Metal–Ligand Coordination for Enhancing Cure Behavior, Mechanical Performance, and Network Reversibility in Epoxidized Natural Rubber

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Abstract

Epoxidized natural rubber (ENR) offers a sustainable approach for developing advanced elastomeric materials through reactive epoxide groups capable of forming coordination crosslinks. In this study, ENR with 25 mol% epoxidation (E25) was compounded with magnesium chloride ($MgCl_2$), stannous chloride ($SnCl_2$), and ferric chloride ($FeCl_3$) at concentrations of 5–7 mmol to investigate their effects on chemical crosslinking propagation, tensile properties, and bonding reversibility. The crosslink network characteristics revealed clear differences among the metal ions. $FeCl_3$ exhibited the fastest crosslinking rate and the highest maximum torque, indicating rapid and extensive E25 network formation, whereas $MgCl_2$ displayed limited reactivity due to its lower charge density and weaker coordination ability. The formation of metal–oxygen coordination bonds was clarified through the infrared spectroscopy among the absorption peak vibration of 451–484 cm^{-1}, in particular the cases of using Fe-containing composites. In addition, the effective crosslink density, determined using the Flory–Rehner equation and supported by temperature scanning stress relaxation (TSSR), showed that the ferric (III) ions (Fe^{3+}) generated the most densely crosslinked and rigid networks, while magnesium (II) ions (Mg^{2+}) had demonstrated the minimal influence. Tensile strength increased significantly from 0.09 MPa for pure E25 to 2.45 MPa for the E25/$FeCl_3$, while $SnCl_2$ provided moderate reinforcement. For the bond reversible, the composites were cut and conditioned at 120°C before measuring the tensile properties. It was found that the coordination bonds can reversibly dissociate and refabricate, allowing recovery of mechanical properties, particularly in $FeCl_3$. This evident was supported by the thermal stability of the composites and observed that the E25 composites with Fe–O bond dissociation had occurred at 120–140°C. These findings suggest that $FeCl_3$ induced coordination crosslinking is a promising strategy for developing ENR based material with enhanced mechanical strength and thermally reversible networks.

Keywords: Epoxidized natural rubber, Metal–oxygen interactions, Reversible network, Coordination crosslinking, Crosslinking density