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CHLOROPRENE RUBBER AND STYRENE
BUTADIENE RUBBER AS AN ACTIVATOR**

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An Analysis upon the Use of Zinc Oxide Nanoparticles in Natural Rubber, Chloroprene Rubber and Styrene Butadiene Rubber as an Activator

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Abstract – Zinc oxide (ZnO) nanoparticles were synthesized by homogeneous precipitation and calcination method and were then characterized by transmission electron microscopy and X-ray diffraction analysis. Synthesized ZnO was found to have no impurity and had a dimension ranging from 30–70 nm with an average of 50 nm. The effect of these ZnO nanoparticles as cure activator was studied for the first time in natural rubber (NR) and nitrile rubber (NBR) and compared with conventional rubber grade ZnO with special reference to mechanical and dynamic mechanical properties. From the rheograph, the maximum torque value was found to increase for both NR and NBR compounds containing ZnO nanoparticles. ZnO nanoparticles were found to be more uniformly dispersed in the rubber matrix in comparison with the conventional rubber grade ZnO as evident from scanning electron microscopy/X-ray dot mapping analysis.

This work focuses on the study the effect of ZnO nanoparticles on the vulcanizate properties of natural rubber (NR) latex films. Zinc oxide nanoparticles were synthesized by a simple and an efficient wet chemical method. The Powder X-ray Diffraction (PXRD) characterization confirmed the successful synthesis of pure ZnO and the average particle size was found to be 50 – 100 nm as indicated by particle size analysis. ZnO nanoparticles thus prepared were surface modified with oleic acid as a capping agent and the modification was carried out under ultrasound sonication in order to provide mechanical forces to separate nanoparticles leading to an efficient surface reaction. The existence of organic layer was confirmed by the Fourier Transform Infrared (FT-IR) spectra.

INTRODUCTION

The nano form of ZnO is typically used in cosmetics, rubber specialty products, and semiconductors. Zinc oxide is used in powders, creams and ointments, and its capability of blocking UVA and UVB rays makes it an indispensable ingredient in sunscreens.

Zinc is a natural component and an inherent part of the environment. Exposure to natural background levels of zinc in the biosphere is essential for all living organisms. Zinc fulfills important metabolic functions in humans, animals and plants. Zinc oxide is recognized as a valuable nutritional additive and is widely used in cosmetic, pharmaceutical and medical applications.

Although zinc oxide is generally recognized as safe, the inhaling of zinc oxide dust and fumes is to be avoided. Regulations are in place to control potential exposure scenarios.

Nano-sized zinc oxide has been used for over twenty years in various applications, mainly as a UV blocker in sunscreens. When the interest in nanotechnology started in the late 1990s, concerns were raised about the safety of nano-sized materials in general as well as for zinc oxide in particular. Due to the existing application in sunscreens and cosmetics, the main concern was possible penetration of small particles into the skin.

Several years and many scientific studies later, it has been demonstrated that nano-sized zinc oxide does not penetrate the skin and does not pose a health risk and that it is very similar in terms of toxicological properties compared to 'regular' zinc oxide (i.e. bulk form).

Natural rubber (NR) is a high molecular weight polymer of isoprene (2-methyl-1,3-butadiene). It is the oldest known rubber and the most versatile one for fabrication of rubber products. The high and reversible deformability of natural rubber is of great

industrial importance. However, its initial modulus and durability are low and an additional reinforcement is required for practical applications. Carbon black and precipitated silica have been extensively used for this purpose. In addition, CaCO₃, ZnO, MgO, talc, mica etc. have also been used.

Zinc oxide is added to rubber compounds as an activator to activate sulfur vulcanization and thereby reduce the vulcanization time. Besides its effect on the curing process, ZnO has many beneficial effects on the physical properties of rubber. Furthermore, ZnO assists in the processing of uncured rubber. ZnO is a dense material that tends to compact and disperse with difficulty. Therefore, it is distributed in the form of crystal particles in rubber mixes. Nieuwenhuizen in his thesis proposed a mechanism in which the ZnO surface function both as a reactant and as a catalytic reaction template, activating and bringing together reactants. Molecules of accelerators, sulphur and fatty acids diffuse through the rubber matrix and are adsorbed onto ZnO with the formation of intermediate complexes. Fatty acids are generally regarded as indispensable activators in conjunction with zinc oxide. The function of fatty acid activators such as stearic acid, is to solubilize the zinc oxide, a secondary effect is an increase in the amount of zinc sulphide produced.⁷ The zinc salts of fatty acids, which are a type of surfactant, also solubilize insoluble accelerators to form the actual catalyst.

Chloroprene rubber is a polar polymer with improved resistance to attack by non-polar oils and solvents. It has high toughness, good fire resistance, good weatherability and is easily bonded to metals. Polychloroprene is widely used for rubber goods subjected to dynamic stressing, for example; damping elements and spring components for motor vehicles and machinery, V-belts and timing belts, bellows, joint protection boots especially axle boots and conveyor belts.

Polychloroprene rubber with mercaptan modified general purpose grade has a medium rate of crystallization and Mooney viscosity [ML(1+4)_{@100C} = 45 – 53]. It provides a good resistance to heat, oil and weather and it has an excellent storage stability.

Mooney scorch and cure rate are quite stable during the storage of raw rubber. Its compounds band well and quickly on mixing mills, and fillers and oil can be incorporated into it rapidly in an internal mixer. The structure of the polychloroprene is such that it is intrinsically highly resistant to ozone.

Earlier study of the thermal destruction of vulcanized and not vulcanised rubber containing chlorine and the investigation of the influence of metal oxides on the degradation have shown that zinc oxide causes considerable changes in the course of degradation of these polymers especially polychloroprene. In the literature there are only a few works concerning the degradation of polymers in the presence of metals.

The works are usually connected with the thermal stability of olefine polymers and polyacrylates concerning their oxidation process.

It has been found that the majority of metals - zinc among others - chemically connected with polymer, or mechanically added (also in the form of oxides and salts) mostly as impurities, generally influenced badly on the thermal stability of polymers. Only in the case of acryl styrene copolymers it has been observed that zinc improves their stability.

It was observed that addition of nano zinc oxide (from precipitation and solid-state pyrolytic method) in polar synthetic rubber has improved the mechanical properties and so the same method was studied in non-polar synthetic rubber, styrene butadiene rubber (SBR). SBR is the most commonly used general purpose synthetic rubber which is a copolymer of styrene and butadiene and the butadiene unit is composed of cis-1,4-, trans-1,4- and vinyl components. They are produced by the copolymerization of styrene and butadiene under controlled conditions of reaction using different techniques of polymerization and the polymer properties vary with the method of polymerization.

The unsaturation in SBR is less than that in NR and the double bonds are chemically less active than the double bonds of the isoprenoid unit in NR.

The compounding of SBR is done in a way more or less similar to that of NR and other unsaturated hydrocarbon rubbers.⁸ All types of SBR require less sulphur than NR for curing. On the other hand SBR requires more accelerators, because of lower unsaturation.

ZINC OXIDE NANOPARTICLES AS AN ACTIVATOR FOR NATURAL RUBBER LATEX

Zinc oxide is one of the basic components of rubber compounds which act as an activator for rubber vulcanization process with sulphur. However, since 2004, the European Union has classified zinc oxide (ZnO) as dangerous for the environment and has legislated that its application in rubber products be reduced and controlled.

According to Beniska and Dogadkin, ZnO promotes the initial response by activating the vulcanization reaction. Moore et al. showed that ZnO plays the role of a catalyst, and Barton et al. argued that ZnO has an influence on the degree of cross linking of natural rubber (NR) and improves the heat resistance of the vulcanizate. .

There are several different methods available in the literature to synthesize ZnO nanoparticles such as high temperature solid-vapor deposition, solution phase methods etc. In the present study, a simple

and an efficient wet chemical method based on sol-gel processing was used.

Hence, the aim of the present study is to investigate the effect of ZnO nanoparticles as cure activator in natural rubber (NR) centrifuged latex. NR latex finds use in industrial and medical gloves, condoms, balloons etc.

NaOH solution of 0.90 M was heated at 55 °C. The Zn(NO₃)₂ solution (0.45 M) was added drop wise (1 drop per 2 seconds) to the heated solution of NaOH under a stir rate of 500 rpm in a magnetic stirrer. The stirring was continued for 2 hours. The precipitated ZnO nanoparticles was washed with deionized water and ethanol, and then dried in air atmosphere at 60 °C. The above reaction was repeated with different rate of additions and stirring rates.

NR LATEX COATED NANO ZNO DISKS

The research on semiconductor nanostructures has great importance in recent years due to their optical, electrical and photocatalytic properties. The unique properties of semiconductor nanostructures are due to quantum effects and increased surface to volume ratio. The different semiconducting nanomaterials of single elements, compound semiconductors and metal oxides have been successfully synthesized and studied. For the last few decades, ZnO has attracted much interest due to its versatile properties such as transparency in the visible range, direct band gap (3.37 eV), large exciton binding energy of 60 meV, absence of toxicity, etc. These qualities make it the best candidate for applications like transparent conducting electrodes in flat panel displays and window layers in solar cells. It also exhibits many potential applications in areas such as laser diodes, solar cells, gas sensors, optoelectronic devices. The ZnO nanoparticles can be synthesized using various techniques such as hydrothermal, sol-gel, wet chemical, precipitation, microemulsion, chemical vapor deposition, solid state reaction and laser ablation. The dielectric properties of an insulating medium can be modified by dispersing electrically conducting particles in the medium. Thus the insulating host material can be modified into conducting or semi-conducting depending on the amount of filler particles dispersed in the medium. Zinc oxide is one of the most important basic components of rubber compounds. In rubber processing, it acts as an activator for the cross linking by sulphur or sulphur donors. The rubber industry, utilized optical, physical and chemical properties of ZnO. It is the most effective activator to speed up the rate of cure. It can improve the resistance to corona effects by its dielectric strength in high-voltage wire and cable insulation. The materials properties such as melting points, mechanical properties, and electrical properties change at nanoscale. The studies on the effect of frequency on the dielectric behaviour and a.c.

electrical conductivity give useful information about the conduction phenomenon in nanostructured materials. It was also noted that premelting of samples greatly depends upon the a.c conductivity. And also the premelting of the mixtures at higher temperature led to a somewhat higher enhancement in a.c conductivity because these temperatures are not high enough to allow for sintering or forming agglomerates. The dielectric properties of particles are due to the contributions from electronic, ionic, dipolar and space charge polarizations. The determination of dielectric properties of the material is also important to assess the usability of the material in various electronic and optoelectronic applications.

VULCANIZATION OF NEOPRENE RUBBER (WRT) BY POLYMETHYLOL RESIN (RESOL)

The vulcanization chemistry of chloroprene rubbers is fundamentally different from that of the other diene rubbers. The carbon-carbon double bonds in the polychloroprene chain are deactivated by the presence of the electronegative chlorine atoms, and one consequence of this is that vulcanization by heating with sulfur occurs to a very limited extent only¹. The reactivity of the chlorine atom varies according to its position relative to the other atoms in an organic molecule.

VULCANIZING AID FOR STYRENE-BUTADIENE ELASTOMER

Presently the nanoscale materials have inspired the scientist and technologists, in the field of composites, by the fact that they often give rise to dramatically improved properties than their macro counterpart. Nanocomposites possess unique properties such as stiffness, strength and barrier action depending on their dispersion structure in the matrix. The nano particles are often used in a blending with polymers but this direct blending cannot avoid the clustering tendency and the polymer matrix must have good process properties.

5 Clay has been used enormously as filler for rubber and plastic in conventional microcomposites. Wang et al., while preparing and characterizing the rubber-clay nanocomposites, suggested the latex method as most convenient in order to use clay as promising reinforcing agent. Although clay nanocomposites have been studied in Nylon-6 and PET as matrix polymer, very little informations are available regarding the use of nano fillers in elastomer composites.

Probably no information is available specially in the field where surface modification of the nanofiller can

affect the composite properties by directly participating in the elastomer vulcanization process.

Efforts have been made in this study, to elucidate the vulcanization mechanisms as affected by the Zn-ion of the Zn-ion coated nano silica filler in the composites based on the styrene-butadiene rubber (SBR) and co-related with the properties thus developed.

SBR 1502 was mixed with nanofiller along with stearic acid, sulfur, N-cyclohexyl-2-benzothiazyl-sulfenamide (CBS) in a two roll open mixing mill at a fixed nip gap at around 35°C. The nanofiller was Zn-ion coated silica having average particle size 15-20 nm, which has been developed following the chemical process in our laboratory. The particles are spherical in shape and amorphous in nature. IR spectroscopy of pure nano silica filler and Zn-ion coated nano silica filler revealed that there is no chemical lattice replacement of Si and Zn rather Zn-ion adsorbed at the surface. The peak at 466 cm⁻¹ is observed in both the cases of nano silica filler with and without Zn-ion coated suggesting Si-O-Si bending vibration remains unaffected. However, the symmetric stretching vibration of Si-O-Si appeared at 799 cm⁻¹ in the case of pure SiO₂ is shifted to 792 cm⁻¹ in the case of Zn-ion coated nano silica filler. The peak at 1547 cm⁻¹ in the case of nano silica filler is shifted to 1420 cm⁻¹ in the case of Zn-ion coated nano silica filler. The IR spectra thus revealed that there is some microscopic interaction between the two-lattice structure. The effect of long chain fatty acid was studied by replacing the stearic acid with diethylene glycol monostearate (DEGS).

EFFECT OF ZINC OXIDE NANOPARTICLES AS CURE ACTIVATOR ON THE PROPERTIES OF NR

Zinc oxide (ZnO) is an important inorganic pigment for the rubber industry, and over the past 100 years, rubber industry has utilized an increasing number of physical and chemical properties of ZnO. ZnO is manufactured industrially by the French and the American processes. In the French process, pure metal is evaporated to obtain a pure oxide, whereas in the American process zinc oxide is obtained directly from a zinc ore by burning it with coal or electrothermally. The conventional rubber grade ZnO has particle size ranging from 0.1 to 0.4 μm and a corresponding specific surface area in the range of 10–20 m²/g. ZnO finds wide application because of its photochemical properties and chemical reactivity. ZnO has proved to be the most cost effective inorganic pigment to activate the rate of sulfur cure with the accelerators. The reaction mechanism for the cure activation is represented in Figure 10. ZnO is also widely used as a UV stabilizer and as an additive having biocidal activity.

Remaining in the invisible form in the finished product, zinc has long been used as an essential compounding ingredient in rubber. It was one of the first pigments extensively used in the rubber products manufacturing.

The first published reference to such application is in a patent granted in 1849.

For better heat conductivity and reinforcement in heavy-duty pneumatic tires, high loadings of zinc oxide are used, since heat-buildup is a critical problem at their higher operating speeds. But some adverse environmental effects of zinc exposure have been reported, which include decline in earthworm population densities, species diversity and the development of tolerant grass species. The main sources of zinc pollution are iron and steel production, nonferrous metals manufacture, road transport, and to a lesser extent coal combustion. The road transport emission is almost entirely because of tire wear. This arises from the zinc content of the tire rubber—around 2% ZnO by weight. For many of its uses, there is currently no other economic alternative at present. Hence, ZnO nanoparticles might help in reducing the level of ZnO in conventional formulations.

There are several different methods available in the literature to synthesize ZnO nanoparticles such as high temperature solid–vapor deposition, solution phase methods, colloidal chemistry techniques, sol-gel method, phase transfer technique, hydrolysis of chelate complex, polymer stabilization, synthesis in reversed micelles, alkoxide based process, precipitation method, microemulsion, spray pyrolysis, hydrothermal method, laser vaporization condensation, and flow injection synthesis.

CONCLUSION

ZnO nanoparticles with an average particle size of 50 nm were successfully synthesized. Agglomeration of the ZnO nanoparticles was prevented by the surface modification with oleic acid. FT-IR results confirm that an organic layer exists and the linkage between inorganic nuclei and organic layer is a chemical bond.

The effects of modified nano ZnO particles on the mechanical properties of natural rubber latex compounds were evaluated. In particular, only about 50 % ZnO nanoparticles, in comparison to commercial ZnO, were sufficient to obtain similar mechanical properties due to the high surface area available and the compatibility with the matrix leading to an increase in the degree of cross linking of the vulcanizates.

Zn-ion coated nano silica fillers are having a dual role in sulfenamide accelerated sulfur vulcanization of butadiene containing elastomers. It can produce bound silica filler containing elastomeric chains with enhanced technical properties.

REFERENCES

- A. Ciesielski (1999). An Introduction to Rubber Technology, Rapra Technology Limited.

- Abdullah, M.; Okuyama, K. (2004). Zinc oxide nanoparticles prepared by a simple heating: Effect of polymer addition and polymer absence on the morphology. *PROC ITB Eng. Sci.* 36, pp. 141–153.
- Abi Santhosh Aprem, Kuruvilla Joseph, Sabu Thomas (2005). *Rubber chemistry and Technology*, 78, p. 476.
- B. C. Sekhar et. al. (2001). *Natural Rubber. Progr.Devclop.*18, p. 78.
- Blackley, D. C. (1997). *Polymer Latices Science and Technology; Application of lattices*; Chapman & Hall: Boundary Row, London, Vol. 3, p. 217.
- C. M. Blow, C. Hepburn (2002). "Rubber Technology and Manufacture", *Plastics and Rubber Institute*, London.
- Chapman, A.; Johnson, T. (2005). The role of zinc in the vulcanization of styrene-butadiene rubbers. *Kautschuk Gummi Kunststoffe*, 58, pp. 358–361.
- Choi S. (2002). Improvement of properties of silica-filled natural rubber compounds using polychloroprene. *Journal of Applied Polymer Science*, 83, pp. 2609–2616.
- Hamed, G. R.; Hua, K. C. (2004). *Rubber Chemistry Technology*, 77, p. 214.
- Invisible partner zinc keeps the bounce in rubber, *International Zinc Association Brussels*, 2000.
- M. R. Kresja, J. L. Koenig (1993). "The nature of sulfur vulcanization" in *Elastometer Technology Handbook*, CRC Press, New Jersey, p. 475.
- R. Galle–Gutbrecht (2002). Presented at the *International Rubber Conference (IRC)*, Prague, Czech Republic.
- Review of Risks from metals in the UK; Presented at *Chemicals Stakeholder Forum CSF/03/68*, Fourteenth meeting 16 December 2003.
- Sadhu, S.; Bhowmick, A. K. (2003). *Rubber Chemistry Technology*, 76, p. 860.
- Shizo Kohjiya, Yuko Ikeda (2000). *Rubber chem. Technol.*, 73, pp. 534- 550.
- W. Hofmann (1994). *Rubber Technology Handbook*, Hanser, New York.
- Z. Fan, J. G. Lu. J. (2005). *Nanoscience and Nanotechnology*. 5 (10), p. 1561.

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