

Crosslinking Control of PDMS Rubber at High Temperatures using TEMPO Nitroxide: Experimental and Modelling

Mani Skander, Cassagnau Philippe, Chaumont Philippe, Bousmina Mosto

A novel composition using 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) and Dicumyl peroxide (DCP) for scorch delay and control of the final network topology of Polydimethyl-vinylmethyl-siloxane (vinyl-PDMS) at high temperatures has been proposed. The evolution of linear viscoelasticity during crosslinking reaction was carried out on parallel plate geometry rheometer. The rubber was crosslinked with different ratio of [TEMPO]/[DCP] in order to control scorch time which is defined as the time during which the PDMS rubber can be worked at a given temperature before crosslinking begins (i.e. the time at which the complex shear modulus suddenly increases). We showed that scorch delay increases according to the amount of TEMPO acting as an inhibitor. Nuclear Magnetic Resonance Spectroscopy ($^1\text{H-NMR}$) has been used to investigate the effect of TEMPO. This study reveals that the delayed action is the result of a TEMPO-grafted polymer action formed by reaction between TEMPO and polymer radicals. Furthermore, polymeric radicals are rapidly trapped by a grafting reaction before they are able to form crosslinks. Differential scanning calorimeter (DSC) was used to characterize the crosslinking reaction. Specific heat data show two exothermic reactions. These reactions may be associated in one hand to the decomposition of DCP and TEMPO grafting in vinyl-PDMS, and on the other hand to the C-C covalent bonds creation. The DSC results indicate that the variation of scorch time with the [TEMPO]/[DCP] ratio is in reasonable agreement with those obtained from rheological measurements. Finally, the variation of the complex shear modulus at different [TEMPO]/[DCP] was modelled from DSC kinetics.