Nanoparticles and their possible use in rubber

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1 INTRODUCTION

Kumho Tire Co. Inc. is part of the Kumho group of companies, one of the most prominent South Korean industrial conglomerates. Kumho Tire is a profitable part of the overall group that has business interests in the chemical industry, transportation and finance, as well as in the construction and leisure industries.

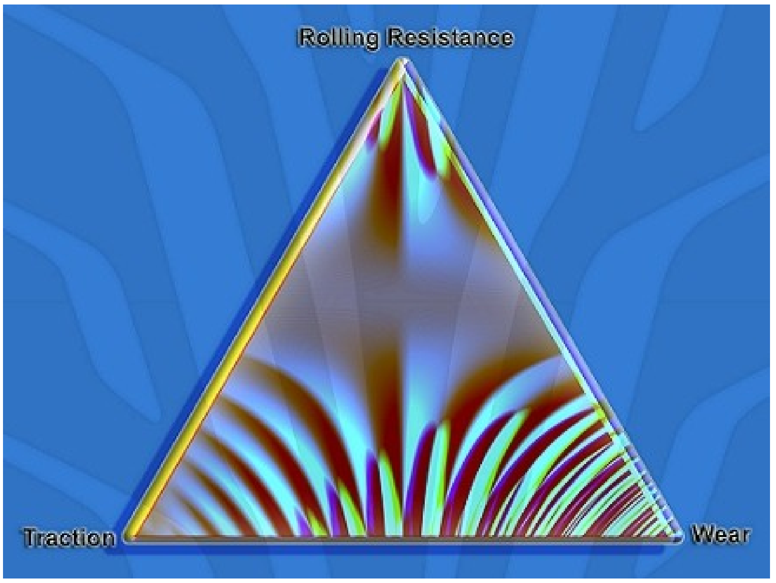
Kumho Tire Co. Inc. has its global headquarters in Seoul, South Korea, its principal research and development centre at Gwangju and local R&D facilities at Akron, Ohio, USA, Birmingham in the UK and Nanjing, China.

Recently tyre materials scientists working at the Kumho European Technical Centre at Birmingham, UK have been investigating the benefits a new nanomaterial might have on the performance of passenger car tyre tread compounds.

2 BACKGROUND

Traditionally the tyre compounder has always been required to possess the skills necessary to be able to adjust and balance various compound physical properties when formulating a tyre tread compound with a specific end use in mind. The compounder is required to deliver acceptable levels of performance in a range of tyre parameters which include rolling resistance, traction in both wet and dry conditions, tyre noise, abrasion resistance, endurance and flat spot performance. Importantly, in what has always been a highly cost limited industry, the compounder is called upon to achieve these performance targets whilst maintaining or even reducing the cost of the product.

Arguably the three tyre performance parameters upon which the compounder concentrates the most are traction, rolling resistance and abrasion resistance. Compounders often refer to these three key tyre properties as forming the 'magic triangle' (See Fig 1 next page). To be able to alter this magic triangle to suit the intended application has been the challenge set before generations of compounders working in the tyre industry, but adjusting one parameter inevitably leads to an associated change in one, or both, of the others. Clearly, it would be a very great advantage to be able to selectively alter any one of the tyre's properties without affecting the others.



In order to adjust the physical properties of any compound the compounder must modify the compound formulation that contains a range of polymers, fillers, additives and curative systems. At his disposal the modern compounder has an enormously extensive array of elastomeric polymers, each of which can be employed for example to generate traction, reduce rolling resistance or improve compound abrasion resistance.

Tyre compounds contain reinforcing fillers that enhance the properties of the polymer system, improving abrasion resistance, traction and many other performance parameters. There are two broad categories of filler in use in the tyre industry today, carbon black and the more recently introduced silica.

Compound formulations for tyres contain a range of oils and chemical additives designed to aid compound processing during manufacturing and to enhance the eventual performance of the compound in the tyre. Finally the formulation contains a curative system, which in the tyre industry still relies almost exclusively on the process of sulphur vulcanisation.

So, it can easily be seen that using such a conventional range of tyre materials, it has always been somewhat difficult to break the compounders' all-important magic triangle and to be able to alter each of the compounds key physical properties in isolation from the others.

One approach taken by compounders to solve this dilemma is to seek novel materials that, when added to a compound might have the ability to selectively modify one of the compounds physical properties. This is the approach that has been adopted by Kumho European Technical Centre when evaluating a new commercially available nanomaterial.

3 POLYHEDRAL OLIGOMERIC SILSESQUIOXANES (POSS)

The nanomaterials currently being investigated by Kumho are polyhedral oligomeric silsesquioxanes, known by the abbreviation POSS. These POSS materials are a commercially available range of nanomaterials developed and supplied by Hybrid Plastics Inc., a company based in the USA.

According to the supplier, the ability of POSS materials to modify the physical properties of a polymeric system has already been successfully demonstrated in plastic materials. But to date experience with the use of these nanomaterials in rubber systems is very limited, especially in the kind of rubber compounds commonly used in tyre applications.

Again, according to the supplier the POSS materials can be shown to be discrete, chemically modified particles of silica. The dimensions of each individual POSS molecule is on a nanometre scale and so their use can justifiably be claimed as an application of nanotechnology.

The POSS materials themselves are described as being ‘hybrid’ because their chemistry combines inorganic, silica based elements as well as organic, carbon based chemical functional groups. The actual chemical composition of the range of POSS nanomaterials studied is between that of silica itself, SiO_2 and the silicones R_2SiO. The chemical structures of the POSS materials are often cage-like with various reactive and non-reactive chemical functional groups on the surface.

The POSS materials can be easily incorporated into polymeric systems either by mechanical blending or by chemically grafting the POSS molecules themselves directly onto the backbone chain of a polymer during the polymerisation stage of the polymer manufacturing process. Also they can be added to a polymeric system as a filler or as a performance-enhancing additive.

Hybrid Plastics claim that once introduced into the types of polymer systems used widely in the plastics industry it has been shown that POSS materials can impart new or improved physical properties to such a system. In particular they claim that the POSS materials have the ability to modify a polymer’s glass transition temperature (Tg). Hybrid Plastics suggest this change is brought about by a modification of polymer chain motion at the molecular level by the POSS materials.

It is this ability to alter Tg that offers the potential for physical property improvement in elastomeric polymer systems such as those used in the tyre industry.

4 TEST COMPOUND FORMULATIONS AND POSS MATERIAL SELECTION

The initial evaluation of the POSS materials by Kumho was designed to demonstrate the ability of POSS to alter the physical properties of a silica filled tread compound formulation of the type commonly employed in passenger car tyres. The technology could equally be applied to carbon black filled compounds for car tyres as well as to compounds for other applications.

Initially Kumho selected the following formulation in which to test the POSS materials:

Ingredient	Loading Level (phr)
Buna VSL 5525-1	110.04
Buna CB22	20.00
Ultrasil VN3	80.00
Silane X50S	12.80
Aromatic Oil	5.00
POSS Material (If included)	3.50
Zinc Oxide	2.50
Stearic Acid	1.00
Santoflex 13	2.00
Antilux 111	1.00
Sulphur	1.40
CBS	1.70
DPG	2.00

The loading for the POSS material was carefully selected such that it represented a typical level of inclusion for a compound performance enhancing additive and not a bulk compound filler.

The rubber compound formulation was mixed using a three-stage laboratory scale process. The first two mixing stages where carried out in a laboratory scale internal mixer and the final stage, where the curative materials were added was carried out on an open two roll mill.

In this initial phase of the investigative work the POSS materials were all added in the second mixing stage. This point of addition was deliberately selected in order to avoid any interaction between the POSS materials and the silica, silane and polymer coupling reaction that occurs in the first mixing stage.

After consultation with Hybrid Plastics, the supplier of the POSS materials and some preliminary pre-sorting investigations, the following two POSS materials were selected for their compatibility with our compound system:

Trisilanol Phenyl POSS (POSS A)

and

Trisilanol Isobutyl POSS (POSS B).

The effect on the compound physical properties of addition of these two materials to the above formulation was then studied in greater detail in a series of laboratory scale evaluations.

5 RESULTS

In order to understand the effect of the POSS materials on the physical properties of the test compound, Kumho conducted a series of physical property tests, both static and dynamic, the nature of which are well known within the tyre and rubber industry. The test methods are not described in detail here, but all tests were conducted in accordance with the appropriate industry standards. The following is a description of the results obtained.

a) Tensile properties

The addition of the POSS materials at the loading selected for this study appeared to produce little discernible change in the tensile strength of the compound compared to the control compound. However, a small increase in elongation at break was noted.

When comparing the tensile modulii of the POSS containing compounds to the control compound a reduction was noticed in both modulii at 100% and 300% extension. This reduction was found to be both significant and also repeatable. Clearly this is a change that could have an effect on the eventual performance of the compound in the tyre and so represents an issue which merits further investigation.

b) Compound hardness

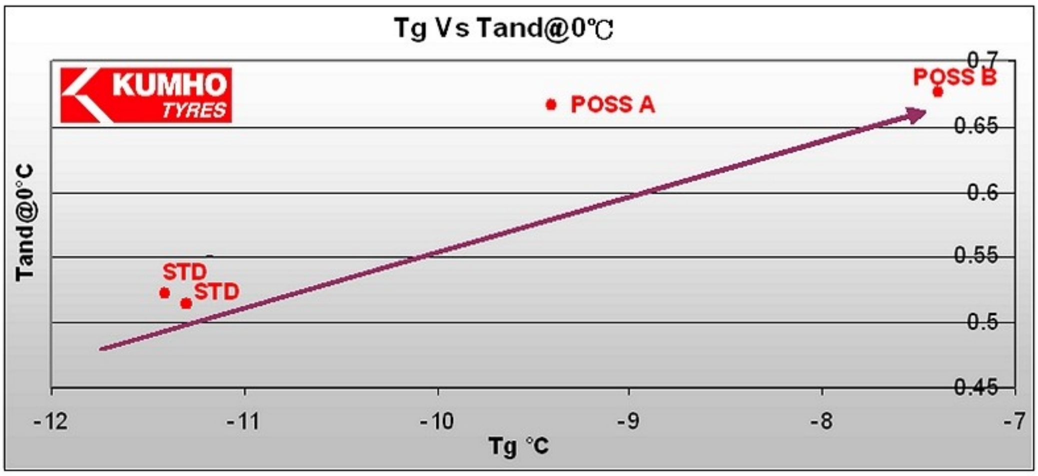
When compound hardness was measured, the POSS compounds were found to be three points or so below the average hardness of the control compound. This result coincides with the reduction in tensile modulii noted previously and also requires further consideration.

c) Viscoelastic properties

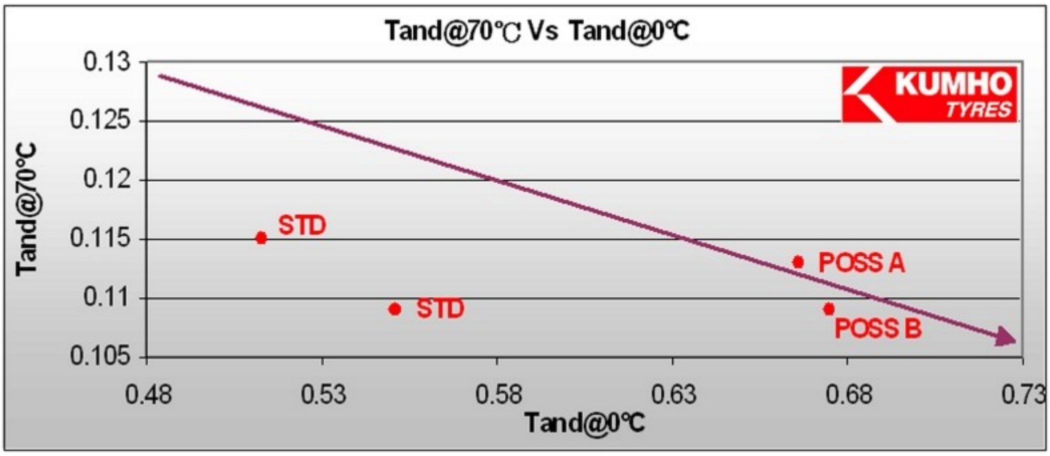
To the compounder it is the dynamic physical properties of a compound that are most important. It is these that correlate most closely with the performance of the compound in the tyre and so offer the compounder the best method of determining the applicability of a particular formulation.

In order to demonstrate the effect of the POSS materials on the viscoelastic properties of the compound, it is possible to plot several key parameters against each other to determine the likely effect on tyre performance.

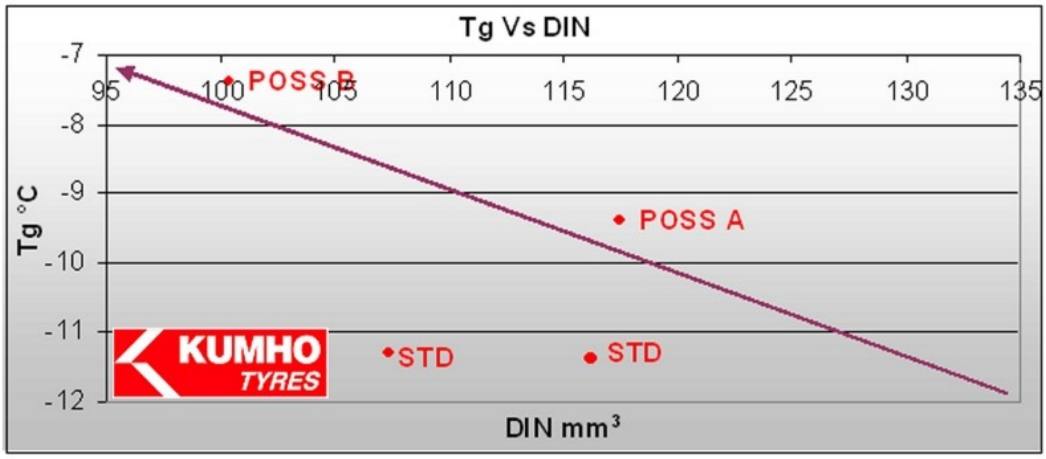
Plotting glass transition temperature against tangent delta at 0°C can be used to give an indication of the effect on compound wet traction. The graph in Fig 2 (below) shows an increase in glass transition temperature and tangent delta at 0°C compared to the control compound for both types of POSS, with POSS B, the trisilanol isobutyl material offering the greatest potential benefit.



A plot of tangent delta at 70°C against tangent delta at 0°C can be used to compare rolling resistance and wet traction. The value for tangent delta at 70°C has been shown to correlate well with tyre rolling resistance and tangent delta at 0°C gives some indication of wet traction performance. In the graph shown in Fig 3 (below), POSS A and POSS B show increases in tangent delta at 0°C without adversely affecting tangent delta at 70°C, suggesting a potential wet grip benefit without an associated deterioration in tyre rolling resistance.



When considering the suitability of a particular tread compound formulation, it is important to asses its abrasion resistance and to compare this result to that of the control compound. It is obviously advantageous to compare this parameter to other compound properties and Fig 4 (below) shows glass transition temperature plotted against the DIN abrasion test result. Since glass transition temperature has an effect on the traction properties of the compound it is possible to compare this with abrasion resistance.



Again POSS B, the trisilanol isobutyl POSS shows the most advantageous properties. This compound variant has the lowest value for DIN, but the highest Tg value, indicating this compound would have the best wet grip, without an associated deterioration in tyre wear properties.

Following these initial, promising, results a further study was carried out.

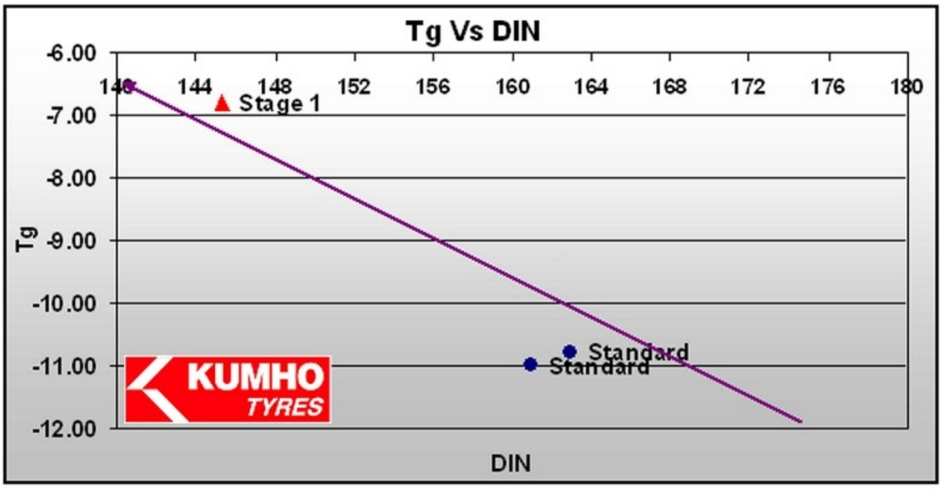
6 SECOND EVALUATION

For the purposes of further study it was decided to concentrate on the trisilanol isobutyl POSS material as this gave the most significant and potentially beneficial changes in compound physical properties in the first evaluation.

In the initial phase of the second evaluation, the previous tests with the POSS material added in the second stage of the same control compound formulation were repeated. The results from this second, repeat evaluation which are not discussed in detail here, confirmed the first trial results given above.

A further batch of compound was mixed with the POSS material included at the same loading as previously, but this time the addition was made in the first rather than the second stage of the compound mixing process. The inclusion of this variant was designed to determine whether the POSS material would take part in the silica, silane and polymer coupling reaction.

Addition of the POSS material in the first stage did not have such a profound effect on compound physical properties as addition in the second stage. The graph in Fig 5 shows glass transition temperature plotted against DIN abrasion.



When the POSS material is included in the first rather than the second mixing stage, it appears to have a more significant effect on DIN abrasion. As noted previously, glass transition temperature is also increased significantly compared to the control compound. This would appear to confirm that the POSS materials do have the ability to interact with the silica, silane and polymer coupling reaction.

7 CONCLUSIONS

It can be concluded from the work carried out by Kumho to date in silica filled passenger car tyre type tread compound formulations, that polyhedral oligomeric silsesquioxane nanomaterials appear to offer potential benefits in terms of compound physical properties. They appear to have the potential to increase wet traction without sacrificing rolling resistance or abrasion resistance. If these changes in physical properties translate into tyre performance, the addition of POSS to a tyre compound could offer the compounder the ability to selectively alter individual tyre performance properties and to break the so-called ‘magic triangle’.

The work carried out by Kumho to date indicates the POSS materials are able to improve compound physical properties by increasing polymer glass transition temperature, and this occurs without adversely affecting other key compound physical properties.

The underlying chemical mechanism by which POSS is able to achieve the changes in physical properties observed is not yet clear, and further work is planned to try to understand this mechanism. However the recent work carried out by Kumho would tend to support the claim by the supplier, Hybrid Plastics that POSS modifies polymer chain motion at the molecular level.

The relatively low loadings of POSS materials employed in these studies (3.5phr) means these results are significant and further work is already in progress to understand in greater detail the effect these materials have on the physical properties of rubber compounds. Also Kumho has applied for two UK patents to protect this technology.

At the present time the cost of the POSS materials remains high in comparison to other types of materials commonly used in tyre compounds, but nevertheless Kumho envisages evaluating these materials in tyres in the future. Currently the supplier of the materials Hybrid Plastics is increasing its production capacity for a wide range of POSS materials, and it is expected this will lead to a future reduction in the purchasing cost.

8 ACKNOWLEDGEMENTS

The author wishes to thank the following people and organisations for providing information and support for this project:

Dr MS Evans – Formerly Kumho European Technical Centre, UK, now retired.
Dr KJ Niderost - Kumho European Technical Centre, UK.
Dr SJ Choi – Kumho R&D Centre, Gwangju, South Korea.
Dr JD Lichtenhan – Hybrid Plastics Inc., USA.

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March 2005