

STABLE FREE RADICAL ASSISTED SCORCH CONTROL IN PEROXIDE VULCANIZATION OF EPDM

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This study demonstrates the capability of a nitroxide stable free radical, 2, 2, 6, 6-tetramethylpiperidine 1-oxyl (TEMPO), to induce sulphur/accelerator like scorch control in peroxide vulcanisation of EPDM. Two commercially used peroxides; butyl 4,4-di(tert-butylperoxy) valerate (BPV) and Di(tert-butyl peroxyisopropyl) benzene (BBPIB) with cure temperatures of 160 °C and 175 °C respectively were used for vulcanisation. TEMPO induced scorch in both systems and the cure curves resembling typical sulphur/accelerator cure curves were obtained. The reduction in cross-link density with the addition of TEMPO was significantly less in BBPIB system. Addition of 4phr of trimethylolpropane trimethacrylate (TMPTM) could regain the loss of cross-links due to the scavenging action of TEMPO. The vulcanisate properties of the EPDM/BBPIB/TEMPO/TMPTM system were determined and compared with a control EPDM compound. The mechanism of scorch control by the stable free radical is also discussed.

Keywords: Peroxide vulcanization, Scorch control, Stable free radicals

INTRODUCTION

Peroxide vulcanisation of rubbers offers various advantages over sulphur vulcanisation like rapid vulcanisation without reversion at higher temperatures, good compression set, excellent heat ageing properties, possibility to co-vulcanise saturated and unsaturated rubber blends *etc.* These are attributed to the C-C cross-links formed during peroxide vulcanisation, which have the same bond strength as the C-C bonds in the polymer main chain. Due to the enhanced performance at high temperature, peroxide vulcanisation covers about 15per cent of the commercial ethylene-propylene-diene rubber (EPDM) applications (Orza *et al.*, 2009).

As per the generally accepted mechanism, peroxide vulcanisation is initiated by the thermal decomposition of organic peroxides to highly reactive free radicals, which then predominantly abstract allyl hydrogen atoms in elastomers with internal double bonds [(R)HC = CH(R')] and pursue addition reaction with elastomers having vinyl pendant groups [$>\text{C} = \text{CH}_2$], either way yielding rubber macro-radicals. These macro-radicals combine to form the cross-links (Dluzneski, 2001). Recent ^{13}C NMR studies on peroxide vulcanisation of EPDM rubber with 2-ethylene-5-norbornene (ENB) as the monomer showed that hydrogen abstraction takes place both at the CH_2 and CH units in the EPM main chain