

Influence of ZnO on the properties of elastomeric compositions and their leached extract

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Abstract

The reduction in zinc oxide (ZnO) content in elastomeric compositions has become a subject due to the deleterious effect of zinc ions on aquatic organisms. The purpose of this study was to develop elastomeric compositions containing 0, 1, 3 and 5 phr of ZnO aiming at assessing the influence of the different contents on the rheometric, mechanical and thermal properties. The release of the zinc (Zn) content by leaching, at each step of the production and after the ageing was also assessed. All ZnO-containing compounds had similar rheometric, thermal and mechanical properties. Also, during and after exposure to accelerated ageing the released contents were similar for all compositions regarding the residual ZnO percent. In conclusion, the utilization of the 3 phr ZnO content is viable for the replacement of the usual amount employed.

Keywords: *leaching, properties, vulcanization activation, zinc oxide.*

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1. Introduction

The reduction in ZnO content in elastomeric compositions has become a subject of technological and industrial interest due to the deleterious effect of zinc ions on aquatic organisms^[1]. Zn release to the environment can occur during production, elimination and recycling of elastomeric products, however it is relevant to keep low ZnO levels in elastomeric formulations, not only for environmental, but also for economic reasons^[2]. Zinc is a metal easily encountered in the environment, however, amounts which exceed the safe limit that an organism can absorb and eliminate may cause a lack of equilibrium in the environment. According to the 2004/73/CE European Norm, Zn is classed as deleterious and toxic for aquatic organisms with lasting effects^[3].

In this sense, Heideman^[4] studied the reduction of ZnO levels during sulfur vulcanization of elastomeric compositions based on poly(ethylene propylene diene) (EPDM) and poly(butadiene styrene) (SBR). The author tried to develop novel activators which would contain only traces of Zn. The results of the studied Zn complexes were similar to those of the current vulcanization system, without harm to the vulcanization process and further increasing the density of the elastomeric composition with half the amount of Zn. In another utilization of zinc stearate as a substitute for ZnO and stearic acid, it was concluded that crosslinking was not effective, compromising vulcanization^[5].

The Zn release and its toxicity on algae and frogs' embryos was studied in NR compositions^[6]. The toxicity test evaluated EC50 which means growth inhibition of 50% of the tested organisms and LC50, the mortality of 50% of

the organisms present in solution. By evaluating Zn release to the eluate with pH varying between 3 and 7, a reduction in release with pH increase could be observed. The authors concluded that Zn release to the environment can occur by means of natural phenomena such as rain and wind, and this can cause toxicity in aquatic species.

Moresco et al.^[7] studied the utilization of an organic Zn composition as compared with the usual ZnO in NR-based elastomeric compositions. The composition of organic Zn exhibited lower Zn content as compared with ZnO. Even at the lower Zn content of the composition, the authors concluded that organic Zn is more reactive, enabling it to be utilized at 3 phr organic Zn, the results obtained being like those obtained when 5 phr of ZnO are used.

In the studies by Pysklo et al.^[1] the influence of particle size on the values of Zn in the leached extract was evaluated. Authors made use of cars' and trucks' tire samples, the particle size distribution varying between 0.5 and 5 mm, as well as the amount of ZnO in phr contents. Samples were assessed after the two extraction forms: with deionized water and with CO₂-saturated water. The ZnO particle size distribution did not influence the Zn release into the leached extract, rather, this resulted from the acidic medium where leaching was performed. When extraction was performed with particles larger than 1 mm, Zn levels in the eluate were reduced of approximately 20% relative to the samples prepared from lower particle size distribution. The authors concluded that not only particle size distribution and surface area, but also the particle shape influences Zn release during leaching.

The amount of leached Zn is reduced with the increase in sample particle dimension.

The objective of this study was to assess the influence of contents of 0, 1, 3 and 5 phr of ZnO for natural rubber-based (NR) compositions on the rheometric, mechanical and thermal properties and on the leached extract of the elastomeric compositions before vulcanization and after vulcanization. The leached extract was also evaluated after thermal-oxidation of the samples.

2. Materials and Methods

2.1 Materials

For the development of this work the following raw materials were employed: GEB 10 NR (Borrachas Quirino/Brazil), stearic acid from animal fatty acid (Sabões Fontana/Brazil) 62.0% purity, ZnO (Votarantin Metais/Brazil) 99.5% purity, sulfur (Intercuf/Brazil), cyclohexyl-2-benzothiazol-sulfenamide accelerator (CBS) (Lanxess/Brazil), toluene (F. Maia/Brazil), glacial acetic acid (Dinâmica) and micro-pearl NaOH (Neon).

Table 1 lists the elastomeric formulations of the present study in accordance with ASTM D312-89, the ZnO content being varied (0, 1, 3 and 5 phr) while the other raw materials contents are fixed.

2.2 Development of the elastomeric compositions

The mixing operation of the raw materials was performed in a Banbury Copé (Brazil) closed mixer with the NR remaining in the mixer for 60 seconds and then vulcanization activators being added. After 24 hours, the mixture was transferred to an open mixer Copé Model Lab Mill 350 (Brazil) with friction ratio between cylinders of 1:1.25. At this step, the mixture was added of accelerator and sulfur. The process of incorporation of the acceleration system was performed at a temperature of 70 °C, for 3 minutes, in accordance with ASTM D312-89.

2.3 Determination of the vulcanization parameters

Vulcanization parameters for the formulations were evaluated by means of an oscillating disk rheometer from Alpha Technologies (USA) model MDR 2000, at the temperature of 150°C, deformation amplitude of 1 and frequency of 1 Hz, in accordance with ASTM D5289-12. The Mooney viscosity of the formulations was obtained with the aid of the Alpha Technologies (USA) Mooney MV 2000 instrument, at the temperature of 100 °C, for 4 minutes, in accordance with ASTM D1646-07.

2.4 Preparation of test specimens

Test specimens were prepared by compression molding in accordance with ASTM D3182-89, in a hydraulic Copé press model Lab Press 215 (Brazil), at the temperature of 50 °C, pressure of 3.5 MPa, the vulcanization time being the optimum vulcanization time (t_{90}) as obtained from the rheometric test.

2.5 Characterization of the elastomeric compositions

Thermal properties were evaluated by thermogravimetry (TGA) in a TGA equipment by TA Instruments (USA) model Q5000, at a heating rate of 20 °C·min⁻¹, in the range of 25°C to 800 °C, under 25 mL·min⁻¹ N₂ flow as reported by Carli et al.^[8].

The crosslinking density of the vulcanized compositions was obtained by adapting the experiment by Khalaf and coworkers^[9] with toluene as solvent. Samples (20 x 20 x 0.2 mm) were submerged in toluene in the dark and at the temperature of 23 ± 2 °C. The samples' mass was registered before and after solvent immersion, with daily mass records, for 7 days, until stabilization. Samples were evaluated in triplicate. Crosslinking density of the elastomeric compositions was determined by equilibrium swelling in toluene on the basis of the Flory-Rehner Equation 1^[10].

$$[X] = \frac{-[\ln(1 - v_r) + v_r + \chi v_r^2]}{V_o \left(v_r^{1/3} - v_r / 2 \right)} \quad (1)$$

Where v_r is the volumetric fraction of the swollen rubber (cm³), χ is the elastomer-solvent interaction and V_o is the solvent molar volume (cm³·mol⁻¹).

For evaluating mechanical properties, tensile strength, modulus at 300% and elongation at break were determined in a universal testing machine EMIC model DL-300 (Brazil) in accordance with ASTM D412-06. Dumbbell shaped test specimens type C, charge cell 5 N at clamp separation speed of 500 ± 50 mm·min⁻¹ was used. Data refer to the average of 5 test specimens with the respective standard deviation. Tear strength of the formulations was determined in accordance with ASTM D624-00, the test being run under the same parameters as the tensile strength test, and in the same equipment. Test specimens were type C and the results refer to the average of 5 test specimens with the respective standard deviation. Hardness of the vulcanized compositions was evaluated in a Shore A durometer by Bareiss (Germany), in accordance with ASTM 2240-05.

Table 1. Composition and coding for the elastomeric formulations.

Codification	Raw material (phr content)				
	NR ^d	ZnO ^e	sulfur	stearic acid	CBS ^f
FC ^a /AE ^c /0 ^g	100	0	2	2	0.6
F1 ^b /AE/1	100	1	2	2	0.6
F1/AE/3	100	3	2	2	0.6
F1/AE/5	100	5	2	2	0.6

^aFC- control formulation; ^bF1-formulation; ^cAE-estearic acid; ^dNR-natural rubber; ^eZnO-zinc oxide; ^fCBS-accelerator; ^gThe number indicates the ZnO content in the composition.

This feature was also observed by Heideman^[4]. Zinc stearate forms complexes with accelerators this in turn promoting, during vulcanization, a crosslinking network, resulting in improved sulfur reaction kinetics^[2]. Data obtained for crosslinking density confirm the values obtained for M_H . Figure 3 depicts the reaction between CBS, sulfur and zinc stearate^[11-14].

At first ZnO reacts with stearic acid forming zinc stearate. The interaction between the accelerator and the activator in the presence of Zn enables the formation of the accelerator active complex. The so-formed complex reacts with sulfur by means of the S_8 ring, forming a sulfurizing agent. Such sulfurizing agent reacts with the elastomer chains to form a crosslinking precursor. The precursor is a polysulfide linked to a moiety of the accelerator molecule. Polysulfide crosslinks are formed through this precursor^[15].

3.2 Characterization of thermal properties

The compositions were evaluated by TGA with only one event of mass loss being observed for NR 99.8%. The different ZnO contents in the compositions did not

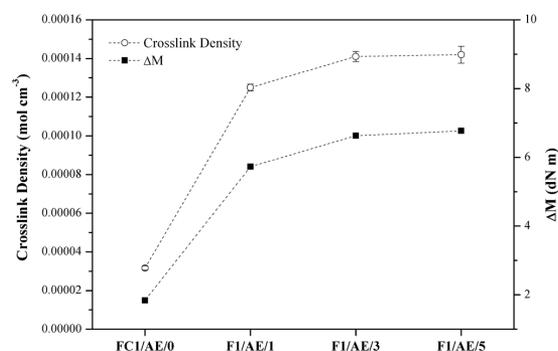


Figure 2. Crosslinking density and vulcanization rate of the elastomeric compositions developed with different ZnO contents in phr.

promote significant differences in TGA curves, exception made to the percentage of residues, the values of which were attributed to the different ZnO contents incorporated into the compositions. Table 3 lists the thermogravimetric data for the studied compositions.

3.3 Characterization of mechanical properties before and after thermo-oxidative ageing

Figure 4 exhibits results for tear strength and hardness for the developed elastomerics. As for tear strength, it could be observed that the results for composition FC1/AE/0 were lower than those for the other studied compositions, and this could be related to its lower crosslinking densities since given the absence of ZnO in the composition, crosslinking formation is compromised.

The lower hardness value of the FC1/AE/0 composition can be explained by the absence of crosslinks formation. Hardness is a measure of the resistance offered by the material to the penetration of a body of higher hardness^[16]. Figure 5 exhibits results for tensile strength, elongation at break and modulus at 300% for the compositions.

For the F1/AE/1, F1/AE/3 and F1/AE/5 compositions, considering standard deviations, tear strength and hardness data were similar, no significant influence resulting from the ZnO content variation in the compositions.

Tensile strength and modulus at 300% of the F1/AE/1, F1/AE/3 and F1/AE/5 compositions exhibited, when standard deviation values are considered, similar results. They are however higher than those for the ZnO- free composition (FC1/AE/0). Tensile strength is directly related to crosslinking formation therefore, data corroborate the crosslinking results found for the compositions. The low result for the modulus at 300% for the FC1/AE/0 composition is related to the incomplete vulcanization resulting from the lack of ZnO in the formulation. The presence of ZnO in the formulation leads to crosslinking, which limits the compositions' deformation capacity. Modulus at 300% and hardness are indicative of

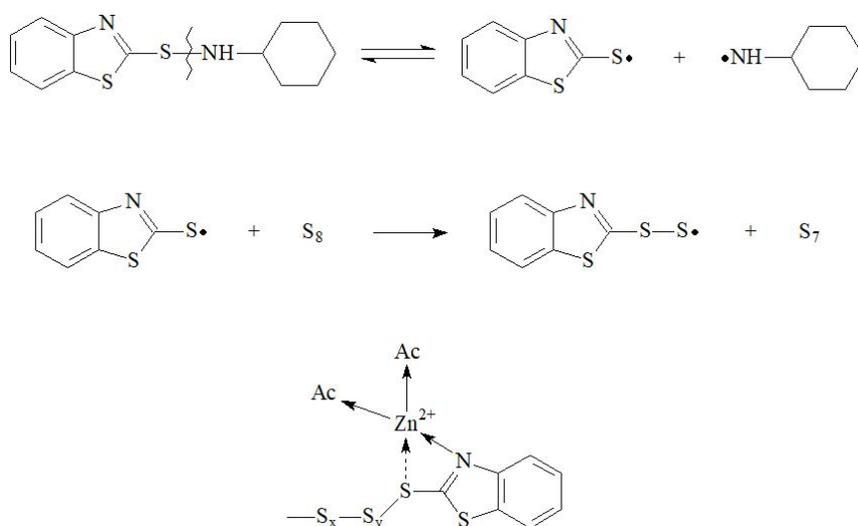


Figure 3. Zinc stearate formation and vulcanization mechanisms for Step 1 compositions. Adapted from Joseph et al.^[14] and Coran^[11].

Table 3. Decomposition temperatures of the elastomeric compositions developed with different ZnO contents in phr.

Compositions	T _{onset} (°C)	T _{endset} (°C)	T _{Max} (°C)	Mass loss (%)	Residues (%)
FC1/AE/0	358.8	411.9	385.7	99.8	0.2
F1/AE/1	359.2	416.0	386.2	98.8	1.2
F1/AE/3	360.2	416.7	386.5	97.2	2.8
F1/AE/5	361.8	417.5	388.2	95.4	4.6

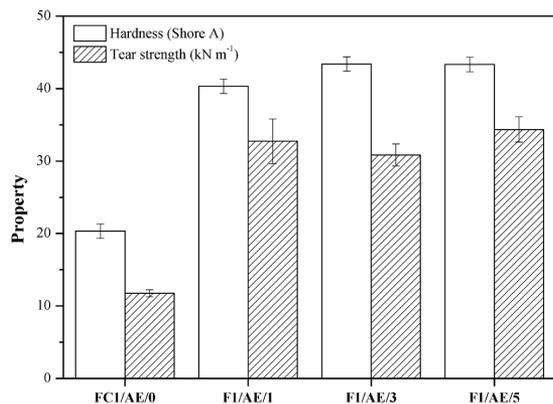


Figure 4. Tear strength and hardness for the FC1/AE/0, F1/AE/1, F1/AE/3 and F1/AE/5 compositions.

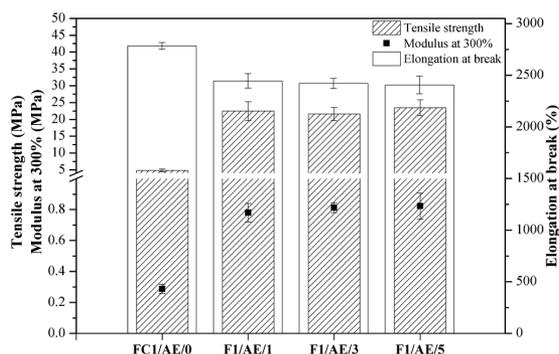


Figure 5. Tensile strength, elongation at break and modulus at 300% for the FC1/AE/0, F1/AE/1, F1/AE/3 and F1/AE/5 compositions.

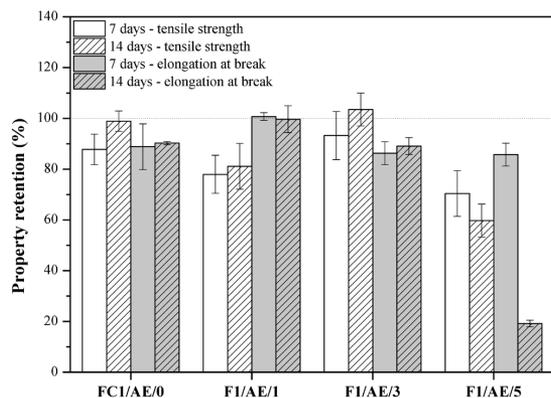


Figure 6. Tensile strength and elongation at break retention for the FC1/AE/0, F1/AE/1, F1/AE/3 and F1/AE/5 compositions after thermo-oxidative ageing during a period of 7 and 14 days exposure (the dotted line corresponds to 100%).

crosslinking formation which confirms crosslinking density data found for the studied compositions. Elongation at break for the ZnO-containing compositions was lower than that for the ZnO-free composition. Elongation at break is related to the elasticity or flexibility of the composition^[17]. In this way, when ZnO is withdrawn from the formulation, crosslinking does not occur in an effective manner, damaging this property since crosslinking formation is diminished. Figure 6 exhibits data for retention of tensile strength for the compositions after 7 and 14 days of thermo-oxidative ageing.

As relates to the results of the tensile strength retention property, it could be observed that all the ZnO-containing compositions exhibited reduction in the property, however, the better performance for the FC1/AE/0 and F1/AE/3 compositions after 14 days ageing should be highlighted. Without ZnO, at first the accelerator reacts with sulfur leading to a polysulfidic structure; this reaction yields an active sulfurous agent. Then the accelerator S-N link is broken, forming a pair of free radicals. One of these radicals reacts with one sulfur molecule yielding a new sulfur atom^[11-14]. At the start of an ageing process of elastomeric compositions, additional crosslinks can be formed because of residual crosslink, rearrangement of the crosslinked sulfur with the residual accelerator molecules and oxidative coupling^[18,19]. Such sulfur rearrangement in a shorter exposure period combined to the post-cure and oxidative crosslinking reactions could explain the increase observed in the tensile strength retention of the compositions.

By checking Figure 6 related to elongation at break retention it was possible to observe that all the compositions exhibited reduction in this property, with the exception of F1/AE/1. Degradation of the elastomeric composition caused by-thermo-oxidative ageing causes reduction in elongation at break^[12-18]. Polysulfidic crosslinkings are more unstable to thermo-oxidative degradation (less binding energy), converting themselves and keeping the mono- and disulfidic links. Such links can impart higher stiffness to the elastomeric system^[20]. The crosslinking density of the F1/AE/1 composition with 1 phr ZnO is lower than that of the other ZnO-containing compositions (F1/AE/3 and F1/AE/5), and as a consequence tolerates better the breaking of the polysulfidic links, its post-ageing deformation ability being more robust.

By examining the lower exposure time, 7 days, smaller losses in elongation at break were observed relative to 14 days losses. One of the possible explanations for the observed pattern is that ageing promotes weakening of the elastomeric matrix by scission of the elastomer main chain besides new crosslinks, which contribute to reduced elongation at break^[12-21]. A further aspect to be considered is that the new crosslinks promote the stabilization of the polymeric chain leading to increased stiffness of the composition^[22]. Upon higher ageing exposure, it is expected that sulfur rearrangement reduces the polysulfide and

increase the monosulfide crosslinks which usually reduce the compositions' mechanical properties. Oxidation-induced crosslinking results in main chain scission and interruption of crosslinks formation^[18,19].

3.4 Characterization of the ZnO content in accordance with the reaction stoichiometry and effectively used mass in phr

Mass contents, considering ZnO and stearic acid purities utilized in the formulations related to the phr employed are presented in Table 4, 13.1 g being the stearic acid mass used in the formulations considering the 2 phr content as fixed.

By replacing x in Equation 2 by the amounts in grams equivalent to the 1, 3 and 5 phr ZnO, the required values in Y are calculated for reacting under the stoichiometric reaction conditions (Table 4).

Considering the stoichiometric coefficients and the molar masses of the stearic acid reaction with ZnO (Figure 1) it could be seen that for the 1 phr ZnO composition 10.7 g ZnO were added to the formulation while according to stoichiometry 74.7 g of stearic acid would be required to react with the whole added ZnO. For the 3phr ZnO composition 31.5 g of ZnO were added while 219.9 g of stearic acid would be needed. The 5 phr ZnO composition would require 360.1 g of stearic acid to react with the 51.5 g of ZnO. In this way, it could be seen that the amount of stearic acid added to formulations (13.1g) was not sufficient to react with all the amount of ZnO added to the evaluated compositions, stearic acid being the limiting reagent, and in view of this it is probable that there is an excess of ZnO in the compositions.

The assessment of the relationship between the stoichiometric amounts in mass and the amounts employed in the development of the elastomeric composition can enable the evaluation of the ZnO contents of the leached extract after each step under study.

Results of Zn content obtained by ASTM 6234-13 followed by data by atomic absorption spectrometry (mg of Zn·L⁻¹)

considering purity and the ZnO release capacity are listed in Table 5.

A gradual increase in Zn release was observed for the leached extract in the evaluated steps. By relating the data for Zn released during leaching with the required amount of stearic acid to react with ZnO (Table 4), it was possible to understand that the amounts of Zn released in leaching are lower than expected. This can be explained in the light of the stability of the salt formed between stearic acid and ZnO. It being a stable salt, it is able to retain Zn in the elastomeric matrix, hindering release.

The highest values were found after thermal oxidative ageing and statistical differences were observed as can be seen in Table 5, this result being explained by chain scission as well as by chemical and physical changes occurring during the elastomer ageing process^[23], influencing Zn release. The Zn percentage released in this study, for the several process steps, was lower than expected. As stated in Table 4, the ZnO amount in the elastomeric matrix is in excess, with the consequence of high probability to release such amount by leaching. However, the salt formed between ZnO and stearic acid is stable^[5] so that release is hindered, besides the fact that ZnO has high thermal stability as stated by TGA in a test performed at the temperature of 800 °C.

Zn release in the leached extract of the present study exhibited lower values than those reported in the studies by Gualtieri et al.^[6] (44,7 mg·L⁻¹) and like those found by Pysklo et al.^[1] (0.04 up to 1.69 mg·L⁻¹) however the particle size employed by the authors was smaller (0.5 and 5 mm) than those of the present study (9 mm). In this way, it is possible that the particle size influenced Zn release. Lower dimension particles have smaller contact areas, releasing higher Zn amounts to the eluate. Zn release to the environment, through small particles generated by the effect of rolling of tires in roads is potentialized because of the huge number of vehicles, which can impart toxicity to the aquatic environment caused by the leaching effect occurring naturally.

Table 4. Stoichiometric ratio of the elastomeric compositions developed with different ZnO contents in phr.

Composition	X ^a (g)	Y ^b (g)	Stearic acid amount employed in the formulation (g)
F1/AE/1	10.7	74.7	13.1
F1/AE/3	31.5	219.9	13.1
F1/AE/5	51.5	360.1	13.1

^aX – ZnO amount utilized in the formulations considering 99.5% purity; ^bY – amount calculated by Equation 2, required for reaction with the ZnO amount employed considering the stoichiometric ratio.

Table 5. Zn content in mg of Zn·L⁻¹ for the elastomeric compositions released in the leached extract in accordance with ASTM 6234-13 with statistical analysis of the samples studied after each step under study.

Composition	Before Cure (mg·L ⁻¹)	After cure (mg·L ⁻¹)	After aging (mg·L ⁻¹)
F1/AE/1	0.18	0.20	0.45
F1/AE/3	0.79	0.69	1.44
F1/AE/5	1.15	1.19	2.16

ANOVA							
Source of variation	SQ	gl	MQ	F	P Value	F critical	Significant
Before Cure	0.86	1	0.86	26.6123	0.035	18.5128	Yes
After Cure	0.81	1	0.81	12.9392	0.069	18.5128	No
After Aging	3.09	1	3.09	23.8828	0.039	18.5128	Yes

4. Conclusions

All the ZnO-containing compounds exhibited similar rheometric, thermal and mechanical properties, except the property of hardness which was 8% higher for the 3 and phr ZnO formulations as compared with the 1 phr ZnO composition. The 3 phr ZnO formulation exhibited the best performances relative to the crosslinking density and consequently to ΔM . Formulations with 0 and 3 phr ZnO after ageing by thermo-oxidation retained 85% of the tensile strength, on the other hand the compound with 1 phr ZnO maintained 100% of the elongation property, indicating lower stiffness in the system. By evaluating the stoichiometry of the stearic acid and ZnO reaction, it was possible to observe that the amount of stearic acid in the elastomer compounds was not sufficient to react with all the ZnO added to the formulations. Upon considering the error in the determination of the leaching assay as 8%, ZnO-containing formulations released similar contents in residual ZnO percent during and after accelerated ageing exposure. Under the point of view of the properties of interest, time of production process and formulation cost the 3 phr ZnO compound is highlighted as the best performing one of this study.

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