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New peroxide systems for crosslinking EPDM in hot air

Novel polyhedral oligomeric silsesquioxane
coagent additives for HNBRs

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Novel POSS coagent additives for HNBRs

by Robert Ou, National Oilwell Varco, and Joseph D. Lichtenhan, Hybrid Plastics

HNBR is a widely used elastomer for which properties can be tailored through variation of the degree of nitrile and olefinic groups along the polymer chain. While partially hydrogenated HNBR can be crosslinked using sulfur and peroxide vulcanization, fully hydrogenated HNBR (*f*-HNBR) can only be crosslinked using peroxides (ref. 1). Therefore, engineering physical properties of crosslinked *f*-HNBR are limited by the number and quality of crosslinks achievable through the peroxide induced abstraction of protons along the elastomer polymer chain.

Coagents, such as triallyl cyanurate, zinc diacrylate, etc., can be utilized to partially rectify the above deficiency by enhancing crosslink quantity and type between *f*-HNBR chains. However, as small molecules, these traditional coagents have only modest ability to control the spacing and thermomechanical dynamics of *f*-HNBR crosslinks. In this work, we introduce a new family of olefinic coagents based on polyhedral oligomeric silsesquioxanes POSS (ref. 2). POSS chemical additives are comprised of a rigid silicon-oxygen ($SiO_{1.5}$) core with external organic groups that impart compatibility and reactivity; while the rigid cage core provides modulus (ref. 3), thermal stability (ref. 4), volume and surface area at the crosslink.

Three olefinic POSS additives were examined: vinyl, allyl and methacrylate POSS. These were also industrial grade cage mixtures comprised predominately (>65%) of cage size 10 decamers (figure 1). The use of POSS systems with a cage size distribution is economically attractive, and a cage size distribution renders a favorable melting point depression that allows these additives to exist as low melting solids and liquids. Due to their lack of crystallinity, POSS cage mixtures are rapidly dissolved and readily dispersed in HNBR and related resins.

From a steric hindrance perspective, varying degrees of reactivity were anticipated and envisioned to follow the reactivity of the olefin on the POSS cage. For example, vinyl POSS (OL1170) was anticipated to achieve a low crosslink density due to steric hindrance of the cage; allyl POSS (OL1175) was envisioned to be a moderate crosslinker due to the increased distance of the olefin from the cage core, and methacryl propyl POSS (MA0735) was expected to achieve the highest crosslink density due to the activity of the olefin and its distance from the cage core.

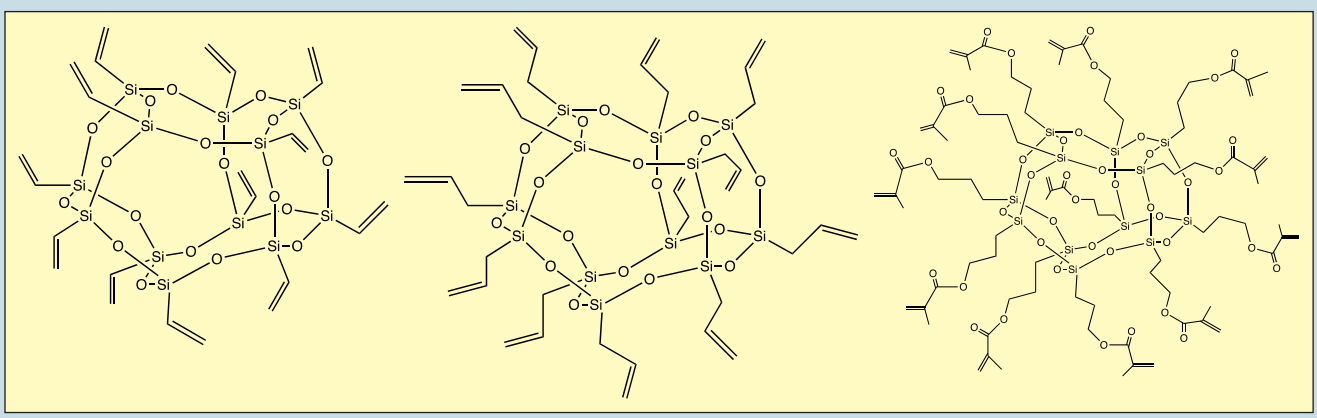
The low degree of unsaturated olefin present on the particular *f*-HNBR chosen minimizes the effect of the HNBR to self-crosslink, and thus highlights the role of crosslinking achievable by the POSS additive. While it is recognized that POSS cages may also self-crosslink, their addition at low percentages into the HNBR and quantified impact on mechanical properties will elucidate the role of the POSS cages to serve as coagents for HNBR crosslinking.

Experimental

Materials and formulations

The *f*-HNBR used in this study is Therban 3407, provided by Lanxess. Peroxide dicumyl (DCP) was obtained from Arkema. The N550 carbon black (Cabot) is used as a reinforcement filler, and zinc oxide (Akrochem) is used as an activator. The HNBR control sample utilizes DCP as a crosslinking agent; however, no coagent (POSS) was added to its formulation. The POSS additives used in this study include methacrylpropyl POSS (MA0735), vinyl POSS (OL1170) and allyl POSS (OL1175). The recipes used in this study are shown in table 1. Formulation levels containing "E" indicate an equivalent molar amount of C=C double bonds (MA0735E, OL1170E, OL1175E). The ENE equivalent weights of MA0735, OL1170 and OL1175 are 179, 79 and 93, respectively. The use of equivalent ENE amounts enables comparisons of coagent crosslinking efficiency between the types of POSS. The samples not designated with an "E" contain approximately twice the amount of ENE as the corresponding "E" designated co-

Figure 1 - structural representations of vinyl POSS (OL1170), allyl POSS (OL1175) and methacryl POSS (MA0735) coagents (left to right)



agent formulation. Finally, the wt.% of POSS is indicated in parentheses next to the phr level.

Mixing was done using a laboratory internal mixer. The HNBR polymer, half of N550 and other raw materials were initially loaded into the mixer. The other half of N550 was added after the mixing chamber reached 70°C. The discharge temperature was chosen to be 95°C in order to avoid scorching. After mixing, the batches were cooled and pelletized on a two-roll mill. Buttons for use in rheometry were collected after 12 hours conditioning under ambient conditions. Vulcanized slabs for tensile tests were prepared according to the ASTM D 3182 protocol.

Moving die rheometer (MDR) tests

The vulcanizing properties of the samples were measured using an MDR according to the ASTM D 5289 protocol. The difference between maximum and minimum torque (MH-ML) is used to compare the rigidity of the samples after vulcanization. Tan δ at maximum torque (MH) is also compared. The time to reach 90% cure (T90) is used to compare the vulcanizing rate of the samples. The testing conditions for this test are 10 minutes at 165°C.

Specific gravity tests

In order to confirm the consistency of sample mixing and molding processes, specific gravity of the vulcanized samples was measured according to ASTM D 297. As the same polymer and carbon blacks are used in all recipes, specific gravity is determined solely by the percentage of each ingredient in the recipe. By measuring the specific gravity, we were able to confirm if there was any significant loss of ingredients during the mixing process.

Tensile properties

Tensile properties of the vulcanized samples were measured according to ASTM D 412C. The elongation and tensile modulus values were used to compare the rigidity of the samples. As raw polymer and fillers are identical in these recipes, it is reasonable to speculate that the rigidity of the samples is attributable to the crosslink density of the vulcanized samples, as they have the same grade and dosage of polymer and filler in the recipes.

Crosslink density tests

The crosslink density of the vulcanized samples was measured using equilibrium swelling. The samples were immersed in a mixture of solvents for 36 hours. Subsequently, the amount of solvent absorbed was measured as the difference between the weight change before and after drying of the immersed samples. The crosslink density was then calculated using the Flory-Rehner equation.

Scanning electron microscopy and energy dispersive x-ray

The degree of dispersion obtained during mixing was optically and elementally determined using a Zeiss Sigma VP FEG-SEM with Thermo System 7 EDS and WDS x-ray detector. The surface and cross-sections of cured elastomers were examined, and elemental maps were created and overlaid relative to optical images.

Results and discussion

Moving die rheometer (MDR) tests

The physical properties resulting from binary blends of POSS coagents relative to *f*-HNBR were determined using a variety of common elastomer characterization techniques. Among these, moving die rheology provides great insight into the processability of the formulations as they progress from the uncured to cured state.

The rheological properties for the formulations are summarized in table 2. We can see the samples containing the POSS additives showed higher MH-ML than the control sample, with the highest increase observed for OL1175 allyl POSS. The increasing trend for MH-ML for all POSS types and contents clearly indicates that POSS helps to increase the efficiency of peroxide curing in *f*-HNBR.

A comparison of the MH-ML values among formulations containing the same ENE amount reveals the activity of the POSS molecules as crosslinking coagents is OL1175 > OL1170 > MA0735E. This finding is counter to our initial prediction that a less sterically hindered olefin, such as the methacrylate, would show the highest activity. The finding also suggests that our initial concerns about sterics were exaggerated. It is particularly interesting to note the vinyl groups on OL1170 and the allyl groups on OL1175 are comparatively more similar in reactivity than the methacryl propyl groups of MA0735. The surprising reactivity of the vinyl POSS OL1170 is preliminarily attributed to the close proximity of the vinyl

Table 1 - elastomer components listed in phr resin and (wt.% total components)

	Therban 3407	*N550*	*ZnO*	*DCP*	*MA0735*	*OL1170*	*OL1175*
f-HNBR control	100	75	4.16	1.25	-	-	-
MA0735E	100	75	4.16	1.25	$5_{(2.69)}$	-	-
OL1170E	100	75	4.16	1.25	-	$2.2_{(1.19)}$	-
OL1175E	100	75	4.16	1.25	-	-	$2.6_{(1.40)}$
OL1170	100	75	4.16	1.25	-	$5_{(2.69)}$	-
OL1175	100	75	4.16	1.25	-	-	$5_{(2.69)}$

Table 2 - moving die rheometer test results

	MH (N.mm)	*ML (N.mm)*	*MH-ML (N.mm)*	*Ts2 (min.)*	*10% cure (min.)*	*90% cure (min.)*	*Tan δ at MH*
f-HNBR control	1,712.78	508.41	1,204.37	0.91	0.62	6.91	0.250
MA0735E	2,137.58	489.20	1,648.38	0.33	0.34	6.45	0.216
OL1170E	2,273.16	407.86	1,865.30	0.79	0.71	6.81	0.178
OL1175E	2,410.99	453.05	1,957.94	1	0.92	7.51	0.168
OL1170	2,588.37	397.69	2,190.68	0.67	0.66	6.68	0.156
OL1175	2,862.91	476.78	2,386.14	0.95	0.98	7.59	0.153

Table 3 - specific gravity and tensile properties

	Specific gravity (g/ml)	*Tensile strength (MPa)*	*Elongation (%)*	*100% tensile modulus (MPa)*	*200% tensile modulus (MPa)*	*300% tensile modulus (MPa)*
f-HNBR control	1.208	16.25	365.5	6.53	12.67	15.55
MA0735E	1.214	16.86	329.7	7.87	13.76	16.61
OL1170E	1.208	19.48	316.8	8.54	16.31	19.29
OL1175E	1.212	19.95	337.4	7.75	15.83	19.39
OL1170	1.213	20.11	277	9.49	17.80	*
OL1175	1.215	21.30	255.5	11.45	19.66	*

* Formulation was not suitable for 300% strain

groups to the electronegative cage core (ref. 5). The prospect of an allylic resonance of the vinyl groups (OL1170) with silicon d orbitals may play a role in its enhanced reactivity. The OL1175 (allyl POSS), however, contains both close proximity to the electronegative cage and easily abstracted allylic protons, thus contributing to its overall high activity.

Comparison of the 10% cure and 90% cure times through MDR reveals the rates of cure are again more similar for the vinyl OL1170 and allyl OL1175 coagents than for methacryl MA0735. The MA0735 showed slightly faster vulcanization. This indicates that the methacrylic group is activated faster than the vinyl groups. However, the slower activation of vinyl OL1170 and allyl OL1175 can be considered advantageous in molding processes, principally because they afford greater scorch safety. This statement is further supported by our TS2 findings.

The tan δ @ MH value provides a good indication of the crosslink density for elastomers. As all the formulations have the same grade and dosage of polymer and fillers, the ratio between the loss and storage modulus can only be affected by crosslink density. Samples with higher crosslink density have lower tan δ due to their higher elasticity. We have observed that all samples with the POSS additive showed lower tan δ values than the control formulation. Again, vinyl OL1170E and allyl OL1175E samples showed a larger decrease in tan δ than the methacryl MA0735E formulation. This indicates that a higher level of crosslinking was achieved for vinyl OL1170 and allyl OL1175 POSS coagents than for the methacryl MA0735 POSS. We conclude the tan δ trend is also in agreement with the MH-ML trend, and it further supports the ability of these POSS additives to function as coagents in *f*-HNBR.

Tensile properties and specific gravity

The specific gravity and tensile properties of the formulations are shown in table 3. The theoretical specific gravity of the control sample was calculated to be 1.207, and the experimentally determined result is in line with this value. Overall, the specific gravity of the vulcanized samples is very consistent. This confirms that the mixing and sample preparation processes are very consistent. In fact, we believe the addition of POSS to the formulations may have enhanced the mixing and homogeneity of the filler with the *f*-HNBR polymer. This observation is consistent with related SBR elastomers for which it was reported that MA0735 POSS improved the interfacial compatibility, and dispersion of silica fillers with elastomer components (ref. 6).

The tensile and modulus data in table 3 reveal significantly higher tensile modulus and slightly lower elongation values than for the control *f*-HNBR. This trend is also in line with the MDR results. The formulations OL1175E and OL1170E and MA0735E showed 18%, 30% and 20% higher tensile modulus at 100% strain than the control formulation samples. A similar trend of tensile modulus was observed for these formulations at 200% and 300% strains. The improvement of tensile modulus followed the following trend OL1170E > OL1175E > MA0735E. It was surprising to observe that the vinyl POSS showed the largest improvements of tensile modulus among the POSS variants.

Commonly, improvement in tensile properties is accompanied by a decrease of elongation. While this was observed, the decrease was relatively minor relative to the control system. For example, OL1175E and OL1170E and MA0735E showed only 7%, 13% and 10% reductions of elongation relative to the control formulation. In consideration of the POSS variants, the POSS cages containing longer reactive arms retained more elongation than the shorter armed vinyl POSS OL1170.

Overall, the tensile property values indicate that POSS coagents help to increase crosslink density of peroxide cured HNBR and increase tensile modulus with an acceptable level of decreased elongation.

Crosslink density

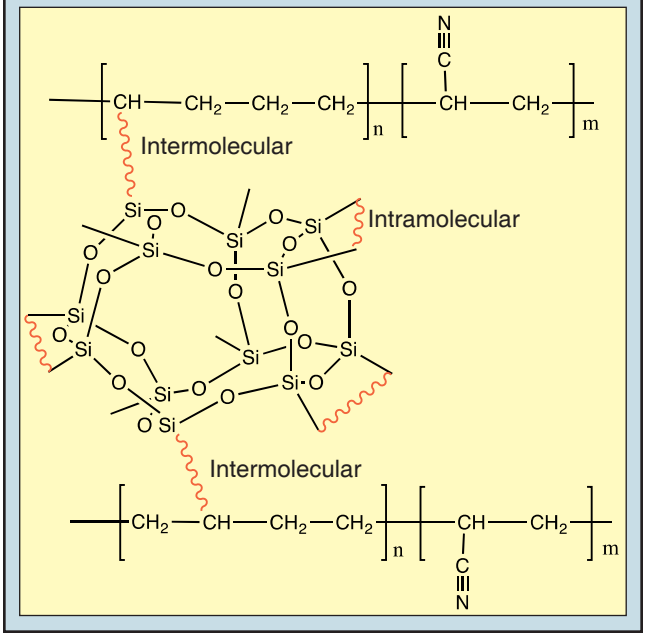
Perhaps the best measure of POSS performance as a vulcanization coagent is crosslink density. Therefore, the equilibrium swelling method was used to directly compare the crosslink density of these formulations. The crosslink density test findings are listed in table 4. It was observed that the POSS additives showed significantly higher crosslink density than the *f*-HNBR control. Specifically, the vinyl containing OL1170 and the allyl containing OL1175 showed higher crosslink density. This finding indicates that vinyl and allyl POSS are more efficient as coagents that the methacryl POSS MA0735. Similar findings have been reported for POSS additives in peroxide cured EPDM (ref. 7). The crosslink density findings are in good agreement with the previously discussed rheological and tensile property trends.

Table 4 - crosslink density of elastomers

	Crosslink density (mol/cm^3)
f-HNBR control	1.55 E-04
MA0735E	2.63 E-04
OL1170E	3.23 E-04
OL1175E	3.58 E-04
OL1170	4.38 E-04
OL1175	4.97 E-04

The crosslink density findings for the non-equivalent ENE containing formulations vinyl OL1170 and allyl OL1175 also reveal an interesting trend. These formulations contain ap-

Figure 2 - illustration of POSS coagent providing inter- and intramolecular crosslinking



proximately twice the ENE content of OL1170E and OL1175E. As expected, the increased ENE content led to higher levels of crosslinking relative to OL1170E and OL1175E. However, the increased crosslink density observed was only 35% and 38%, respectively, of what would have been expected based on ENE loading level. This discrepancy is potentially explained by the ENE groups on the POSS cage reacting with each other (intramolecular), rather than functioning as a coagent with the HNBR (intermolecular) (figure 2).

In this light, we also postulate the MA0735 methacryl POSS may self-react to a higher degree than can occur for OL1170 and OL1175 POSS. If this is the case, it would explain the observed lower degree of coagent reactivity and lower achievable

Figure 3 - SEM/EDS image showing dispersion of MA0735 POSS

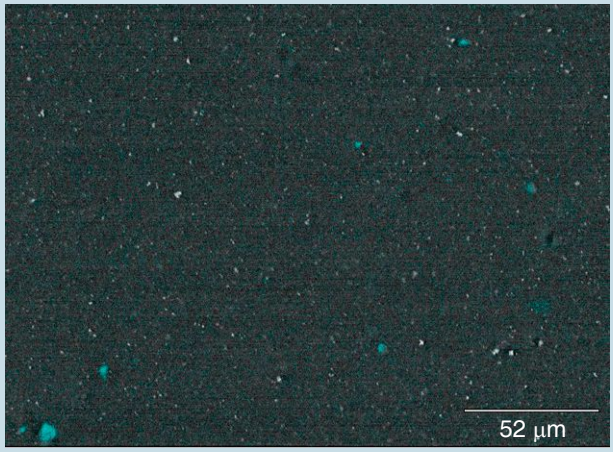
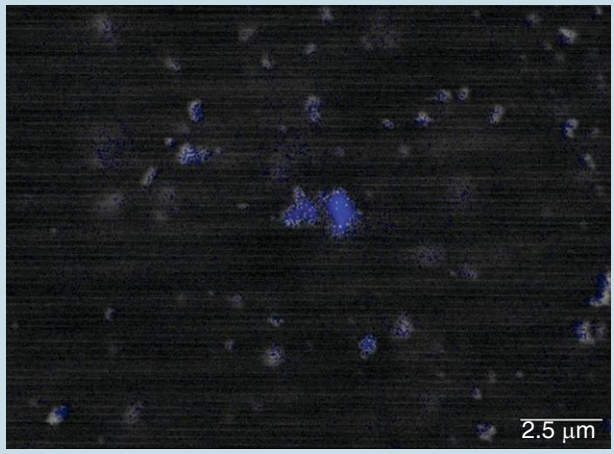


Figure 4 - SEM/EDS image showing 200-500 nm white silicon domain on ZnO particles



crosslink density for MA0735 POSS which contains the reactive methacrylate olefin.

Scanning electron microscopy and energy dispersive x-ray

Using SEM EDS, we were able to examine the dispersion state of the coagent in the formulations. Overall, SEM indicated very high homogeneity of components within the elastomer, which is attributed to thorough mixing and compatibility of formulation components (figure 3). The creation of elemental maps for silicon was particularly informative, as POSS is the only source of silicon in the formulation. However, the low loading level of POSS and its high compatibility did prove to be challenging. Comparatively, all POSS additives disperse within the elastomer; however, some intramolecular aggregation of MA0735 was identifiable by the observance of 200-500 nm domains relative to micron sized zinc oxide particles (figure 4). This finding is in agreement with the postulated activity of the methacrylate POSS at high loading levels in *f*-HNBR.

Conclusions

The purpose of the present work was to challenge POSS cages bearing reactive groups to crosslink fully hydrogenated HNBR using traditional peroxide vulcanization. The ability of olefinic POSS to serve as a crosslinking coagent in peroxide vulcanization of *f*-HNBR has been demonstrated. As expected, the crosslink density correlates the olefin (ENE) loading provided by POSS. Significant improvements in rheological and tensile properties resulted from incorporation of the POSS additive at loading levels ranging from 1.19 to 2.69 wt.%.

In contrast to original expectations, the POSS cages bearing vinyl groups were surprisingly effective as coagents; as were POSS cages bearing allyl groups. The methacryl POSS cages were also effective as a coagent, but exhibited comparatively lower enhancement of mechanicals, crosslink density and rheological properties relative to the other POSS types. It is postulated the decreased coagent activity for methacryl POSS is attributed to rapid reaction with itself (presumably intramolecu-

lar), as opposed to crossover reactivity with the fully saturated *f*-HNBR.

This article is based on a paper presented at the 194th Technical Meeting of the Rubber Division, ACS, October 2018.

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