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Role of various coagents in peroxide vulcanization of natural rubber

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INTRODUCTION

Peroxide vulcanization is an alternate vulcanization method for rubbers. The drawbacks of peroxide vulcanization such as poor mechanical property can be overcome by introducing suitable co-curing agents (coagents) in the formulation. Coagents are multi-functional organic molecules and are highly reactive towards free radicals (Dluzneski, 2001). The mechanism of incorporation of coagents and property improvement of several synthetic rubbers has been extensively investigated. Very little work has been done to study the effect of these coagents on the peroxide cured natural rubber. Hence, the role of various coagents such as zinc diacrylate (ZDA), trimethylolpropane trimethacrylate (TMPTMA) and triallyl cyanurate (TAC) was studied by Fourier Transform infrared spectroscopy. Crosslinking mechanism of peroxide in natural rubber is also interpreted.

MATERIALS AND METHODS

Natural Rubber used was ISNR 5 grade, obtained from the Pilot Crumb Rubber Factory, Rubber Board, Kottayam, India. Dicumyl peroxide (DCP, 40%) was used as the crosslinking agent (Arkema Peroxides India Private Limited, Cuddalore, Tamil Nadu). The coagents ZDA, TMPTMA and TAC were supplied by Meen Been Elastomers Private Limited, Gurgaon, India.

Preparation of compounds

The compounds were prepared in a two-roll mixing mill as per the ASTM D 3182-07. Cure characteristics were measured using a Monsanto Rheometer. The compounds were vulcanized in a hot press at 160°C to their respective optimum cure time.

FTIR Analysis of the vulcanizates

The FTIR ATR spectra were recorded using an IR spectrometer (Thermo Nicolet, Avatar 370) having a resolution of 4 cm^{-1} in the range 500 - 4000 cm^{-1}. The existence of coagent bridges were established by the selective cleavage of ester linkages in the vulcanizates (Dikland *et al.* 1993).

Measurement of mechanical properties and swelling studies

Tensile specimens were cut from the cured sheets and the measurements were carried out according to ASTM D 412 (Zwick, Model 1474) and crosslink density was determined using Flory- Rehner equation.

Determination of ionic crosslink density of ZDA

ZDA impart ionic as well as covalent crosslinks in polymer. An analytical method has been developed for the quantification of relative amount of ionic crosslinks formed in peroxide-metallic coagent cured networks. The ionic crosslink density can be calculated using following equation.

Total crosslinks = Covalent crosslinks + Ionic crosslinks..........(1)

RESULTS AND DISCUSSION

FTIR Spectroscopy

The mechanism of peroxide vulcanization of natural rubber is interpreted by comparing the FT IR spectra of vulcanized and unvulcanized rubber. The important peaks under consideration are 838cm^{-1}(=CH out-of-plane bending), 1025cm^{-1}and 1141cm^{-1}(C-C stretching) and 1654cm^{-1}(C=C stretching). The abstraction mechanism does not yield a reduction in unsaturation whereas if the addition reaction predominates there will be considerable reduction in the intensity of absorption bands corresponding to the -C=C- stretch/deformations of polyisoprene. Comparison of spectra suggests the predominance of abstraction route over radical addition in the peroxide vulcanization of natural rubber at 160°C.

ROLE OF COAGENTS IN PEROXIDE VULCANIZATION OF NATURAL RUBBER

Zinc diacrylate (ZDA)

FT IR spectrum of coagent ZDA is compared with those of vulcanizate with coagent. Then the latter is compared with vulcanizate without coagent. This confirms the addition of coagent in to the vulcanizate.

Trimethylolpropane trimethacrylate (TMPTMA)

The comparison of FT IR spectra of cured (NR- DCP) vulcanizate and those with coagent TMPTMA showed that, during vulcanization coagent molecules are incorporated into the network. This is further confirmed by the controlled cleavage of ester linkage of the vulcanizate.

Triallyl cyanurate (TAC)

During vulcanization with TAC, the intensity of absorption band at 1024 cm^{-1} (C-C stretch) is considerably reduced. The radicals produced may abstract hydrogen from polymer to form polymer macro-radical or at the same time it can facilitate the isomerisation of coagent triallyl cyanurate to triallyl isocyanurate. When the concentration increased, homopolymerization predominates and TAC form a dispersed phase and it is incompatible with natural rubber.

Coagent selection for peroxide vulcanization of natural rubber

Crosslink density of vulcanizates with various coagents is measured using equilibrium swelling studies. Comparison of crosslink density and delta torque (M_H-M_L) of various coagents with control (gum vulcanizate) is given in Fig. 1. Coagent TMPTMA produced maximum crosslink density and tensile strength is highest with ZDA. The ionic crosslink density of coagent ZDA is calculated and is found to have 20 per cent ionic crosslink density. Ionic bonds exhibit both good heat aged stability and the ability to slip along the hydrocarbon chain, even break and reform to impart the best mechanical properties.

CONCLUSION

FT IR spectroscopy along with swelling studies successfully explained the role metallic coagent ZDA, methacrylic coagent (TMPTMA) and allylic coagent (TAC) in the peroxide vulcanization of natural

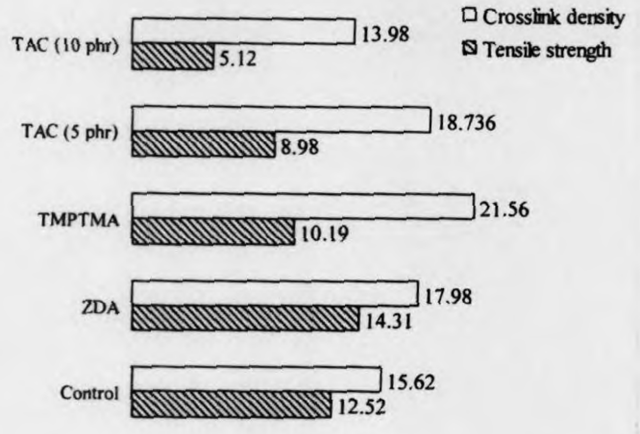

Fig. 1. Comparison of crosslink density and tensile strength of various coagents with control

rubber. Coagent TMPTMA is applicable where, high modulus, low set, hardness and heat ageing resistance is required. Allylic coagent TAC is not suitable for highly unsaturated rubber like natural rubber. ZDA impart ionic and covalent crosslinks in the vulcanizates and is a unique system having the best characteristics of both the peroxide and sulphur cure systems.

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