

THE ROLE OF ZINC OXIDE IN THE COMPOUNDING OF CARBOXYLATED NITRILE RUBBER FOR DIPPED PRODUCTS

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Abstract

The emulsion copolymer of butadiene, acrylonitrile and methacrylic acid, known industrially as nitrile latex, has found extensive use in the manufacture of elastomeric gloves. Nitrile gloves are produced by dipping a hand-shaped mould into a bath of compound comprising a mixture of the emulsion copolymer, vulcanization chemicals, colorants and foam control additives (1). For historical reasons, the vulcanization materials used in nitrile latex are very similar to those traditionally added to natural rubber and comprise sulphur, accelerator(s) and zinc oxide. In natural rubber processing, zinc oxide acts as an activator for the vulcanization reaction.

By compounding standard nitrile latex with the separate vulcanization components, it was shown that the dipped film tensile properties depended completely on the ZnO, with a negligible contribution from sulphur and accelerator. In the absence of ZnO, even high levels of sulphur and zinc-free accelerator failed to produce any measurable effect on tensile properties.

Model experiments, in which nitrile latex was compounded only with ZnO, showed that its effect on film properties developed rapidly. Optical microscope examination of liquid mixtures of nitrile latex and modest levels of ZnO, indicated that the ZnO particles had dissolved. A more extensive study using centrifugation showed that dissolution was rapid and stoichiometric with respect to the carboxylation present in the latex. The solubility is explained by the formation of the zinc salt of the polymerized methacrylic acid.

KOH titration of a series of nitrile latexes containing various levels of carboxylation showed good stoichiometric neutralization. This result demonstrates the ready accessibility of the carboxyl groups in these nitrile latexes.

An examination of the effect of increasing levels of ZnO on the tensile properties of XNBR was carried out. The overall effect was consistent with crosslinking, with increases being seen in tensile strength and modulus, together with a decrease in elongation at break.

Since the primary role of ZnO is to neutralise the copolymerized carboxylic acid groups, a further series of experiments was carried out in which potassium hydroxide was used as an alternative base. It was found that neutralisation with KOH modified the tensile properties of XNBR in a similar way to ZnO. This finding clearly demonstrated that the crosslinking effect of ZnO was not due to simple zinc dicarboxylate formation. The property changes that are seen on neutralisation are consistent with the formation of an ionomer structure in which ionic clusters act as crosslink points within the rubber matrix. Nitrile rubber ionomers, produced by adding zinc oxide to the solid rubber at elevated temperature, have been described previously in the literature (2, 3).

The nitrile latex system used in glove dipping is interesting because the ionomer formation begins, with great efficiency and at room temperature, in aqueous polymer dispersion. Where ZnO is used, this requires the transport of zinc ions through the aqueous phase of the latex. The concentration of zinc ions produced by ZnO in water by hydrolysis is pH dependent and it was seen that the successful addition of ZnO also depended on nitrile latex pH.

References

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