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Opinion
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A Review of Sulfur Vulcanization of Rubber

Ali Ansarifar*

Department of Materials, Loughborough University, UK

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***Corresponding author:** Ali Ansarifar, Department of Materials, Loughborough University, UK, Email: M.A.Ansarifar@lboro.ac.uk

Opinion

Charles Goodyear discovered in 1839 that heating raw rubber with sulfur modified the rubber to retain its shape. Over the years, there has been an increasing trend to use more chemical curatives in rubber compounds. Excessive use of the chemical curatives is harmful to health, safety and the environment and their use is restricted by the new European chemicals policy, Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) and various legislations for environment and safety [1,2]. Sulfenamide accelerators and zinc oxide (ZnO) are used extensively to cure a wide range of industrial rubber articles. However, these chemicals cause eye, skin and respiratory irritation in human and are harmful to aquatic life.

Zinc oxide was treated with N-tert-butyl-2-benzothiazole sulfenamide (TBBS) accelerator in ethyl acetate solvent to provide a convenient single material component to use as an additive. The quantity of TBBS required to provide monomolecular coverage of the zinc oxide was determined to be 35mg/g based on the approximate surface areas of the TBBS molecule ($6x10^{-19}m^2$) and the ZnO ($50m^2$) used. Gradually, the amount of TBBS to coat the zinc oxide was increased from 100mg/g to 350mg/g to find a material with optimum properties. The material with 35 mg/g TBBS led to a very slow cure, but material with 350mg/g gave a good cure comparable to much higher loadings of TBBS. A large batch of the surface modified zinc oxide was then prepared with this ratio from 202.0g of ZnO and 70.7g of TBBS which was mixed in 100ml of ethyl acetate in a 500ml beaker. The suspension stirred magnetically for 15min at room temperature (21.5 °C) to ensure uniform coating. The mixture was filtered under suction using an electric diaphragm vacuum pump (capable of achieving 50mmHg). The white solid was left to dry overnight and then further dried in a vacuum oven at 50 °C. Evaporation of the filtrate on a rotary evaporator indicated the mass lost was 0.110g, indicating the bulk of the TBBS was absorbed onto the ZnO. The surface modified additive will be referred to as the "powder". In another experiment, the loading of the powder with 350 mg/g of TBBS was increased progressively to determine its effect on the cure properties of the rubber. The raw rubber was mixed with the powder and sulfur to produce compounds. The cure properties of the rubber compounds were measured at 160±2°C according to the British Standard ISO 3417. All the indications are that a much lower consumption of ZnO and TBBS in sulfur vulcanization, by almost 77wt%, yields significantly shorter cure cycle and a more efficient cure. For example, the optimum cure time of the powder-based system was 32% shorter than that of some commercial sulfur cure systems and its rate of cure higher by 41%. Other benefits include improvement in health, safety and the environment as well as major cost reduction. It seems that treating the surface of ZnO with TBBS to produce a single additive component is a more efficient method of using these chemicals in rubber vulcanization than the methods which are currently in use. This has the added advantage of eliminating secondary accelerators and stearic acid which is used as secondary activator with ZnO, and minimizing ZnO in the cure system. The sulfur cure systems currently in use in industrial rubber articles are inefficient, too costly, damaging to human health and the environment and no longer viable. A cure system based on a single TBBS/ZnO composite powder and sulfur is a more efficient way to reduce chemical curatives and to make green compounds for industrial applications.

References

1. Regulation (EC) No 1272/2008.
2. European Directive 98/24/EC. Risks related to chemical agents at work.

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