

Functionalization of Ethylene-Propylene-Diene Terpolymer via the Alder Ene Reaction

M. R. THOMPSON, C. TZOGANAKIS,* and G. L. REMPEL

Department of Chemical Engineering
University of Waterloo
Waterloo, Ontario, Canada N2L 3G1

An ethylene-propylene-diene rubber (EPDM), containing 5 wt% 5-ethylidene-2-norbornene, was functionalized with maleic anhydride through the Alder Ene reaction at temperatures above 200°C in a co-rotating twin screw extruder. Characterization of the maleated product included FT-IR, ^1H and ^{13}C NMR, and GPC. The degree of functionalization was determined by infrared analysis and by the mechanical properties of an ionic network formed by neutralizing the maleated rubber with zinc oxide. Increased temperature and maleic anhydride reactant concentration were found to improve the extent of reaction. Several Lewis acid species ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{RuCl}_n \cdot x\text{H}_2\text{O}$ and AlCl_3) were tested as catalysts, and they were found to have a small effect on the degree of functionalization. This effect improved with reduced acid concentration. Among the Lewis acids examined, AlCl_3 gave rise to the greatest improvement of succinyl anhydride incorporation into the rubber.

INTRODUCTION

The non "site-specific" functionalization of ethylene-propylene-diene terpolymer (EPDM) rubber, in particular maleation, involving free-radical reactions often leads to undesirable rheological changes in the product owing to chain scission and crosslinking as well as confusion over the structure of the bound comonomer. It is thought that peroxide-induced grafting of maleic anhydride produces single succinyl anhydride groups (1, 2) attached to the backbone of EPDM, similar to other ethylene-based or propylene-based polymers, although oligomeric or polymeric maleic anhydride grafts have also been proposed (3, 4) despite the monomer's being used above its ceiling temperature of 150°C (5). Maleic anhydride is attached through chain addition to the polymer at a macroradical site, yielding a succinyl anhydride radical (2, 6). The strong tendency of the succinyl radical to terminate by chain transfer as well as the presence of maleic anhydride excimers leads to numerous side reactions in the presence of free radicals. The radical grafting efficiency (ratio of grafted maleic anhydride to peroxy radicals), which can be used as a measure of the degree of chain transfer occurring in the reaction system, is characteristically high, always greater than unity (7–10). The radical grafting efficiency increases with temperature according to the activation energy of the chain transfer

mechanism and decreases with increased peroxide and maleic anhydride reactant concentrations because of excimer quenching. Degradation of the EPDM chain results from macroradicals formed through chain transfer with no maleic anhydride neighboring the radical site.

Investigation of the simultaneous mechanisms of scission and crosslinking during maleation (6, 10, 11) has shown β -scission to dominate, according to rheological measurements (10), with crosslinking occurring only at high peroxide concentrations. The possibility of the observed crosslinks occurring through succinyl anhydride radicals was dismissed by Gaylord *et al.* (6), who stated that the formation of crosslinks was simply due to the less favored abstraction of hydrogen (compared to tertiary hydrogen abstraction leading to β -scission) from a backbone methylene carbon in EPDM. Reducing the degree of degradation prevalent during free-radical maleation required chemical species such as dimethylformamide and stearamide, which have been found to interfere/quench maleic anhydride excimers (6, 10).

Recently, several studies have been reported on alternative methods of functionalizing EPDM including the Diels-Alder and Alder Ene mechanisms, in an effort to reduce material degradation resulting from free radicals. Diels-Alder reactions to attach 1,2-dihydro-4-chloroformylbenzocyclobutene end-capped polymers (12) onto EPDM have been performed in a Brabender batch mixer at high temperatures (250–280°C). The ring formed by the reaction gave an aromatic ring adduct, which was considered to be thermally irre-

*To whom correspondence should be addressed.