A Novel Method to Determine the Chemical Composition of Polyisobutylene-Based Oil-Soluble Dispersants by Fluorescence

Solmaz Pirouz, Yulin Wang, Michael Chong, Jean Duhamel
Institute of Polymer Research (IPR), Department of Chemistry, University of Waterloo

INTRODUCTION

Succinimide dispersants are among the most important additives that are currently used in engine oils. They adsorb on the surface of carbon-rich particles generated during engine operation, stabilizing them in solution, and consequently reducing the emission of ultrafine particles (**UFPs**) and the formation of sludge. This research intends to characterize the chemical composition of a series of succinimide-based dispersants. The chemical composition of polyisobutylene succinic anhydride (**PIBSA**) and a series of polyisobutylene succinimide (**PIBSI**) dispersants were determined by more common characterization methods such as ^{1}H NMR, FTIR, UV-Vis, and a procedure based on GPC analysis. Steady-state and time-resolved fluorescence measurements were used as a new and unique method to determine the chemical composition of PIBSI dispersants.

PROBLEMS

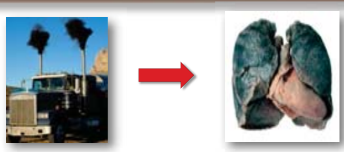


Figure 1. *Lung failure caused by UFPs emission in to the air*

UFPs are typically formed by the incomplete oxidation of fuel during ignition and can be released into the air. Since releasing UFPs from engines into the air can cause heart and lung failure, governmental regulations were issued to reduce their emission. This, in turn, results in higher concentrations of UFPs in the engine oil which leads to sludge formation. To prevent this phenomenon, dispersants were added to the engine oil.

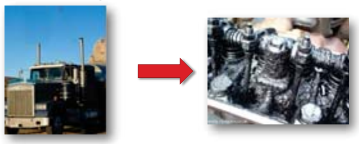


Figure 2. *Sludge formation caused by circulating the exhaust gas back into the oil*

SOLUTION

UFPs which are smaller than 100 nm in diameter have polar groups on their surface which are generated by the oxidation of the oil during engine operation. In apolar oil, UFPs self–aggregate into large particles (**LPs**, d_{LP}= ~1 μm) to minimize their surface exposure to the oil.

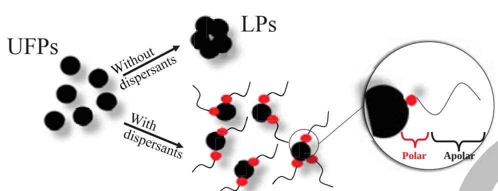
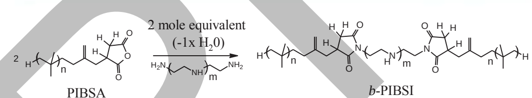


Figure 3. *UFPs in the oil: (top) aggregated UFPs in the absence of dispersant, (bottom) stabilized UFPs in the presence of dispersant*

LPs can cause sludge formation resulting in oil blockage and engine failure. Therefore, dispersants are added to the engine oil to minimize UFPs aggregation into LPs. Dispersants are typically composed of a polar head group and an oil-soluble apolar tail. The polar core of the dispersant is expected to be adsorbed onto the surface of the UFPs, whereas the apolar tail stabilizes the particle in the oil.

SYNTHESIS PROTOCOL



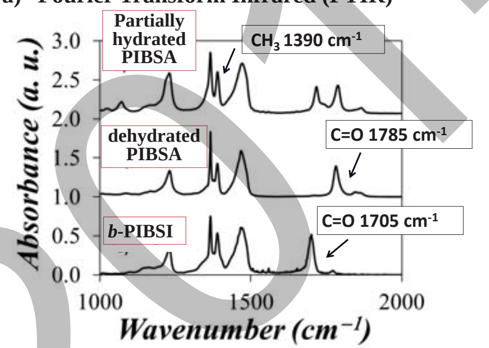
Scheme 1. *Synthesis of succinimide dispersants*

Diethylenetriamine (DETA)	$H_2N-(CH_2CH_2-NH)_1-CH_2CH_2-NH_2$
Triethylenetetramine (TETA)	$H_2N-(CH_2CH_2-NH)_2-CH_2CH_2-NH_2$
Tetraethylenepentamine (TEPA)	$H_2N-(CH_2CH_2-NH)_3-CH_2CH_2-NH_2$
Pentaethylenehexamine (PEHA)	$H_2N-(CH_2CH_2-NH)_4-CH_2CH_2-NH_2$
Hexamethylenediamine (HMDA)	$H_2N-(CH_2)_6-NH_2$

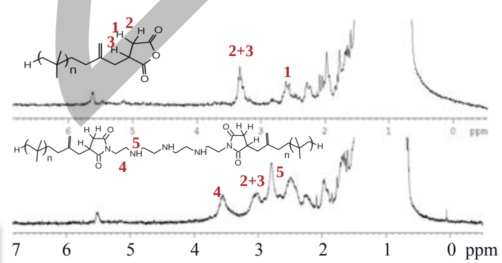
RESULTS

Determination of Chemical Composition

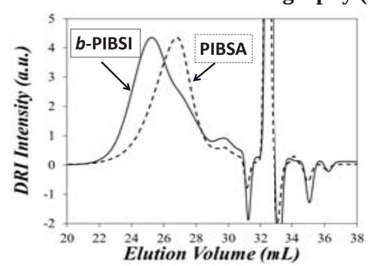
a) Fourier Transform Infrared (FTIR)



b) Nuclear Magnetic Resonance (^{1}H NMR)



c) Gel Permeation Chromatography (GPC)



d) UV-Visible Spectrophotometry (UV-Vis)

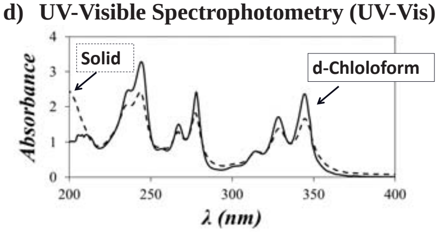
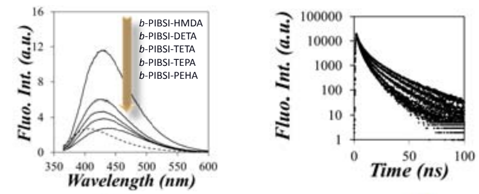


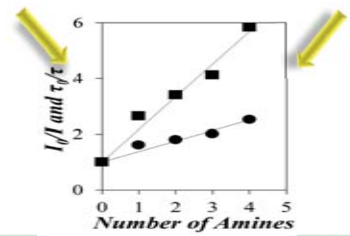
Table 1. *Summary of PIBSA and PIBSI Chemical Compositions*

Dispersants		^{1}H NMR	FT-IR (Peak Height)	GPC	UV-Vis
PIBSA	N_{SA} / N_{IB}	1:55±2	1:49±1	1:52	-
b-PIBSI	N_{SI} / N_{IB}	1:31±3	1:39±2	-	-
m-PIBSI-PyNH$_2$	N_{SI} / N_{IB}	1:45	1:44	-	1:55

Pirouz, S.; Wang, Y.; Chong, M.; Duhamel, J. "Characterization of the Chemical Composition of Polyisobutylene-Based Oil-Soluble Dispersants by Fluorescence", *J. Phys. Chem. B* 2014, 118, 3899-3911

e) Fluorescence Measurements





SUMMARY

- The chemical composition of PIBSA and PIBSI dispersants were characterized quantitatively by using a novel characterization method
- This study confirmed the existence of H-bonds between the secondary amines of the polyamine spacer and the succinimide carbonyls of the *b*-PIBSI dispersants
- Stern−Volmer plots of the ratios I_0/I and τ_0/τ as a function of the number of secondary amines showed a linear behavior suggesting that fluorescence quenching measurements can provide a reliable measure of the secondary amine content of a given *b*-PIBSI dispersant.

ACKNOWLEDGMENTS

The authors thank Imperial Oil and NSERC for funding.