ABSTRACT

Different activator systems containing zinc oxide, zinc stearate, calcium oxide, thiodiglycol metal complexes and nano-zinc oxide were applied for sulphur vulcanization of NR/SBR blend. The systems were chosen in order to have better dispersion in rubber matrix, better metal ion release in vulcanization process and lower zinc content. The cure characteristics and physicomechanical properties were investigated. Results showed that zinc oxide could be reduced from 4 to 2 phr in the formulation, without any detrimental effects on properties. Zinc stearate was not a good activator but it could be employed in combination with zinc oxide to improve tensile properties. Calcium oxide did not show satisfactory results. Zinc complex of thiodiglycol was an acceptable substitute for zinc oxide due to better dispersion in rubber matrix and better ability for zinc ion release. Zinc content could be reduced to about 4.5 mmol per 100 g of rubber by using this complex. Calcium complex of thiodiglycol was not a good choice either and showed detrimental effects on properties. Application of nano-zinc oxide did improve abrasion and tensile properties due to better surface effects. An alternative mixing method which was used to improve the zinc oxide and nano-zinc oxide dispersion was good and showed better abrasion and tensile properties. The results are presented as patterns to achieve the desirable properties.

INTRODUCTION

Nowadays there is clear evidence that zinc plays an important role in the efficiency of cross-linking systems. Zinc oxide is the most common activator used in rubber industry for improving the vulcanization rate and efficiency. There is general agreement that zinc cations from zinc oxide react with organic accelerators to form an active zinc-accelerator complex which is one of the main steps in the vulcanization process [1-4]. This complex reacts with sulphur to form an active sulphurating agent which interacts with allylic sites of the rubber to form cross-links. Although addition of zinc oxide enhances the vulcanization efficiency and vulcanizate properties and reduces the vulcanization time, there are three major problems associated with its application in rubber compounds.

The first problem is the low affinity of zinc oxide towards most elastomers, so it is very difficult to incorporate it efficiently into rubber matrix. The second problem is mould fouling, that during...
vulcanization, a layer of zinc sulphide is deposited on the wall of the mould and builds up gradually with each subsequent production cycle [5,6]. Reduction of zinc content in rubber formulary has significant effects in producing less deposition. The third problem concerns the zinc release into the environment from rubber products during production, service life, disposal and recycling as its toxicity has detrimental effect on the living environment and organisms [7,8].

The desire to optimize the cure process and decrease the zinc content in rubber products, has led to search for other alternatives for conventionally activator system, containing zinc oxide. Today the researchers focus on reduction of zinc oxide content and finding new activator systems in order to improve dispersion in rubber matrix, higher solubility in hydrocarbons for raising the availability of Zn^{2+} ions. Heideman et al. have reduced zinc oxide content in SBR and EPDM compounds to 1 and 2 phr, respectively [3]. Chapman has reduced zinc oxide content in NR, EPDM, SBR, and NBR compounds [9]. Pysklo et al. have also reduced zinc oxide in IR and SBR in the presence of a phase transfer catalyst [10]. In their report Duchacek et al. discuss the efficiency of different metal stearates on the cure properties of NR and attribute them to electron configuration of metals [11]. Garreta et al. have likewise considered different metal oxides in model compound vulcanization of NR [12]. Tulyapitak has studied the curing and mechanical properties of carboxylated nitrile rubber vulcanized by alkaline earth metal compounds [13]. Umland has disclosed vulcanization activators based on zinc salts of organic carboxylic acids being homogeneously dispersed in rubber matrix [14]. Henning has used zinc salts of acrylic and methacrylic acid and explored the mechanism of network enhancement through the use of these salts [15]. Wei et al. have reported that nano-zinc oxide in NR/BR compounds has improved their tear strength [16]. By applying nano-zinc oxide into SBR masterbatch Jincheng et al. have found improvement in mechanical properties [17]. Pysklo et al. have used 2 phr nano-zinc oxide in IR without any detrimental effects on its properties [18].

NR/SBR blend is investigated because of its common application in tire treads. The work was designed to provide different activator systems in order to reduce zinc content and achieve better dispersion and distribution of metal ion in rubber matrix. The effects of each system on the properties of the products were investigated and their advantages and disadvantages were concluded. The conventional zinc oxide was decreased in compound formulation in the first step. Zinc stearate was applied as an activator, due to its higher affinity towards elastomers which gave better dispersion in rubber matrix. Calcium oxide was designated as a conceivable alternative. Zinc and calcium complexes of thiodiglycol were synthesized and considered as new vulcanization activators. This choice was due to accessibility of raw materials for thiodiglycol synthesis, in petroleum industries, like ethylene oxide and hydrogen sulphide. Furthermore thiodiglycol is a potential tridentate ligand capable of bonding with metals through the sulphur and hydroxyl groups [19-21].

Thiodiglycol complexes can homogeneously disperse in rubber by common mixing procedure because of their organic nature and better metal ion release due to coordination bond between metal ion and thiodiglycol ligand in comparison with the ionic bond in zinc oxide. The effect of zinc ion on rubber properties could be confirmed by comparing the zinc and calcium complexes of thiodiglycol. Nano-zinc oxide was designated as another activator system as the properties change in nanoscale, because of increasing surface area to volume ratio and quantum effects that have impact on the behaviour of materials. The efficiency of zinc oxide and nano-zinc oxide during vulcanization can be enhanced by maximization of the particles contacts with the accelerator in rubber formulation. To achieve this goal an alternative mixing method was investigated for better dispersion and distribution of zinc oxide and nano-zinc oxide. The results of applying different activator systems were reported as viable patterns to choose effective vulcanization system that establish the desired compound properties.

EXPERIMENTAL

Materials
The materials used in the experiments are listed in Table 1. Thiodiglycol metal complexes and nano-zinc
oxide were prepared in laboratory.

**Instruments**

The elemental analysis was made by a CHN analyzer 2400 Perkin Elmer. H NMR 500 MHz Varian was used for \(^1\)H NMR analysis. IR analysis was carried out on KBr pellets of samples and the spectra were taken on a FTIR Spectrum GX, Perkin-Elmer. Transmission electron microscopy (TEM) image was obtained by a Philips EM 208 transmission electron microscopy. Particle size distribution (PSD) was measured by an Optilab Wyatt, Sematech laser light scattering. Particle specific surface area was measured by Brunauer, Emmett and Teller method (BET) and ChemBET 3000 Quantachrome TRP.

The cure characteristics of different compounds were measured at 160ºC with MDR 900, HIWA Company, Iran. The compounds were cured in a laboratory press PTP 600, PGH Company at 160ºC and 220 KN. Density was measured by immersion method. Hardness of the samples was measured by a Bareiss 49038 Hardness-meter Shore A Type, according to ASTM D2240. Abrasion was measured by Bareiss 2243 according to ASTM D5963. Fatigue tests were performed by HIWA 600, HIWA Company according to ISO 6943. Tensile tests were carried out on dumb-bell shaped specimens by M-350-5019, Testometric Company, according to ASTM D412.

**Preparation of Thiodiglycol Zinc Complex**

In a flask 8.5 g (0.06 mol) of ZnCl\(_2\) was dissolved in 200 mL of methanol, followed by addition of 200 mL...
of a methanol solution containing 19 g (0.15 mol) thiodiglycol. The mixture was stirred over a day and then it was concentrated to 200 mL by passing the slow diffusion of diethyl ether vapours from the solution. The zinc complex of thiodiglycol was formed which was confirmed by CHN analysis, H NMR and IR spectroscopies [19,20].

CHN analysis for C₈H₂₀O₄S₂Cl₂Zn: calculated: C 25.21, H 5.25; found: C 25.09, H 5.11.

1H NMR (500 MHz, D₂O) (δ, ppm): 2.55 (t, 4H, CH₂-S), 3.15 (br, 2H, OH), 3.55 (t, 4H, CH₂-O).

IR (ν, cm⁻¹): 3383, 2924, 2876, 2048, 1648, 1408, 1286, 1063, 657.

Preparation of Thiodiglycol Calcium Complex

Four grams of CaCl₂, 2H₂O (0.03 mol) was dissolved in 100 mL of methanol and 100 mL of a methanol solution containing 9 g (0.07 mol) thiodiglycol was added into the flask. The mixture was stirred over a day and then it was concentrated to 100 mL, by passing the slow diffusion of diethyl ether vapours from the solution. The calcium complex of thiodiglycol was formed which was confirmed by CHN analysis H NMR and IR spectroscopies [21].

CHN analysis for C₈H₂₀O₄S₂Cl₂Ca: calculated: C 27.01, H 5.35; found: C 26.85, H 5.23.

1H NMR (500 MHz, D₂O) (δ, ppm): 2.67 (t, 4H, CH₂-S), 3.11 (br, 2H, OH), 3.75 (t, 4H, CH₂-O).

IR (ν, cm⁻¹): 3391, 2930, 2888, 2051, 1666, 1429, 1277, 1090, 683.

Preparation of Nano-size Zinc Oxide

One hundred milliliter aqueous solution of 1 M zinc acetate was mixed with 100 mL aqueous solution of 2 M sodium hydroxide. After stirring for 6 h, 5 mL of triethanolamine (TEA) was slowly added to the reaction mixture. It was then stirred for extra 10 minutes. Finally, the mixture was placed under microwave irradiation (20% power) for 20 min. The white solid product was vacuum filtered, washed with distilled water and dried in air at room temperature. It was then calcinaited at 900°C for 1 h [22]. The prepared nanoparticles were investigated by TEM (Figure 1), PSD (Figure 2) and BET analysis. The nano-size zinc oxide particle dimension was in the range of 30–70 nm with specific surface area 39.7 m²/g.

![Figure 1. TEM image of synthesized zinc oxide nanoparticles.](image1)

![Figure 2. Nano-zinc oxide particle size distribution.](image2)
combinations in MB and NMB preparation.

RESULTS AND DISCUSSION

Reducing of Commercial Zinc Oxide

Zinc oxide content was reduced from 4 to 1 phr in the compounds Z4 to Z1. Figure 3 and Table 3 have shown rheometric curves and different properties of the compounds, respectively. $M_H$ which has shown the maximum torque in a cure curve is decreased by reducing the zinc oxide content as it is also confirmed being decreased in the cure state. $T_{90}$ defined as the time to reach 90% of the maximum torque, was highly decreased in compound Z1 and it confirmed the delaying effect of zinc oxide in vulcanization process which was caused by delaying in the disappearance of the cross-link precursors. $T_S$ that is scorch time and process safety has shown the minimum value using 1 phr of zinc oxide. Density was decreased by reducing the zinc oxide level, as it is a dense material. Hardness was decreased by using 1 phr of zinc oxide and

![Figure 3. Rheometric curves of the compounds Z4-Z1.](image)

Table 2. Compounds recipe.

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<th>Label</th>
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<th>CB</th>
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(a) Stearic acid; (b) zinc stearate; (c) calcium complex of thiodiglycol; and (d) zinc complex of thiodiglycol.
confirmed the lower cure stage. Abrasion was increased by reducing the zinc oxide level and confirmed the lower cure state and cross-link densities. Fatigue was increased by reducing the zinc oxide level that may be caused by polysulphidic linkage. Tensile strength was slightly changed in compounds Z4 to Z2 and it clearly showed the effective vulcanization process in these three compounds, although it was highly decreased in compound Z1 and confirmed the lower cure state. Modulus of 100% has shown good results for all compounds but the modulus of 300% decreased for compound Z1, confirming the lower cure rate as MH results have shown before. Elongation-at-break has presented the maximum value for compound Z1. From the discussion it can be concluded that zinc oxide content can be reduced successfully from 4 to 2 phr (50%) in the compound without any detrimental effects on the properties.

Application of Zinc Stearate

Three compounds S3 to S1 were considered using 4 to 2 phr of zinc stearate and compound S4 using 1 phr of zinc stearate in addition with synergic effect of 1 phr zinc oxide. Figure 4 and Table 4 show the rheometric curves and different properties of the compounds, respectively. MH was decreased in comparison with the system containing zinc oxide and this lower torque was caused by lubricant effects of zinc stearate. The presence of zinc oxide in compound S4 as zinc oxide is a dense material. Hardness was highly decreased by using the zinc stearate and confirmed the lower cure stage in comparison with zinc oxide curing system. Abrasion was increased in the compounds containing zinc stearate which established the lubricant symptoms and a non-effective cure system, which was improved by applying zinc oxide in the formulation. Fatigue was more than 300 KC for all the compounds and showed good results. Tensile strength was highly increased in compound S4 which demonstrated release ability from covalent bond in zinc stearate in comparison with ionic bond in zinc oxide which was confirmed by the delay action in the vicinity of zinc oxide. Density was not significantly changed in compounds S3 to S1 but it was increased in compound S4 as zinc oxide curing system. Abrasion was increased in the compounds containing zinc stearate which established the lubricant symptoms and a non-effective cure system, which was improved by applying zinc oxide in the formulation. Fatigue was more than 300 KC for all the compounds and showed good results. Tensile strength was highly increased in compound S4 which demon-

<table>
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<th>Label</th>
<th>Density [±SD] (kg/m³)</th>
<th>Hardness [±SD] (Shore A)</th>
<th>Abrasion [±SD] (mm²)</th>
<th>Fatigue [±SD] (KC)</th>
<th>Tensile strength [±SD] (MPa)</th>
<th>Modulus 100% [±SD] (MPa)</th>
<th>Modulus 300% [±SD] (MPa)</th>
<th>Elongation-at-break [±SD] (%)</th>
</tr>
</thead>
</table>

(a) Standard deviation.

Figure 4. Rheometric curves of the compounds S4-S1.
strated the more effective vulcanization process in the presence of zinc oxide. Modulus 100% and modulus 300% both showed similar behaviour. Elongation-at-break has presented the acceptable values. Application of zinc stearate has shortened the vulcanization time due to faster releasing of zinc ions being incorporated in vulcanization process. The above results have shown the synergistic effects of zinc oxide and further activation of rubber-sulphur-accelerator-zinc oxide system in presence of fatty acid salts due to higher affinity of activator system towards rubber matrix with higher effectiveness. Higher amounts of zinc stearate were not recommended because of its high abrasion results and mixing problems.

### Application of Calcium Oxide

Three compounds C3 to C1 were considered, using 4 to 2 phr of calcium oxide. Figure 5 and Table 5 have shown the rheometric curves and different properties of the compounds, respectively. $\text{MH}$ was decreased in comparison with the system containing zinc oxide and this lower torque was caused by curing reduction. During active complex formation, the $\text{Zn}^{2+}$ ions act as Lewis acid and the accelerator acts as Lewis base. The acidity of metal ion is dependent on its size and charge, according to eqn (1) [23]:

\[
\text{Cation acidity} = \frac{KZ^2}{r}
\]

where $Z$ is charge of the cation, $r$ is radius of the ion, and $K$ is constant.

Since for $\text{Zn}^{2+}$ and $\text{Ca}^{2+}$ ions the charges are equal, the size of the cation is the main factor which influences the acidity of ions. The ionic radius of $\text{Ca}^{2+}$ is larger than $\text{Zn}^{2+}$ and shows more basic characteristic and slight tendency to form complexes. This leads to lower curing state. $T_c90$ was decreased in compounds containing calcium oxide and showed a faster cure system. This was due to increased pH that activated the accelerated properties of amines. Density values have shown some acceptable values. Hardness has highly decreased by using calcium oxide and presented the lower cure state. Abrasion has highly increased by using this activator system, as much as compound C1 has fully chafed before finishing the test. Fatigue has shown good results. The results obtained for tensile strength and modulus 300% are not acceptable due to non-effective

### Table 4. Properties of the compounds S4-S1.

<table>
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<tr>
<th>Label</th>
<th>Density [±SD] (kg/m³)</th>
<th>Hardness [±SD] (Shore A)</th>
<th>Abrasion [±SD] (mm³)</th>
<th>Fatigue (KC)</th>
<th>Tensile strength [±SD] (MPa)</th>
<th>Modulus 100% [±SD] (MPa)</th>
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<th>Elongation-at-break [±SD] (%)</th>
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<td>7.5696 ±0.3893</td>
<td>0.7733 ±0.0187</td>
<td>2.8059 ±0.1044</td>
<td>603 ±14</td>
</tr>
<tr>
<td>S1</td>
<td>1083 ±1</td>
<td>45 ±1</td>
<td>250 ±6</td>
<td>&gt;300</td>
<td>5.7289 ±0.1861</td>
<td>0.7187 ±0.0556</td>
<td>2.3125 ±0.01657</td>
<td>567 ±12</td>
</tr>
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</table>

Figure 5. Rheometric curves of the compounds C3-C1.
vulcanization system but modulus 100% and elongation-at-break were settled in the acceptable range. From the discussion it could concluded that calcium oxide is not a good substitute for conventional zinc oxide.

**Application of Thiodiglycol Complexes**

Figure 6 presents the rheometric curves of the compounds containing thiodiglycol in comparison with compound Z2 and their properties are tabulated in Table 6. $M_H$ was not significantly changed in compounds TZ1 and TZ3 but highly decreased in other compounds and produced a non-effective vulcanization system. $T_{e90}$ has shown higher values for compounds TZ1 and TZ3, and other compounds have presented faster curing. This behaviour is due to the absence of zinc oxide in TZ2 and basicity of Ca$^{2+}$ ions in TC1 and TC2. $S_{25}$ was decreased by using the complexes but still acceptable for the compounds TZ1 and TZ3. Density was decreased a little in compounds TZ1, TZ2, and TZ3 and more increased in compounds

![Rheometric curves of the compounds containing thiodiglycol complexes in comparison with Z2.](image-url)
TC1 and TC2 as zinc oxide (a dense material) was used together with higher values of complexes in two foregoing compounds. Hardness was decreased by using the complexes but still acceptable in cases of TZ1 and TZ3. These two compounds presented similar abrasion behaviour towards Z2 and gave an effective cure system. TC1 and TC2 could not pass the test as they chafed fully. Fatigue has shown good results by applying zinc complex and the compounds containing calcium complex could not pass the test due to non-effective vulcanization system. Tensile strength was slightly changed in TZ1 and TZ3 with obvious change in the effective vulcanization process of these two compounds but decreased in others. Modulus 100% and modulus 300% have also shown good results for TZ1 and TZ3. Elongation-at-break has shown the same behaviour. From the discussion it may be concluded that TZ1 and TZ3 were good substitutes for Z2 which was considered as a reference compound here, without detrimental effects on properties. The results have shown that calcium complex was not a good substitute for a conventional activator in spite of the synergetic effects of zinc oxide.

Table 7 has presented the zinc content of different compounds. There is lower zinc in TZ1 in comparison with TZ3, so it is a better choice for substitution and reduced zinc content about 4.5 mmol per 100 g of rubber due to homogeneous dispersion and distribution of zinc ions in rubber matrix.

### Application of Nano-size Zinc Oxide

Figure 7 shows the rheometric curves and Table 8 gives the properties of different compounds. $M_{H}$ presents acceptable value by applying 2 phr of nano-size zinc oxide. $T_{90}$ and $T_{32}$ are increased in the compounds NZ2, MB, and NMB. Reduction in the dimension and surface area of zinc oxide in the compounds NZ2 and NMB, in addition with better distribution of zinc ions in the compounds MB and NMB, has facilitated the formation of an active complex with sulphur and accelerator, which have led to formation of an increased number of vulcanization precursors and their delayed disappearance and increased cure time. Density has increased in compounds MB and NMB, which may be due to the improvement of zinc distribution, which has reduced void volumes generated by agglomeration. Hardness is decreased slightly by using nano-size zinc oxide which may cause clustering of particles and the improvement is noticed by using the alternative mixing method. Abrasion is reduced using nanoparticles and alternative mixing method as it has increased interfacial interaction between zinc oxide nanoparticles and rubber matrix because of the reduction in size and increase in surface area. Fatigue has demonstrated good results (more than 300 KC for the compounds NZ1, NZ2, MB, and NMB). Tensile strength modulus 100% and modulus 300% have been highly increased in the compounds NZ2, MB, and NMB which were confirmed on the more effective symptoms. It could be concluded that reduction of zinc oxide content from 2 to 1 phr is impossible by using this kind of nano-size zinc oxide particles, without any detrimental effects on properties. Applying 2 phr of nano-size zinc oxide.

<table>
<thead>
<tr>
<th>Label</th>
<th>Zn (mmol)/rubber (100 g)</th>
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<tbody>
<tr>
<td>Z2</td>
<td>22.42</td>
</tr>
<tr>
<td>TZ1</td>
<td>18.21</td>
</tr>
<tr>
<td>TZ2</td>
<td>14.05</td>
</tr>
<tr>
<td>TZ3</td>
<td>21.08</td>
</tr>
<tr>
<td>TC1</td>
<td>11.18</td>
</tr>
<tr>
<td>TC2</td>
<td>11.18</td>
</tr>
</tbody>
</table>
zinc oxide can highly improve abrasion and tensile properties. The usage of alternative mixing method has led to greater improvement in abrasion and tensile properties due to better dispersion of activator in rubber matrix.

CONCLUSION

It can be concluded from the results that for the CBS-accelerated sulphur vulcanization of NR/SBR blend, the conventional zinc oxide content could be reduced successfully from 4 to 2 phr (50%) without any detrimental effects on the properties. Zinc stearate curing takes place faster due to better zinc ion release ability but the cure rate is decreased. It is essential to have synergetic effects of zinc oxide to maintain the properties of the compound. Calcium oxide is not a good substitute for conventional zinc oxide. Calcium ion has basic characteristic in comparison with zinc ion. This causes slight tendency to form active complexes and lower cure rate. Conventional zinc oxide can successfully be substituted by thiodiglycol zinc complex and the zinc content is reduced to about 4.5 mmol per 100 g of rubber. Calcium complex of this ligand is not a good choice. Zinc content cannot be reduced to 1 phr by using this kind of nano-size zinc oxide but tensile and abrasion properties can be highly improved using 2 phr of nano-zinc oxide due to increased interfacial interaction between the nanoparticles and rubber matrix because of reduction in size and increase in surface area.

Usage of alternative mixing method has shown greater improvement in abrasion and tensile properties due to better dispersion of activator in the rubber matrix.

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SYMBOLS AND ABBREVIATIONS

\[ M_H \] : Maximum torque in cure curve
\[ T_{90} \] : Time to reach 90\% of the maximum torque
\[ T_{S2} \] : Scorch time
\[ K \] : Constant
\[ Z \] : Cationic charge
\[ r \] : Radius of the ion
TEM : Transmission electron microscopy
PSD : Particle size distribution
BET : Brunauer, Emmett, Teller

REFERENCES

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