Synthesis of derivative of zinc dithiocarbamate of piperazine (ZDPC) and its application as a safe accelerator for the vulcanization of natural rubber latex

Síntese do derivado do ditiocarbamato de zinco da piperazina (ZDPC) e sua aplicação como um acelerador seguro para a vulcanização do látex de borracha natural

Síntesis de un derivado del ditiocarbamato de zinc de piperazina (ZDPC) y su aplicación como acelerador seguro para la vulcanización del látex de caucho natural

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ABSTRACT
Derivative of zinc dithiocarbamate of piperazine (ZDPC) prepared in the laboratory acts as an accelerator for the vulcanization of natural rubber latex based formulations. The ZDPC synthesized in our laboratory was characterized by FTIR spectroscopy, UV-Visible spectroscopy and CHNS analysis. Results of the MTT assay show that the ZDPC is a safe (non-carcinogenic) rubber chemical. For comparable dosages of the accelerator, the ZDPC based natural rubber latex vulcanizates show improved mechanical properties as compared to zinc diethyl dithiocarbamate (ZDEC) based vulcanizates. ZDPC may be considered as a safe replacement for the nitrosamine generating ZDEC in natural rubber latex based formulations.

Keywords: vulcanization, natural rubber latex, non-carcinogenic, accelerator, nitrosamine
RESUMO
O derivado de ditiocarbamato de zinco de piperazina (ZDPC) preparado em laboratório atua como um acelerador para a vulcanização de formulações à base de látex de borracha natural. O ZDPC sintetizado em nosso laboratório foi caracterizado por espectroscopia FTIR, espectroscopia UV-Visível e análise CHNS. Os resultados do ensaio MTT mostram que o ZDPC é um produto químico de borracha seguro (não carcinogênico). Para dosagens comparáveis do acelerador, os vulcanizados de látex de borracha natural à base de ZDPC apresentam propriedades mecânicas aprimoradas em comparação com os vulcanizados à base de dietil ditiocarbamato de zinco (ZDEC). O ZDPC pode ser considerado um substituto seguro para o ZDEC, gerador de nitrosaminas, em formulações à base de látex de borracha natural.

Palavras-chave: vulcanização, látex de borracha natural, não carcinogênico, acelerador, nitrosamine

RESUMEN
El derivado del ditiocarbamato de zinc de piperazina (ZDPC) preparado en el laboratorio actúa como acelerador de la vulcanización de formulaciones a base de látex de caucho natural. El ZDPC sintetizado en nuestro laboratorio se caracterizó mediante espectroscopia FTIR, espectroscopia UV-Visible y análisis CHNS. Los resultados del ensayo MTT muestran que el ZDPC es un producto químico del caucho seguro (no cancerígeno). Para dosis comparables del acelerador, los vulcanizados de látex de caucho natural a base de ZDPC muestran mejores propiedades mecánicas que los vulcanizados a base de dietil ditiocarbamato de zinc (ZDEC). El ZDPC puede considerarse un sustituto seguro del ZDEC, generador de nitrosaminas, en las formulaciones a base de látex de caucho natural.

Palabras clave: vulcanización, látex de caucho natural, no cancerígeno, acelerador, nitrosamina.

1 INTRODUCTION

Nitrosamines are known to cause significant carcinogenic effects in laboratory animals. However there is no direct evidence to prove that they cause cancer in humans. Nitrosamines have been detected in various rubber products such as baby teats, condoms, gloves and balloons which are used in our daily life [1],[2],[3],[4]. N-nitrosamines are formed by the interaction between amines and atmospheric nitrosating agents [5]. The amines originate from the rubber chemicalsthat are added during processing as accelerators or retarders of the vulcanization process [6].

During the vulcanization process, dithiocarbamates, thiurams and some sulfonamides get converted to secondary amines. In the presence of nitrosating agents, secondary amines react to form nitrosamines [7][8][9][10]. Some of the nitrosamines
that are found in rubber industry are: N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosodibutylamine (NDBA), N-nitrosopiperidine (NPIP), N-nitrosomorpholine (NMoR) and N-nitrosoethylphenylamine (NEPhA)[11][12].

Zinc salt of various dithiocarbamates are widely used as accelerators for the vulcanization of natural rubber latex because of the excellent properties of the vulcanizates produced. Unfortunately, dithiocarbamates, being secondary amines, produce harmful N-nitrosamines. Substitution of these accelerators with safe (non-carcinogenic) accelerators requires thorough investigation to prove that the substitutes give vulcanizates of acceptable properties [13][14].

Nitrosamine are formed during vulcanisation using conventional accelerators like zinc diethyl dithiocarbamate (ZDEC) as the ethyl groups present in ZDEC is not a constraint for the amine group to react with nitrogen oxide in the air to form N-nitrosodimethyl amine (NDEA). It has been reported that N-nitroso diethyl amine is one of the most potent carcinogens [15].

The replacement of the ethyl groups present in the ZDEC with a bulky group such as piperazine may result in the formation of non-regulated (safe) nitrosamine. The synthesis of novel derivative of zinc dithiocarbamate of piperazine (ZDPC) (Figure 1) and its application as safe accelerator in natural rubber latex formulations are discussed in this paper.

Figure 1. Structure of derivative of zinc dithiocarbamate of piperazine.

Source: own research work

2 EXPERIMENTAL

2.1 MATERIALS

Centrifuged Natural Rubber Latex (high ammonia (HA) type) as per ASTM D1076 – 2010 was obtained from Central Experimental Station, Rubber Research Institute of India, Kottayam.
Figure 2. Reaction scheme for the synthesis of derivative of dithiocarbamate of Piperazine.

Zinc oxide (ZnO) was supplied by M/s. Meta Zinc Ltd. Mumbai. Zinc diethyl dithiocarbamate (ZDC), zinc 2-mercaptobenzothiazole (ZMBT), tetramethylthiuramdisulfide (TMTD), styrenated phenol (SP) and sulphur were supplied by M/s. Associated Rubber Chemicals (Kochi) Pvt. Ltd. Potassium hydroxide and potassium oleate were of the laboratory reagent grade.

Zinc dipiperazine dithiocarbamate (ZDPC) was synthesized in our laboratory. The materials for the synthesis (piperazine, carbon di sulphide, zinc acetate, triethyl amine and methanol) were supplied by M/s. Alpha Chemicals and Diagnostics Ltd., Kochi, India.

2.2 SYNTHESIS OF ZDPC (DERIVATIVE OF ZINC DITHIOCARBAMATE OF PIPERAZINE)

Zinc dipiperazine dithiocarbamate was prepared by the following method. Piperazine (1 mol) was dissolved in methanol. Triethyl amine (1 mol) was added to this solution drop by drop and cooled below 5°C. Carbon di sulphide (1 mol) was slowly added to the cold solution. The piperazine salt formed in the nitrogen atmosphere was precipitated by the addition of zinc acetate dissolved in methanol. The precipitate formed was filtered, washed with methanol-water mixture and dried. The proposed mechanism for the formation of ZDPC is shown in Scheme 1.
2.3 CHARACTERIZATION TECHNIQUES

2.3.1 FTIR Spectroscopy

FTIR spectroscopic analysis of the synthesized ZDPC was conducted using Thermo Nicolet Avatar 370 FTIR spectrometer in the spectral range of 400 – 4000 cm\(^{-1}\) using horizontal attenuated total reflectance assembly.

Figure 2. – FTIR Spectrum of derivative of zinc dithiocarbamate of piperazine.

2.3.2 CHNS analysis

Sulphur content was analysed using CHNS-O Analyser (Thermo Fisher Scientific, Model- Flash 2000, Detector-TCD (Thermal conductivity detector)).

2.3.3 UV spectroscopy

UV-Visible absorption spectra were recorded with Thermo Scientific Evolution 201 UV-Visible Spectrophotometer operating between 200 nm – 900 nm.

2.3.4 MTT assay

Cytotoxicity of the newly synthesized ZDPC was measured from the percentage viability of the cells by using the method of MTT (3-(4,5 dimethylthiazol-2-yl)-2,5-
diphenyltetrazoliumbromide) assay and the test procedure is based on ISO 10993-5. The MTT enters the cells and passes into the mitochondria where it is reduced to an insoluble, coloured (dark purple) formazan product. The cells are then solubilized with an organic solvent (dimethyl sulfoxide DMSO (Himedia)) and the released, solubilized formazan product was measured at 540 nm. Since reduction of MTT can only occur in metabolically active cells, the level of activity is a measure of the viability of the cells. Optical density was read at 540 nm using DMSO as blank in a microplate reader (ELISASCAN, ERBA). Control samples are the cells (L929 cells) to which the ZDPC solution is not added.

The percentage viability of the cells was calculated using the formula:

\[
\text{Percentage viability} = \frac{\text{Optical density of test specimen}}{\text{Optical density of control}} \times 100 \quad (1)
\]

Table 1 - Formulation of Mixes (NR LATEX)

<table>
<thead>
<tr>
<th>Formulation</th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>C₄</th>
<th>C₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR latex (g)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Potassium oleate (g)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>ZnO dispersion (phr)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>SP emulsion (phr)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>ZDEC dispersion (phr)</td>
<td>0.75</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ZDPC dispersion (phr)</td>
<td>0</td>
<td>0.25</td>
<td>0.50</td>
<td>0.75</td>
<td>1</td>
</tr>
<tr>
<td>TMTD dispersion (phr)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>ZMBT dispersion (phr)</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>Sulphur dispersion (phr)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

*based on the dry weight of rubber in the latex and dry weight of the ingredients in the dispersion/emulsion.

Source: own research work

Figure 3. UV Spectrum of derivative of zinc dithiocarbamate of piperazine.
2.4 PREPARATION OF THE MIXES

Mixing of the natural rubber latex based formulations was carried out using mechanical stirrer. The natural rubber latex was stirred and the ingredients were added in the order - stabilizer, anti-oxidant, activators, accelerators and the vulcanizing agent. The mix was kept for 24 hours for maturation. Films were cast using the mixes on a glass plate, dried and cured at 70°C for 24 hours [16]. The film vulcanizates prepared using ZDEC (control) is designated as C₀ and the vulcanizates prepared using varying dosages of ZDPC are designated as C₁, C₂, C₃, C₄ and C₅ (Table 1).

2.5 TESTS ON VULCANIZATES

The tensile strength, tear strength, elongation at break and modulus at various percentages of elongation were measured using Shimadzu Universal Testing Machine, model-AG-1 series (10 KN) at a cross head speed of 500 mm/min, as per ASTM D 412.

The crosslink densities of the vulcanizates were determined using the equilibrium swelling method.

Source: own research work
3 RESULT AND DISCUSSION

3.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY

IR spectrum of the compound (Figure 2.) showed bands at 3387 cm\(^{-1}\) representing N-H stretching. The peak at 3183 cm\(^{-1}\) represents aromatic C-H stretching. The band at 2901 cm\(^{-1}\) represents C-H stretching. The bands at 994, 909, 874, 857 and 815 cm\(^{-1}\) are stretching frequencies of C=S. The peaks at 677 and 617 cm\(^{-1}\) represent C-S stretching and peaks at 1155, 1112 and 1090 cm\(^{-1}\) represent C-N stretching [17].

3.2 UV SPECTRUM

The UV spectrum of the compound is shown in Figure 3. The peak of absorbance at 273 nm represents metal-sulphur linkage [18].

3.3 CHNS ANALYSIS

Table 2 shows the result of CHNS analysis. The theoretical values of CHNS for ZDPC are in very good agreement with the CHNS experimental value obtained from synthesized ZDPC.

<table>
<thead>
<tr>
<th>% of constituents</th>
<th>Theoretical value</th>
<th>Experimental value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>31.00</td>
<td>30.69</td>
</tr>
<tr>
<td>H</td>
<td>4.65</td>
<td>5.1</td>
</tr>
<tr>
<td>N</td>
<td>14.47</td>
<td>14.01</td>
</tr>
<tr>
<td>S</td>
<td>33.07</td>
<td>33.16</td>
</tr>
</tbody>
</table>

Source: own research work

3.4 CYTOTOXICITY

The cytotoxicity of the synthesised ZDPC was evaluated by checking the cell viability through MTT assay. Cell morphology of control of MTT assay and confluent tested cell containing extract of ZDPC (6.25, 12.5, 25, 50 and 100(\(\mu\)g/mL)) were determined using phase contrast image as shown in Figure 4.

Controlled sample of MTT assay show large number of fibroblastic cell. But in the case of the confluent cell containing the extract of ZDPC, considerable reduction in
the number of viable cells was noticed. The reduction in the number of viable cell in the
case of confluent cell containing the extract of ZDPC was evident from the lower values
of optical density as compared to the control cell. The sample containing the extract of
ZDPC was found to possess 98.3%, 92.1%, 88.4%, 84.2% and 81.6% of viable cells. Thus
the result of MTT assay showed that ZDPC accelerator is safe (non-cytotoxic). The
cytotoxicity result of the synthesized ZDPC is as shown in Figure 5.

Figure 5. Cytotoxicity analysis of derivative of zinc dithiocarbamate of piperazine at
different concentrations.

3.5 MECHANICAL PROPERTIES

The mechanical properties of control sample (ZDEC) and different concentrations
of synthesised samples (ZDPC) are shown in Table 3. There is change in the mechanical
properties of synthesized sample with respect to the dosage (phr). The tensile strength,
modulus, elongation break and tear strength of the vulcanizates increases as the dosage
of ZDPC increased. At the comparable dosages of the accelerators the vulcanizates
prepared using the safe accelerator shows better mechanical properties compared to the
vulcanizates prepared using the control. The crosslink density is almost similar in the
case of the novel safe accelerator and the control for comparable dosages of the
accelerators.
### Table 3 - Properties of vulcanizates (from NR latex) prepared using ZDEC (C₀) and ZDPC

<table>
<thead>
<tr>
<th>Properties</th>
<th>C₀</th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>C₄</th>
<th>C₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>18.21</td>
<td>14.66</td>
<td>16.10</td>
<td>18.19</td>
<td>19.66</td>
<td>20.05</td>
</tr>
<tr>
<td>Modulus at 300 % elongation (MPa)</td>
<td>1.69</td>
<td>1.45</td>
<td>1.81</td>
<td>2.03</td>
<td>2.70</td>
<td>3.17</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>1441</td>
<td>1552</td>
<td>1342</td>
<td>1048</td>
<td>953</td>
<td>942</td>
</tr>
<tr>
<td>Tear strength (N/mm)</td>
<td>25.1</td>
<td>23.6</td>
<td>24.3</td>
<td>25.3</td>
<td>26.5</td>
<td>27.4</td>
</tr>
<tr>
<td>Crosslink density × 10⁵ (mol/g)</td>
<td>3.35</td>
<td>3.28</td>
<td>3.30</td>
<td>3.37</td>
<td>3.41</td>
<td>3.48</td>
</tr>
</tbody>
</table>

Source: own research work

### 4 CONCLUSION

Derivative of zinc dithiocarbamate of piperazine (ZDPC) could be prepared in the laboratory using piperazine, carbon disulphide, zinc acetate, triethyl amine and methanol in nitrogen atmosphere. The results of characterization tests (FTIR spectra, UV-Visible spectra and CHNS analysis) confirm the formation of ZDPC. MTT assay test results shows that the newly synthesized ZDPC is a safe (non-carcinogenic) rubber chemical. ZDPC acts an accelerator for the vulcanization of natural rubber latex based formulations. Mechanical properties of the vulcanizates improve as the dosage of ZDPC increases. For comparable dosage the ZDPC based vulcanizates show mechanical properties comparable with the vulcanizates prepared using ZDEC in the case of natural rubber latex based formulations. Thus ZDPC may be used as a safe (non-carcinogenic) replacement for ZDEC.

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