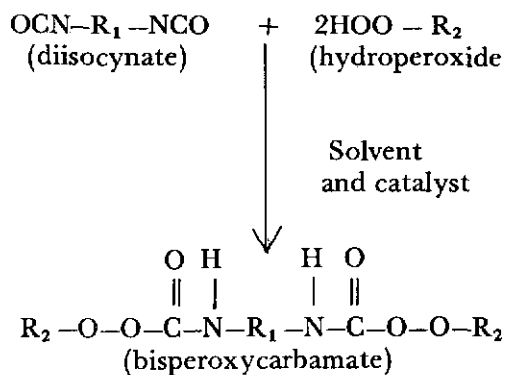


Thesis Summaries

Bisperoxycarbamates as Crosslinking Agents for Natural and Polyisoprene Rubbers

Most of the early studies using peroxycarbamates concerned their synthesis, decomposition and use as initiators in vinyl or diene polymerisation. The only attempt to use one as a crosslinking agent was reported in 1960 for a plastic. The interest in the present research consists of the synthesis of new bisperoxycarbamates and evaluation of these materials as novel crosslinking agents in natural rubber (DPNR) and polyisoprene rubber (Cariflex IR 305).

Bisperoxycarbamates were prepared by the method shown below:



With a variation of the structure of R_1 , it was found that the rates of reaction of the diisocyanates with a given hydroperoxide were dependent on the specific structures and steric effect of the diisocyanates. The order of reactivity was found to be a aromatic diisocyanate > aliphatic diisocyanate > aliphatic/cyclic diisocyanate > cyclic diisocyanate.

Seven bisperoxycarbamates were prepared and evaluated as crosslinking agents in the natural and polyisoprene rubbers. The investigated bisperoxycarbamates were:

- I – Bisperoxycarbamate prepared from 1,6 hexamethylene diisocyanate and cumyl hydroperoxide (aliphatic)
- II – Bisperoxycarbamate prepared from 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl - isocyanate (IPDI) and tertiary butyl hydroperoxide (aliphatic/cyclic).
- III – Bisperoxycarbamate prepared from methylene-bis-(4-cyclohexyl isocyanate) and tertiary butyl hydroperoxide (cyclic)
- IV – Bisperoxycarbamate prepared from a polyurethane prepolymer based on 1,4 butane diol reacted with excess IPDI (block ratio 1:2); this polyurethane type was then reacted with tertiary butyl hydroperoxide to form the bisperoxycarbamate (prepolymer).
- V – Bisperoxycarbamate prepared from 2,4 tolylene diisocyanate dimer and tertiary butyl hydroperoxide (aromatic)
- VI – Bisperoxycarbamate prepared from Polyester /TD1 prepolymer and tertiary butyl hydroperoxide (prepolymer)
- VII – Bisperoxycarbamate prepared from polycaprolactone/methylene

bis-4-(cyclohexyl isocyanate) prepolymer and tertiary butyl hydroperoxide (prepolymer)

The relative effectiveness of the prepared bisperoxycarbamates as curing agents in the two rubbers was found to be dependent on the structures of the diisocyanate backbones investigated; cyclic > aliphatic/cyclic > aliphatic. The bisperoxycarbamates studied, based on the aromatic and prepolymer diisocyanate backbones, were found to be relatively ineffective crosslinking agents for natural and polyisoprene rubber. However, the three bisperoxycarbamates I-III were found to be effective crosslinking agents for rubbers, two of which were investigated in detail, DPNR and IR 305.

Of the three bisperoxycarbamates I-III, the cyclic bisperoxycarbamate III demonstrated comparable ultimate tensile strength and resistance to thermal oxidative stress-relaxation and hot air oven ageing with the DPNR control cured using dicumyl peroxide.

It was found necessary to use a special gas absorption additive system to avoid porosity in vulcanisates cured with high proportions of the bisperoxycarbamates as carbon dioxide is liberated during cure. Three systems were examined and found to eliminate porosity:

- Trimethylol propane trimethacrylate (Sartomer SR-350)
- N, N'-M-phenylene dimaleimide (HVA-2)
- $\text{Ca(OH)}_2 + \text{CaO}$.

Of these the $\text{Ca(OH)}_2 + \text{CaO}$ system was considered the most suitable with respect to the versatility and cost.

For applications involving white and black filled mixes the cyclic bisperoxy-

carbamate III gave a satisfactory cure in the presence of fillers such as precipitated silica (Ultrasil VN3) and the following carbon blacks: SRF (Regal SRF), MT (Sevacarb MT), and Acetylene (Shawinigan Acetylene). However with SAF black (Vulcan 9) and HAF black (Vulcan 3) cure interference occurred and this was considered due to the presence of relatively high content of organic groups based on H₂O and S in the carbon blacks.

ABU BIN AMU

Awarded the degree of Ph.D. by the School of Pure and Applied Science, Loughborough University of Technology, 1981.

A Contribution to the Study of Metalation of Polyisoprene

The use of organolithium as metalating agent is becoming important in organic chemistry. Metalation is a reaction between a hydrocarbon containing a labile proton and the organolithium. The metalated polymer, containing a lateral bond of carbon to lithium can be further utilised for the preparation of polymer containing pendant groups. One possible application of this chemical route is to form a graft polymer by further reaction of the metalated polymer with monomers which can polymerise by anionic polymerisation. The preparation of graft polymer by this technique is the objective of this study.

From the study of the NMR spectrum of the silylated product after metalation of oct-4-ene (molecular model of polybutadiene), by the secondary butyllithium—N,N,N',N'—tetramethylethylenediamine (*sec*-Buli-TMEDA) (1:0.5), it was

shown that metalation occurred only on the allylic carbons. Similarly, the NMR spectrum of silylated 4-methyl-oct-4-ene indicated the presence of various microstructures in accordance with the mechanism of metalation of polyisoprene.

The conditions of metalation of polyisoprene complex, *sec*-Buli-TMEDA, were optimised. The reactivity of the complex was very much dependent on the reaction conditions. In certain cases, experimental results have shown that the metalation reaction was first order with respect to butyllithium and the number of isoprene units. The variation of the ratio of Buli to TMEDA has a preponderant influence on the rate of metalation. The kinetic result was confirmed by a similar study on the metalation of 4-methyl-oct-4-ene (a molecular model of 1,4-polyisoprene).

The effects and efficiency of other complexing agents with *sec*-Buli were studied. Only the *sec*-Buli-TMEDA complex and *sec*-Buli-*t*-Buok (potassium *t*-butoxide) gave positive results and the yields were further improved by the *sec*-Buli-*t*-Buok-TMEDA (1:1:1) complex.

Based on the results obtained it is concluded that the metalated polymer can be best used for the preparation of polymer containing a pendant group. The carbonionic sites obtained can react with classical organo reagents for the preparation of polymers containing a pendant group of alcohol, amine, acid, *etc.*, and silver salt, mercury salt or diazonium halides.

ZAINUL ABDIN BIN MAIDUNNY

Awarded the degree of Docteur du 3^{eme} Cycle by the Universite du Maine, Le Mans, France, 1980.

Composites of Natural Rubber and Polyaramid Short Fibres

The present work was carried out to study the properties of natural rubber composites reinforced by short polyaramid fibres with natural rubber laminates. Natural rubber composites reinforced by filament polyaramids, formed the experimental controls. Two different types of bonding polyaramid to rubbers are resorcinol-hexamethylene tetramine-silica (HRH) and sulphur, and blocked diisocyanate with diurethane crosslinker. Each system was found to offer a different type of adhesion, the HRH forms physical bonds and the NCO/urethane chemical links between fibre and rubber. When the proportions of these bonding agents were optimised in the NR rubber compound for example, vulcanisate properties were significantly improved.

Further studies on composites with polyaramid short fibres demonstrated the necessity to optimise the proportions of blocked diisocyanate in the composite to achieve maximum strength properties, e.g. unoptimised with 30% fibre gave tensile strength of 26.66 MPa, optimised with 30% fibre gave tensile strength of 34.38 MPa. Post-treatment of composites and laminates by heating or with high-energy radiation, using a Co⁶⁰ source, improved the quality of adhesion still further by the formation of more chemical links between polyaramid and rubber.

Diisocyanate was found unsuitable for use in a sulphur curing system. It formed complexes with the accelerator DCBS and sulphur, reacted with zinc salts and acted as a crosslinker for rubber. Resorcinol-hexamethylene tetramine-silica system contributed a type of physical adhesion, possibly by hydrogen bonding, between polyaramid and rubber. The resin formed

in situ during vulcanisation of rubber was found to crosslink the rubber, and reaction mechanisms were postulated. The potential of the composite as a tyre material was examined as it had low heat build-up characteristics. Only composites with a minimum of 20% volume/volume fibre were considered satisfactory as tyre construction materials. The potential of

these composites as ballistic garment material was investigated. The conclusions were indecisive and further investigation and improvement were necessary.

YUSOF BIN AZIZ

Awarded the degree of Ph.D. by the Loughborough University of Technology, United Kingdom, 1981.