

Reducing zinc oxide in rubber industry use through the development of mixed metal oxide nanoparticles

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Zinc oxide is a widely used compound in rubber industry due to the excellent properties that shows as activator for sulphur vulcanisation. The tire industry remains the largest single market for ZnO, consuming more than half of the total worldwide demand of 1,200,000 metric tons¹. Traditionally, ZnO is used in rubber formulations in concentrations of 3–8 parts per hundred rubber (phr).

Despite its superior characteristics, there is an increased concern about the environmental effects that zinc oxide causes and over the years lower levels of zinc have been tried in order to decrease its impact and to minimise the production costs. Different approaches have been considered for reducing zinc levels. Between all the alternatives proposed, the use of nano-sized ZnO particles with high surface area seems to be promising. However, it was found that the use of more active forms of zinc oxide did not substantially reduce further the minimum zinc content that can be achieved with conventional zinc oxide although the dispersion of high surface area ZnO during mixing was found to be significantly better, which could enable low levels of this zinc oxide to be used in industry with more confidence².

There have been a number of studies comparing different metal oxides as vulcanisation activators in order to find substitutes for zinc oxide. Several metal oxides have been used, CaO, MgO, CdO, CuO, PbO and NiO. Among them, MgO is the most promising candidate since it is a non heavy metal oxide that provokes the breakdown of the accelerator to be faster than when ZnO is used and it is able to form active sulphurating agents. However the crosslink level achieved is lower than that obtained with zinc oxide, which has limited its industrial application.

In this article, a new approach to overcome the problems between ZnO and MgO is presented. It consists in the development of a new activator based in the mixture of both mixed oxides at nanoscale to take advantage of the behaviour of both zinc and magnesium oxides as nanoparticles. The new activator is nanometer-sized mixed metal oxide particles of zinc and magnesium ($Zn_{1-x}Mg_xO$) with very precise stoichiometry prepared employing a polymer-based method. In this accelerator, magnesium is incorporated into the ZnO structure and this inclusion and its size are expected to show a better performance taking advantage of the behaviour of both ZnO and MgO in sulphur vulcanisation.

Basically, the method consists on the preparation of a polymer/metal salt complex that is water-soluble, its purification by precipitation/redissolution cycles and finally the calcination of the dried purified complex to give nanosized crystals³. The polymer used to form the polymer/metal salt complex is poly [acrylic acid]. Magnesium nitrate hexahydrate, and zinc nitrate hexahydrate are the starting materials.

Dynamic Light Scattering was employed to measure the particle size of the $Zn_{1-x}Mg_xO$ particles, which was found to be in the range of 100 to 175 nm with a narrow distribution as seen in Figure 1. No apparent dependence of the particle size with the magnesium content was found.

X-Ray diffraction was employed to characterise the crystal structure of the mixed metal oxide particles. Figure 2 shows the X-ray diffraction patterns of the oxide products obtained in the different syntheses. The patterns of the pure ZnO are indexed according to the known hexagonal phase (zincite)⁴, and that of MgO is indexed according to its cubic phase (periclase)⁵. In **¡Error! No se encuentra el origen de la referencia.**, the vertical line corresponds to the standard reflections of the ZnO phase and the dashed vertical lines are the standard reflections of the MgO phase which planes are indicated with a star. The scans showed a weak (200) peak of the MgO phase, which demonstrates that the material is mostly present in the hexagonal phase (zincite) and that magnesium has been incorporated into the ZnO structure. In addition, the lattice constant c of the synthesized nanoparticles has decreased in comparison to the corresponding ZnO phase. As magnesium replaces zinc in the hexagonal phase, due to the smaller radius of Mg^{2+} than that of Zn^{2+} , there is a shrinking of the lattice constant along the c -axis and a displacement of the diffraction peaks to higher angles. These findings indicate Mg^{2+} ions replace the Zn^{2+} ions into the zincite.

The model compound vulcanisation (MCV) approach with squalene as a model molecule for natural rubber and N-Cyclohexylbenzothiazole-2-sulphenamide (CBS) as accelerator has been used to study the role of the mixed metal oxide along the reaction. The results obtained with $Zn_{1-x}Mg_xO$ nanoparticles

as activator for sulphenamide accelerated sulphur vulcanisation have shown when $Zn_{1-x}Mg_xO$ nanoparticles are used it is possible to take advantage of the behaviour of both ZnO and MgO in sulphur vulcanisation. It has been seen that the reactions that take place during the scorch time, the breakdown of the accelerator and the formation of MBT occur faster, which could be due to the presence of magnesium into the zinc oxide structure.

Nevertheless, the crosslink degree achieved is higher than those obtained with zinc oxide nanoparticles. It is worth noting that mixed metal oxide nanoparticles of zinc and magnesium lead to around a 30 % higher crosslink degree than the one obtained with standard zinc oxide. This effect can be partly attributed to the small particle size of the $Zn_{1-x}Mg_xO$ since Bhowmick et al.⁶⁻⁷ found that ZnO nanoparticles (30-70 nm) increased the crosslink degree by 15 % compared with standard ZnO. On the other hand, the fact that, even with bigger sizes, higher amounts of crosslinked products are formed suggests that $Zn_{1-x}Mg_xO$ nanoparticles are more active and more effective transporting sulphur into the hydrocarbon chain than ZnO nanoparticles. Therefore, $Zn_{1-x}Mg_xO$ nanoparticles not only overcome the disadvantages of the use of a mixture of ZnO and MgO reported previously in the literature⁸, which shows a crosslink degree similar to the one obtained with magnesium oxide, but a better performance is achieved.

References

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Figures

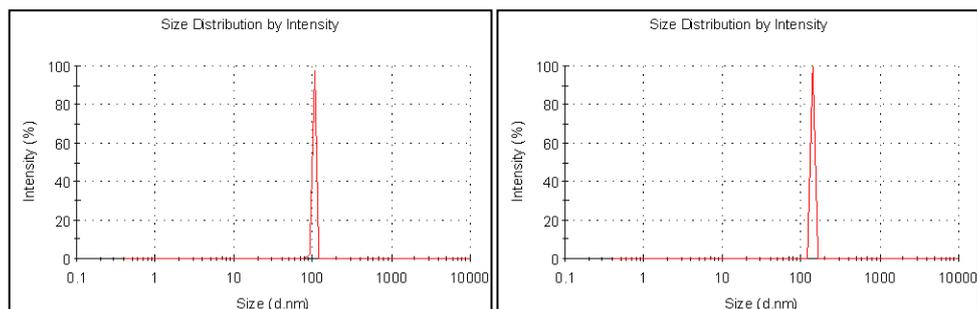


Figure 1. Particle size measurement of a) MG1.2 and b) MG1.5.

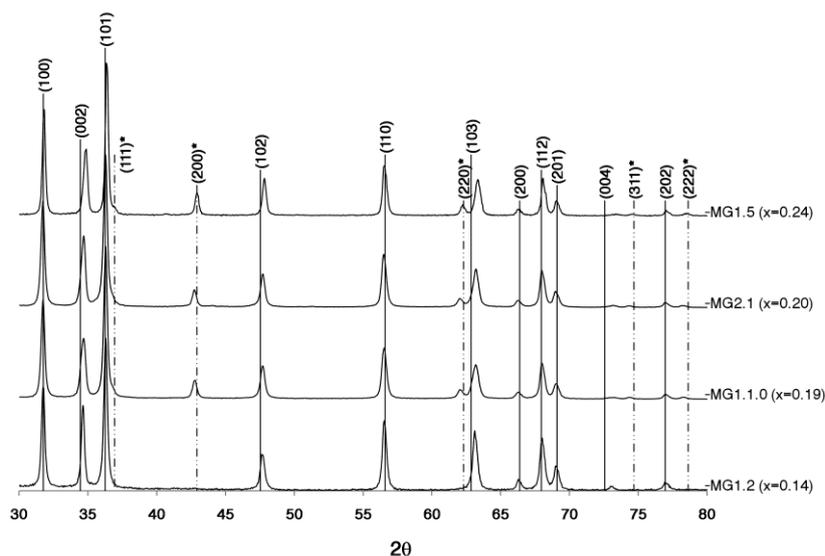


Figure 2. XRD patterns of $Zn_{1-x}Mg_xO$.