibility within silica-reinforced rubber compounds is a crucial factor affecting the ultimate tensile properties. The rubber compound with OCT which shows lowest filler-filler interaction, has a tensile strength and elongation at break that are closest to the reference compound with DPG.
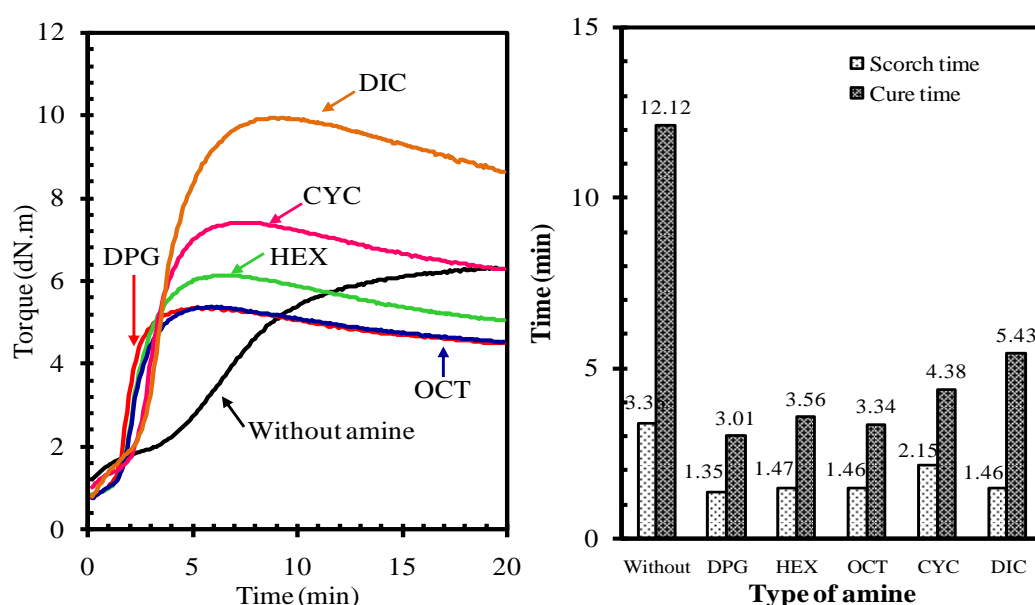

Fig. 4. Cure curves, scorch times and cure times of silica-reinforced rubber compounds with different amine types.
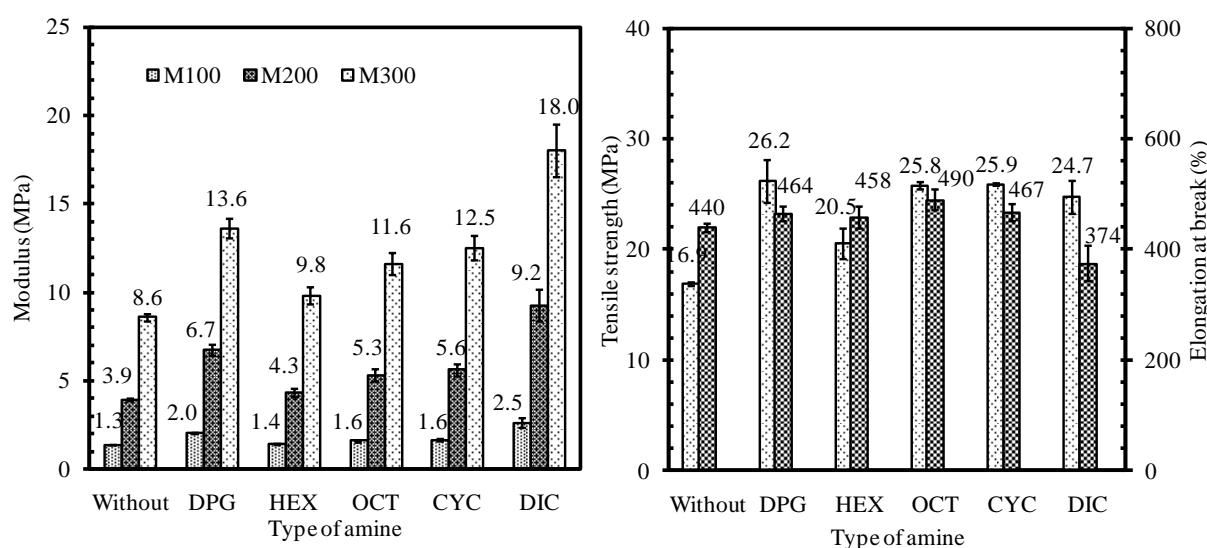

Fig. 5. Tensile properties, i.e. modulus, tensile strength and elongation at break, of silica-reinforced rubber compounds with different amine types.

4. Conclusions

The rate constant of the primary silanization reaction of a silica/silane model system with different amine types is investigated. The presence of all amine types promotes a higher rate constant of the primary silanization reaction compared to the system without amine. Linear aliphatic amines give a higher rate constant than the ones with cyclic aliphatic amines. An increase of carbon atoms in the linear amine structure from 6 to 18 decreases the rate constant. An increase of the cyclic aliphatic from 1 to 2 cyclic rings also decreases the rate constant of the reaction, caused by steric hindrance of the amine molecules that reduces the accessibility of the amines onto the silica surface. With regard to practical silica-reinforced rubber compounds, the Payne effect of the compounds with amines corresponds well with the rate constant of the primary silanization reaction, except for the linear aliphatic amines. The OCT-containing rubber compound shows the lowest Payne effect due to a shielding effect by the long alkyl-chains that promote hydrophobicity and interfacial compatibility. The use of all amines improves the cure properties, in which the linear aliphatic amines give faster cure than the cyclic ones. But, the use of CYC and DIC gives a higher maximum cure torque and torque difference, thus results in higher modulus in the rubber vulcanizates. Among the alternative amines studied, tensile strength and elongation at break of the OCT-containing compound are highest and closest to the reference compound with DPG, as influenced by optimized interfacial compatibility involving both chemical and physical interactions.

Acknowledgements

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