AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

ABSTRACT

This study describes how changes made to the modification of a polyolefin affect the solution properties of these modified polyolefins in apolar solvents. The modified polyolefins of interest are maleated ethylene-propylene random copolymers (EP-MAH) reacted with *N*-phenyl-*p*-phenylenediamine (NP_3D) to yield NP_3D-EP-MAH. NP_3D-EP-MAH is used as a dispersant by the oil-additive industry and solution properties such as self-aggregation, rheological behaviour, and its efficiency at stabilizing carbon black particles (CBPs) were investigated. The maleation of the polyolefin was characterized in terms of succinic anhydride (SAH) content and level of SAH clustering along the polymer backbone by FT-IR and UV-Vis absorption and steady-state and time-resolved fluorescence. The self-aggregation of the modified polyolefins was characterized in hexane by replacing NP_3D with 1-pyrenemethylamine and using fluorescence to probe excimer formation between an excited and a ground-state pyrene. The rheological behaviour exhibited by the solutions of modified polyolefins was characterized from the viscosity profiles of the solutions obtained as a function of polymer concentration. Finally, the adsorption of the modified polyolefins onto CBPs was characterized by analysis of Langmuir isotherms, which yields both the equilibrium constant and the maximum coverage for the binding of the modified polyolefins onto CBPs. The conclusions reached in this thesis are that clustering of the SAH pendants along the EP backbone enhances the ability of the modified polyolefin to self-aggregate in apolar solution. In turn, self-aggregation led to enhanced thickening of the NP_3D-EP-MAH solutions and stronger adsorption onto CBPs. This thesis establishes how the level of SAH clustering affects self-association and establishes its consequence on the rheological properties and adsorption isotherms of NP_3D-EP-MAH samples in apolar solvents.

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CBPs : Carbon black particles

CRPs : Carbon rich particles

DETA: Diethylene triamine

EP: Ethylene-propylene copolymer

EP-MAH: Maleated ethylene-propylene copolymer

FT-IR : Fourier transform infrared

ΔG : Gibbs free energy

I_E: Total excimer fluorescence intensity obtained from the emission spectrum of the pyrene-labeled polymer

I_E/I_M: Excimer to monomer fluorescence intensity ratio

I_M: Total monomer fluorescence intensity obtained from the emission spectrum of the pyrene-labeled polymer

k_{-1}: Rate constant of excimer dissociation

M_n: Number-average molecular weight

M_W: Weight-average molecular weight

M_w/M_n : Polydispersity index

M_z: Z-averaged molecular weight

MAH: Maleic anhydride

P_A: Peak-to-valley ratio for the pyrene absorbance

PEHA: Pentaethylene hexamine

PIB: Polyisobutylene

PIBSI: Polyisobutylene succinimide

PMA: 1-Pyrenemethylamine

Py: The pyrene chromophore

Py*: The excited pyrene group

Py-EP-MAH: Pyrene-labeled polymer

NMR: Nuclear magnetic resonance

NP_3D: *N*-Phenyl-*p*-phenylenediamine

NP_3D-EP-MAH: Modified ethylene-propylene copolymer

NP_3D-Su: *N*-Phenyl-*p*-phenyleneaminesuccinimide

REX: Reactive extrusion

SAH: Succinic anhydride

THF: Tetrahydrofuran

UV: Ultraviolet

λ_{em}: Emission wavelength

λ_{ex}: Excitation wavelength

λ_{py}: Pyrene content

λ_{NP3D}: *N*-Phenyl-*p*-phenylenediamine content

λ_{SAH}: Succinic anhydride content

τ: Excited state lifetime

$1/\tau_E$: Rate constant of the excimer emission

$1/\tau_M$:: Rate constant of the monomer emission

K: Binding equilibrium constant

Γ_{max}: Maximum adsorption of the dispersant onto carbon black particles