

Research Paper

Environmental-Friendly and Non-Toxic TBSI as an Alternative for MOR Accelerator

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Abstract

In the solid tyre rubber industry, most accelerators can produce n-nitrosamines as a by-product during the vulcanization process. As many n-nitrosamines are carcinogenic, they are highly regulated in final rubber articles and during manufacturing process. 2-(Morpholiniothio benzothiazole (MOR) is the primary accelerator used in vulcanizing systems. It produces nitrogen toxic gases (nitrogen oxide and amine gas) which are carcinogenic. In this research MOR was successfully replaced with N-tert-butyl-2-benzothiazole sulfenimide (TBSI) accelerator which has no carcinogenic effect. The main objective of this research is to maintain its original properties while replacing MOR with TBSI accelerator. This study was conducted and test samples were made of bonding rubber compound that is used to make the bonding layer of tyres which is the common part in all type of solid tyres. Physical-mechanical and bonding properties were analyzed for MOR and TBSI added bonding compound samples. Tensile, hardness, density and rheological using Oscillating die rheometer properties were also measured to maintain the quality of the tyre. The property change of bond layer can affects the other tyre layers. So, it can lead to failure of curing process or failure in performance of the tyre during the applications. The TBSI curing characteristics are closer to MOR sample. However other physical properties like hardness and density of TBSI samples were bit lower but they were in the required level as a bonding layer compound. Substitution of MOR by 'safe TBSI' compounds are still active as accelerators, but do not form carcinogenic gases.

Keywords: accelerator, bonding compound, carcinogenic effect, MOR, TBSI

Introduction

An accelerator is a chemical compound that increases the speed of vulcanization process of rubber with a crosslinking agent like sulfur and peroxide examples like thiurams, hexamethylenetetramine and benzothiazoles. choice of an accelerator system for the vulcanization is tough. Parameters, like processability, scorch, crosslinking and raw rubber storage stability should be considered when opting a proper accelerator for a compound [1].

Accelerators increase curing and efficiency of sulfur bonding to rubber molecules. The accelerators employed in vulcanization significantly reduce time need for vulcanization reaction. They reduce the temperature and sulfur content in the rubber [2]. Most of the accelerators have an effect on the properties of vulcanizates, specially, ageing resistance

[2]. They should reduce the possibility of pre-vulcanization and reversion and probability of sulfur blooming on rubber surface [1].

In 19th century, inorganic compounds were used as accelerators such as hydroxides and oxides of lead, calcium, zinc and magnesium [3]. After some years later amine and its derivatives, piperidine, dimethylamine, trimethylamine and their alkaline derivatives were largely used [3].

Accelerators can be divided into four groups according to their activity in vulcanization process, slow (guanidines, some aldehydamines), fast (thiazole), very fast (thiurams) and ultra-fast accelerators (dithiocarbamates, xanthates) [4]. Primary accelerators are generally providing considerable scorch delay and better cross link development and secondary accelerator usually scorch and fast curing.

Accelerator activity in vulcanization process depends on type of rubber, rubber composition, accelerator concentration and conditions of vulcanization [5]. So the same type of accelerator provides different impact in different compounds. For an example, thiazoles are fast accelerators in most of the compounds but they act as weak accelerator in chloroprene rubber compounds. Accelerators additionally act as a slow bond formation compound [6].

Different quantities of accelerator are used in rubber compounds. The amount depends on the rubber type and vulcanization processing conditions. Normally, very little volume of accelerator is more effective as a result of smaller amount of sulfur is required to achieve the expected vulcanization properties [7].

Very fast accelerators offer high network densities of cross-linking. Thiazole type accelerators used as fast accelerator in tyre industries and these accelerators are appropriate for vulcanization of butadiene rubber, styrene butadiene rubber, natural rubber and other low unsaturated rubbers. They have low cross-linking densities and broad vulcanization plateau compared to thiurams [8].

A solid tyre, resilient or press on type consists a bonding layer. Commonly bonding compounds are used to adhere metal parts with rubber materials. Bonding compound in resilient solid tires is attached to the bead (steel) wires as a bonding (adhesion) coating and used as bonding layer in press on tyres between steel band and rubber layers. These compounds prepared with primary accelerator. MOR, N,N-diisopropylbenzothiazole-2-sulfenamide(DIBS) and N,N-dicyclohexylbenzothiazole-2-sulfenamide(DCBS) are frequently used accelerators for steel and brass.

MOR is an excellent and N-oxy-diethylene -2- benzothiazole sulfonamide (NOBS) type accelerator having an excellent delayed action ensure scorch safety. MOR has good properties such as easy to disperse, changing the product color slightly, suitable for

natural and synthetic rubbers and also can be used to make products that need to bear great tension [2]. Not only that also it shows excellent physical properties such as hardness and tensile. But, because of the carcinogenic effect in MOR, it was decided to replace MOR by TBSI.

TBSI is a primary accelerator however also can be used as secondary accelerator. It is an amine-based accelerator. It does not generate the nitrosamines. NOBS is carcinogenic that produces toxic gases like nitrogen oxides. MOR has nitrogen and oxygen atoms that turn out toxic gases. So, it can be replaced by TBSI with excellent physical properties.

Materials and Methods

Materials

Bonding rubber compound was made in two stages.

RSS (Ribbed Smoke Sheet) 3, carbon N 330, C5 resin, 6PPD(N-1,3-(dimethylbutyl)-N-phenyl-1,4-benzenediamine), rescorcin/ 80 SBR, stearic acid, TMQ(poly(1,2-dihydro-2,2,4-trimethyl-quinoline), zinc oxide, and silica were added as first stage material. Sulphur, PVI (pre vulcanization inhibitor), insoluble sulphur and MOR/TBSI accelerator were added as second stage materials. All the materials were mixed with respective Phr amounts.

Methods

Test Sample Preparation

Table 1- Test sample formulation of second stage bonding compound

Material	Phr
First stage compound	78
Sulphur	12
MOR/TBSI	0.7
PVI	0.25
Insoluble Sulphur	10

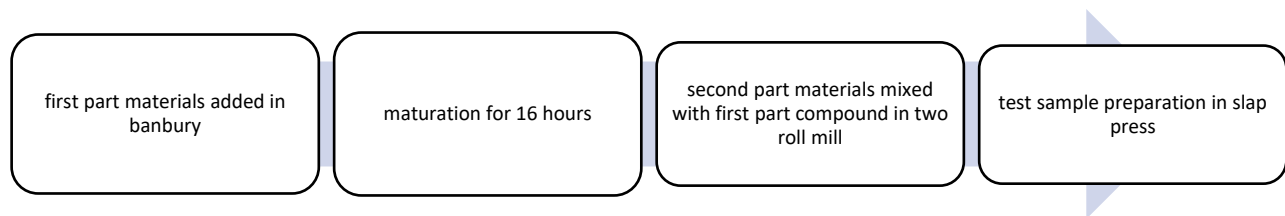


Figure 1. Flow chart of sample preparation

The bonding compound was made in two stages. In first stage, materials were masticated in internal Banbury mixer. According to the formula in Table 1, the second stage compound materials were added with first stage compounds and mixed in two-roll mill. Test samples were prepared by adding TBSI as an accelerator while control sample was prepared by adding MOR as an accelerator. All other test conditions kept same while changing only the accelerator type. During this study TBSI accelerators were used from two different manufactures (TBSI-SI and TBSI-hayleys). Ash content of TBSI is 0.5 % and MOR is 0.3 %. The purity of MOR is 98% and TBSI is 88%.

Physical and mechanical properties were tested using different standard methods. Tensile and elongation at break was measured using ASTM D412 method while the force maintained at 500 N, density was measured using ASTM D1817 method and hardness was measured using ASTM D2240-00 technique. Physical test and rheometer test samples were prepared using rubber compound sheet 20 cm × 15 cm in slap press and it was maintained at 150 °C for 30 minutes. Thickness of the samples were 0.5 cm. All MOR, TBSI-SI and TBSI-HEYLIS were prepared and performed for replicates.

Tensile set is defined as the extension remaining of a specimen after it has been stretched and allowed to relax for a period. It is expressed as a percentage of the original length. The tensile properties are more important in any type of rubber product.

Bead Wire Bonding Test

Bead wire bond strength is an adhesion strength that holds the steel wire and the rubber layer. This test method was performed according to ASTM D1871 standards. Bonding was done by using UTM (Universal Tensile Machine). Specially this test was carried out only for bonding compounds. The test sample was prepared in the two-roll mill. The samples were cut in to 5 cm × 5 cm size and thickness of the sample was 1 cm. Bead(steel) wire was placed with in the slap press hot plate then the sample was inserted into the hole of the hot plate cavity. Slap press was maintained at 150 °C for 30 minutes.

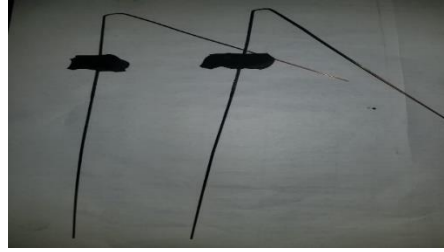


Figure 2- bead wire test sample

Rheometer- Viscosity Test

Rheometer-viscosity tests were performed according to ASTM D2084 standard in Oscillating Die Rheometer (ODR). The test result was given using computer with aid of EKTRON software.

Results and Discussion

Sample	Tensile (kg/cm ²)	Elongation at break (%)	Hardness (shore A)	Density	Bead wire bond strength (kg/cm ²)
MOR	118.099	70.66	89.00	1.33	56.75
TBSI-HAYLEYS	104.242	70.00	89.00	1.33	50.1045
TBSI-SI Group	111.259	99.666	88.00	1.32	51.679

Table 2. Physical properties test results

The average test results of physical-mechanical properties of vulcanized bonding rubber compound samples shown in Table 2. TBSI accelerator samples were shown low tensile strength than the MOR accelerator. Furthermore, TBSI-SI samples were shown higher tensile strength than TBSI- hayleys. The low tensile property was occurred in TBSI samples as an accelerator has high butyl-2-benzothiazole structure [9] and it has high quantity of Carbons and Hydrogens in the structure than MOR [9]. The tensile property is necessary in bonding and the strength should be compromised with steel.

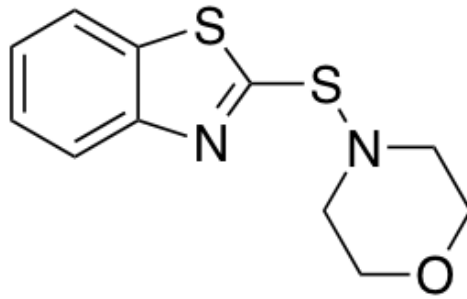


Figure 3. MOR(2-(Morpholinothio)benzothiazole) structure

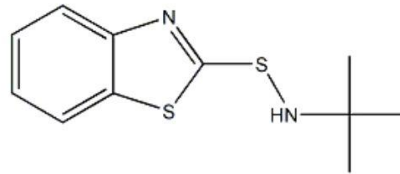


Figure 4. TBSI structure

MOR and TBSI-hayleys samples show good elongation at break but TBSI-SI samples show poor performance while showing higher value of elongation where the bonding compound is not required high amount of elongation [10]. MOR samples and also the TBSI- hayleys were shown almost same hardness near value whereas TBSI- SI samples were shown the lower hardness. The hardness was high in most of the samples because of the high ash content and high carbon bond in the accelerators [11]. Hardness of the rubber mostly depend upon the materials used in the compound specially the filler type. As in bonding compound, same quantity of carbon filler was used in all tested samples given the same hardness value in test samples.

The densities of the MOR samples and the TBSI-hayleys samples were same. The density of TBSI-SI is low compared to TBSI-hayleys samples. Non aging samples (samples tested before 24 hours) results were shown in Table 2. Same as hardness property, the densities of the samples were depended within the chemicals used in the test samples. Mostly density was affected by the rubber and filler used in the compound. However, accelerator had significant amount of effect in density and hardness as the cross-link density occurred by vulcanization system. The results should be in the value range of standard compound values which is used to predict the test result. All tested properties were attained the standard test values.

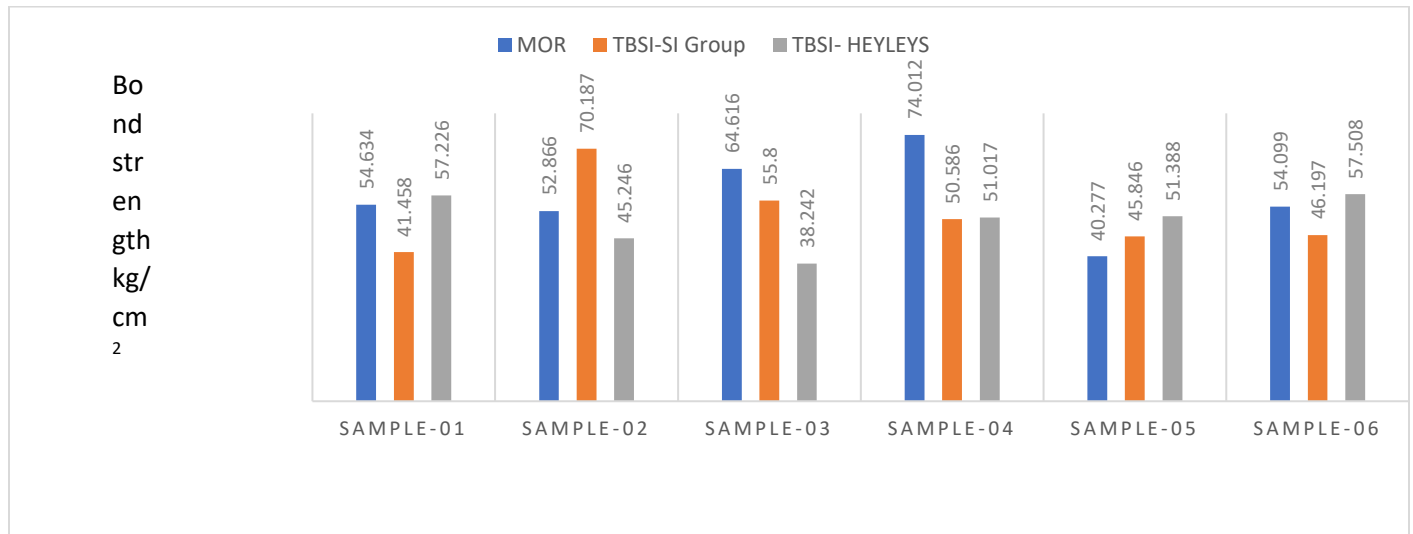


Figure 5. Bead wire bonding strength result according to the accelerator type

As shown in Figure 5, the column chart indicated that TBSI -SI replicate samples were shown better bead wire bonding properties compared to TBSI- hayleys samples. Bead wire bonding properties should not be less than 28. All tested samples (MOR, TBSI hayleys and TBSI-SI) were in required levels. MOR had high bonding strength as it has benzene ring structure [11]. Normally 50-70 MPa bonding strength should be required.

Bead wire bonding testing is the most important property test for the bonding compound. The steel bead and rubber adhesion should be maintained by adhesive and cohesive forces in the steel and rubber molecules. Then only the correct property range occurs.

Rheometer Cure Characteristics

Table 3. Rheometer test results

sample	sample No	ML(dN/m)	MH(dN/m)	TS2(seconds)	TC90(seconds)
MOR	1	7.16	170.58	48	247
TBSI hayleys	2	5.78	176.02	42	248
TBSI SI	3	6.58	170.78	44	249

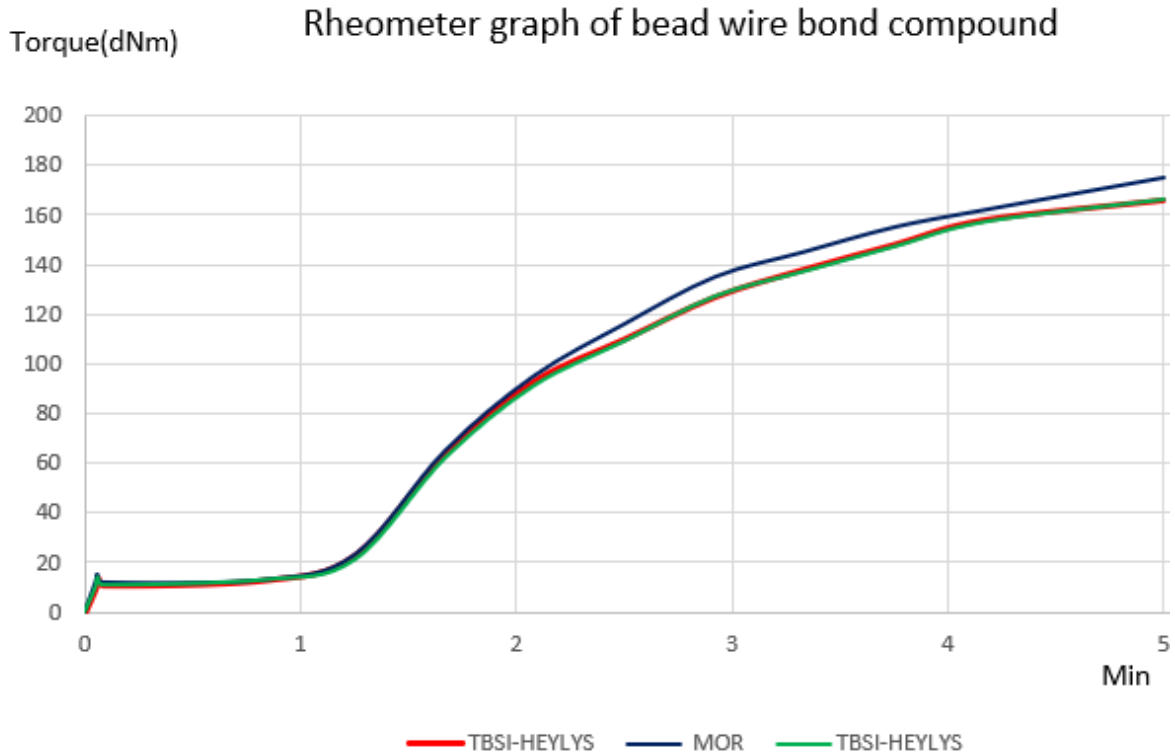


Figure 6. Rheometer graph of bead wire bond compound

Figure 6 shows that all samples were good at cure characteristics including ML, MH, TS2 and TS90. As the Table 3 indicates the MOR and TBSI-SI samples were shown same cure properties and values.

ML (Minimum Torque)

This was the initial cross-link density of the compound and given the concerning idea about the uncured rubber. The initial cross-links were formed during the first stage mastication. MOR accelerator was shown high ML thus it was given high initial cross links than TBSI accelerator.

MH (Maximum Torque)

Maximum torque value was given the idea about where the high cross-link happened. As the value the TBSI hayleys sample was given high value. So, the cross-link amount with TBSI was higher than MOR.

TC90(90%torque)

TC90 was achieved very late by tested samples. However, the MOR and TBSI samples passed the TC90 values and all samples were given the plateau curve. It was indicated the 90% cross-link density. At this point all samples were shown closer values.

Conclusion

MOR accelerator releases toxic gases while handling and curing at high temperatures. These toxic compounds pollute the atmosphere and cause cancers according to the earlier studies done by scientist. Substitution of the MOR compounds by safe TBSI accelerators shows promising results with no carcinogenic effect. As TBSI has no oxygen atoms it is difficult to produce carcinogenic NOBS gases. According to this study, MOR, TBSI- hayleys, TBSI-SI samples analyzed as an accelerator specification of bonding compound properties. Among TBSI samples, SI samples were shown higher tensile properties and bead wire bonding properties compared to TBSI-hayleys samples. The hayleys samples were shown good hardness and density properties than TBSI-SI samples. The difference properties were given by TBSI samples because the properties differ with purity of TBSI which differ with manufactures. It was occurred because of the quality and purity of the TBSI material. All tested samples were passed to reach the expected level of rheometer TC90 value and given better cure properties. TBSI-SI was shown promising properties. These accelerators could be used with natural or synthetic rubbers like butadiene and styrene butadiene rubbers along with zinc oxide and antioxidants. Bonding rubber compound was used to coat the steel wires and used as bonding layer in solid tyre production which used to enable the bonding between different hardness of layers. In this study the bonding compound (used to adhere steel and rubber) was taken to replace the MOR without harming to its original properties. TBSI samples were succeeded to replace the MOR accelerator by maintaining its original properties of bonding rubber compound used in bonding layers. Therefore, the TBSI accelerator type is the best alternative to replace the MOR accelerator.

Conflicts of Interest

Authors declare no conflicts of interest

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