Dissolution of Perfluoroalkyl Oligomers in Lubricating Oil for Enhancing Wear Resistance and Fuel Economy

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SYNOPSIS

Perfluorobutyl-1,1,2-tri-H-1-hexene and perfluoroalkyl methacrylate have been solubilized in lubricating oil by single-step free radically grafting onto poly(ethylene-co-propylene). Perfluoroalkyl-1,1,2,2-tetra-H-ethanol and perfluoropolyether carboxylic acid were solubilized by condensing with poly[(ethylene-co-propylene)-g-glycidyl methacrylate], generating the corresponding perfluoroalkyl ether or ester, respectively. Solubilization of 1,1,2,2-tetra-H-ethanol was also achieved by condensing with poly[(ethylene-co-propylene)-g-2-isocyanoethyl methacrylate] to the corresponding perfluoroalkyl urethane. Scar diameter reductions ranged from 9.4 to 58% using perfluoro-modified graft copolymers as determined using the Four Ball Wear Test, although optimum reductions were obtained using perfluoroalkyl urethane-modified graft copolymers. Moreover, a semiquantitative correlation of scar reductions and thermal instability was determined. Sequence VI engine testing of perfluoroalkyl urethane graft copolymers containing pendant perfluoroalkyl chain lengths of 8.2 and 7.2 had an Equivalent Fuel Economy Index of 4.33 and 4.27, respectively. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Despite its routine use in waxes and greases as a friction modifier, polytetrafluoroethylene (PTFE) has limited application in lubricant formulations because of its poor oil solubility. Circumventing these solubility restrictions using PTFE colloidal dispersions or microemulsions routinely achieves less than optimum friction reduction when used in lubricant formulations.[1] Our method of solubilizing perfluoroalkyl or perfluoropolyether oligomers in lubricating oils entails grafting onto an oil-soluble polymer. This method is well documented in the literature, although others report using polyalkyl methacrylates[2] or polyalkyl ether as the polymeric substrate.[3] The oil-soluble polymeric substrate is a random olefin copolymer viscosity index improver, poly(ethylene-co-propylene) (OCP) (*I*):

Structure I

$$---[(CH_2-CH_2)_a--(CH_2CH)_b]_c$$
$$\overset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$$

Poly(ethylene-co-propylene)
OCP
(I)
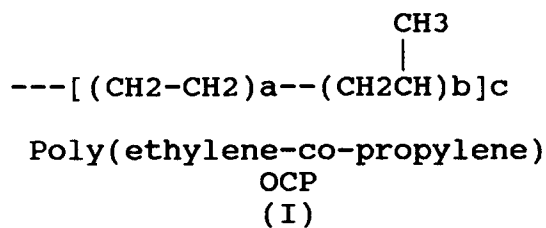
This methodology offers distinct advantages over other methods that utilize PTFE dispersions or suspensions in lubricating oils. First, OCP polymers containing chemically grafted perfluorooligomers are completely soluble in a wide variety of solvents including lubricating oils. This permits wear-resistance properties to be imparted to lubricating oils in a wide variety of temperatures and under adverse conditions. Second, the grafting methodology is sufficiently general that it has wide application to other polymeric materials.

The chemical modification can be accomplished in either a one- or two-step process. In the single-

step process, pendant perfluoroalkyl groups are grafted directly onto the polymeric substrate. This is illustrated in eq. (1): using perfluorobutyl-1,1,2-tri-H-n-1-butene:

(1)
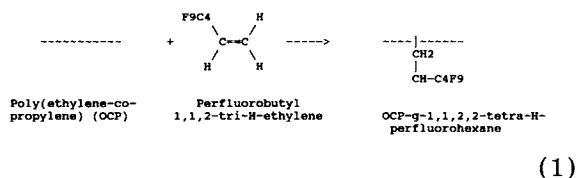
A summary of one-step monomers along with the perfluoroalkyl distribution is provided in Table I. In the two-step process, glycidyl methacrylate (**II**) or 2-isocyanoethyl methacrylate (**III**) is free radically grafted onto the OCP and subsequently condensed with either perfluoroalkyl-1,1,2,2-tetra-H-ethanol (**IV**) perfluoroalkylpolyether carboxylic acid (**V**). This is illustrated in eq. (2) using glycidyl methacrylate and perfluoroalkyl-1,1,2,2-tetra-H-ethanol. Summaries of perfluoroalkyl and perfluoropolyether nucleophiles along with their perfluoro distributions and OCP perfluoro graft copolymers are provided in Tables II and III, respectively.

(2)
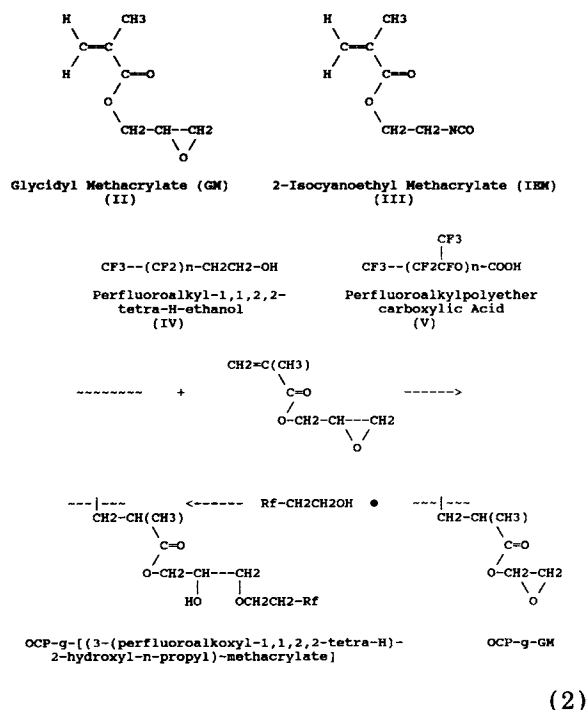
EXPERIMENTAL

All reactions were conducted under nitrogen. Glycidyl methacrylate, isocyanomethacrylate, tetrabu-

tylammonium hydroxide, and solvents were obtained from the Aldrich Chemical Co. and were used as received. Dicumyl peroxide was obtained from the Hercules Chemical Co. and also used as received. Poly(ethylene-co-propylene) consisting of 59 mol % propylene and 41 mol % ethylene with an M_n of 70,000 amu was obtained from the Copolymer Chemical and Rubber Co. and purified by dissolution in n-heptane and precipitation in methanol. Perfluoroaliphatic alcohols Zonyl BA-L, Zonyl BA, and Zonyl BA-N, perfluoroalkylpolyether carboxylic acids FS low and medium, in addition to the single perfluoroolefin, Telomer B, were manufactured and obtained from DuPont and used as received.

Infrared spectra were recorded neat on potassium chloride plates using a Nicolet 5-DX spectrometer. Thermal gravimetric analyses were obtained on 5–15 mg samples with a Perkin-Elmer Series 7700 Thermal Gravimetric Analyzer at a heating rate of 200°C/min over a temperature range of 30–600°C.

SINGLE-STEP PREPARATIONS

1. Preparation of OCP-g-Perfluorobutane-1,1,2-tri-H-n-hexane

A 1.0 L three-neck round-bottom equipped with a mechanical stirrer, thermometer, and condensor with a nitrogen gas tube is charged with 200 g of poly(ethylene-co-propylene) consisting of about 59 mol % propylene having an M_n of approximately 70,000 dissolved in 1440 g of solvent neutral oil and 10 g perfluorobutyl-1,1,2-tri-H-n-1-hexene. The mixture is heated to 160°C under nitrogen and 1.5 g of dicumyl peroxide dissolved in 2.5 g solvent neutral oil is added and the reaction mixture held at 160°C for 3 h before filtering through a 200 mesh screen. The graft copolymer is isolated by precipitating the reaction mixture into a copious amount of acetone. It is purified by dissolving in n-heptane and reprecipitating in acetone, the process being repeated three times.

OCP-g-perfluoroalkyl methacrylates: Preparation of Monomers

Perfluoroalkyl-1,1,2,2-tetra-H-methacrylate containing an average perfluoroalkyl chain length of 7.3. A 500 mL four-neck round-bottom equipped with a 1 in. Teflon-coated magnetic stirrer, thermometer, and condensor equipped with a nitrogen egress tube is charged with 100 mL anhydrous THF containing triethylamine and 50 g

Table I   Summary of Perfluoroalkyl Intermediates Grafted onto an OCP Polymeric Substrate Using the One-Step Process

Material Name	Perfluoroalkyl Chain Length (Wt %)					
	C4	C6	C8	C10	C12	< C14
Perfluoroalkyl (N = 7.2)methacrylate	4	50	29	11	4	2
Perfluoroalkyl (N = 8.2)methacrylate	4	35	30	17	8	6
Perfluoroalkyl (N = 9.0)methacrylate	0	6	50	29	11	4
Perfluorobutyl-1,1,2,2-tetra-H-ethanol	100					

Nos. in parentheses represent the average perfluoroalkyl chain length.

(0.48 mol) of methacryloyl chloride. The mixture is cooled to −5 to 0°C using brine and 225 g (0.50 mol) of sodium salt of perfluoro-1,1,2,2-tetra-H-ethanol having an M_n of 443 amu (Zonyl BA-L) dissolved in 100 mL THF added dropwise at such a rate the temperature never exceeds 10°C. The reaction mixture is refluxed for 5 h and filtered and the crude product isolated by high-vacuum removal of reaction solvent and unreacted reagents and methacrylic acid. The product is purified by extracting with trichloroethylene and is isolated as an amber solid.

Perfluoroalkyl-1,1,2,2-tetra-H-methacrylate containing an average perfluoroalkyl chain length of 8.2. The aforementioned synthetic procedure is again utilized substituting 238 g perfluoroalkyl-1,1,2,2-tetra-H-ethanol with an M_n of approximately 475 amu (Zonyl BA).

Perfluoroalkyl-1,1,2,2-tetra-H-methacrylate containing an average perfluoroalkyl chain length of 9.0. The aforementioned synthetic procedure is again utilized substituting 257 g per-

fluoroalkyl-1,1,2,2-tetra-H-ethanol with an M_n of approximately 514 amu (Zonyl BA-N).

2. Preparation of OCP-g-perfluoroalkyl (N = 7.2)-1,1,2,2-tetra-H-methacrylate

The aforementioned grafting procedure illustrated in Example 1 is again utilized substituting 20 g of purified perfluoroalkyl (N = 7.2) methacrylate.

3. Preparation of OCP-g-perfluoroalkyl (N = 8.2)-1,1,2,2-tetra-H-methacrylate

The aforementioned grafting procedure illustrated in Example (1) is again utilized substituting 20 g of purified perfluoroalkyl (N = 8.2) methacrylate.

4. Preparation of OCP-g-perfluoroalkyl (N = 9.0)-1,1,2,2-tetra-H-methacrylate

The aforementioned grafting procedure illustrated in Example (1) is again utilized substituting 20 g of purified perfluoroalkyl (N = 9.0) methacrylate.

Table II   Summary of Perfluoroalkoxy and Perfluoropolyether Nucleophiles Postreacted with OCPs Containing Grafted Reactive Intermediates

Material Name	Perfluoroalkyl Chain Length (Wt %)						Molecular Weight Range (amu)
	C4	C6	C8	C10	C12	< C14	
Perfluoroalkyl (N = 7.2)-1,1,2,2-H-ethanol	4	50	29	11	4	2	—
Perfluoroalkyl (N = 8.2)-1,1,2,2-H-ethanol	4	35	30	17	8	6	—
Perfluoroalkyl (N = 9.0)-1,1,2,2-H-ethanol	0	6	50	29	11	4	—
Perfluoropolyether carboxylic acid-A							~ 2500
Perfluoropolyether carboxylic acid-B							~ 3750

Nos. in parentheses represent the average perfluoro chain length.

Table III   Summary and Material Designations of One and Two Perfluoroalkyl Graft Polymers Using a Viscosity Index Improver as the Polymeric Substrate

Polymeric Substrate	Perfluoro Monomer	Perfluoro Graft Polymer	Designation
OCP	Rf–alkene	OCP-g-perfluorobutyl-tetra-H-hexane	(OCP-g-Rf)
OCP	Rf–methacrylate	OCP-g-perfluoroalkyl methacrylate	(OCP-g-FM)
OCP-g-IEM	Rf–alcohol (N = 7.2; 8.2; and 9.0)	OCP-g-perfluorourethane methacrylate	(OCP-g-FPU)
OCP-g-GM	Rf–alcohol (N = 7.2; 8.2; and 9.0)	OCP-g-perfluoroether methacrylate	(OCP-g-FGM)
OCP-g-GM	Rf–polyether acid	OCP-g-perfluoroester methacrylate	(OCP-g-FE)

TWO-STEP PREPARATIONS

5. Preparation of OCP-g-glycidyl methacrylate

The aforementioned grafting procedure illustrated in Example (1) is again utilized substituting 20 g of glycidyl methacrylate.

6. Preparation of OCP-g-[(3-(perfluoroalkoxy (N = 7.2)-1,1,2,2-tetra-H)-2-hydroxyl-n-propyl)methacrylate

In a typical condensation reaction, purified OCP-g-GM from Example 5 is treated with a 50%
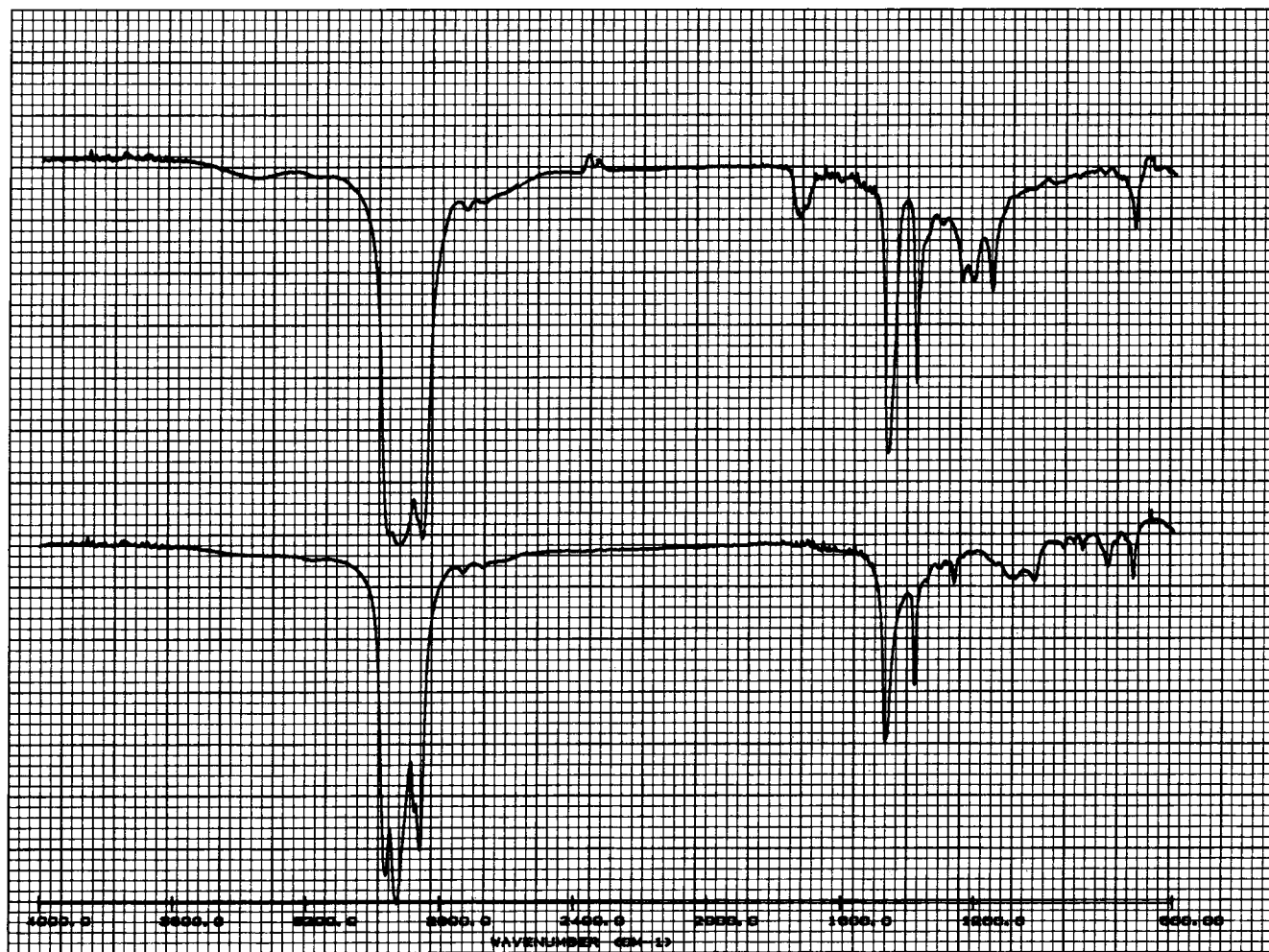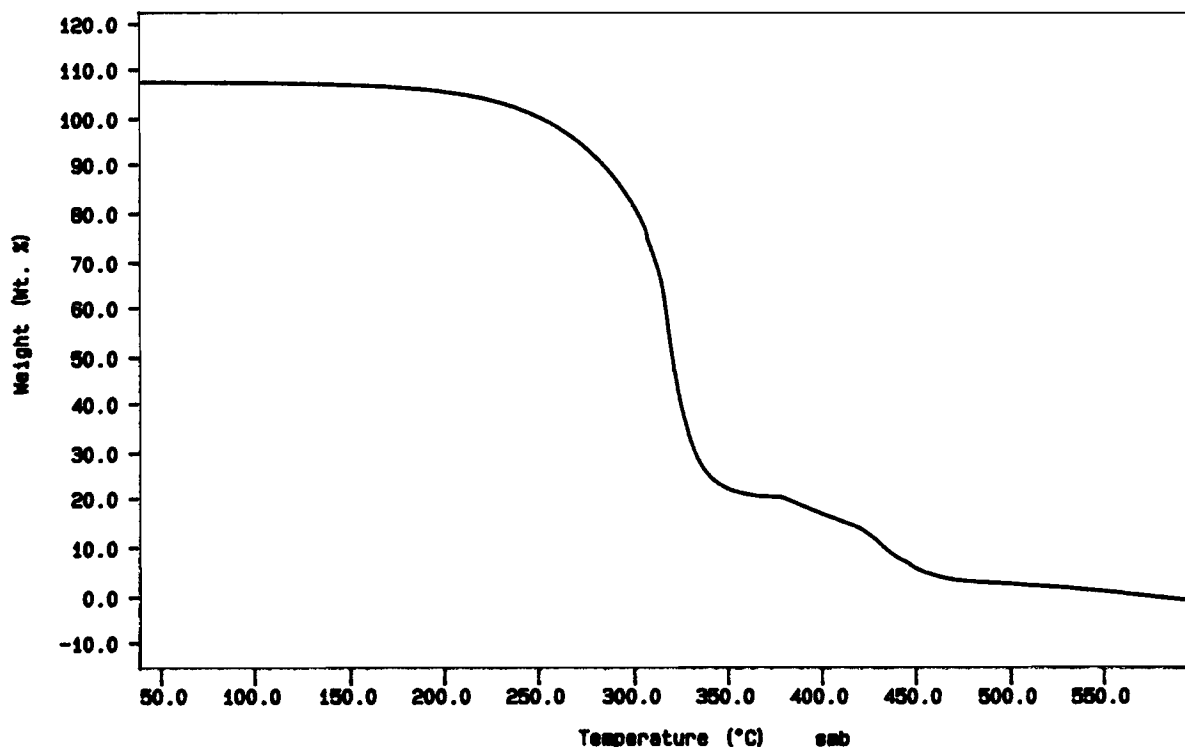

Figure 1   Infrared absorbance spectra for (bottom) unmodified poly(ethylene-co-polymer) and poly[(ethylene-co-propylene)-g-((2-perfluoroalkyl(N = 7.2)urethane)-ethyl)methylmethacrylate].

TGA File Name: sb2
Sample Weight: 14.839 mg
Wed Aug 04 13:12:54 1993
 F40399.61

PERKIN-ELMER
7 Series Thermal Analysis System

Figure 2   Thermogravimetric analysis perfluoroalkylpolyether carboxylic acid (MW
~ 2500 amu) conducted under nitrogen at a heating rate of 20°C min^{-1} where a 50 wt %
loss was obtained at 369.5°C.

stoichometric excess of perfluoroalkyl (N = 7.2)-
1,1,2,2-tetra-H-ethanol (Zonyl BA-L) based upon
the initial glycidyl methacrylate grafting charge and
the mixture heated to 150°C for approximately 4 h.
Excess alcohol is removed by adding the reaction
mixture to a copious amount of acetone precipitating
the rubber while retaining the perfluoroalcohol in
solution. The rubber is dissolved in n-heptane and
reprecipitated in acetone, the process being repeated
three times.

**Table IV   Lubricating Oil Composition Used in
Assessing Antiwear Properties in the
Four Ball Wear Test**

Component	Parts by Weight
Solvent Neutral Oil A	83.50
Solvent Neutral Oil B	5.00
Experimental polymer	11.50

7. Preparation of OCP-g-[(3-(perfluoroalkoxy(N = 8.2)-1,1,2,2-tetra-H)-2-hydroxyl-n-propyl)methacrylate

The experimental condensation protocol from Ex-
ample 6 is again utilized substituting 50% stoicho-

**Table V   Monomer Grafting Efficiencies Using
Poly(ethylene-co-propylene) as the Polymeric
Substrate and Dicumyl Peroxide as the
Free-radical Initiator at 165°C for 2.5 h**

Material	Grafting Efficiency (%)
Glycidyl methacrylate	77
2-Isocyanoethyl methacrylate	83
Perfluoroalkyl (N = 7.2)methacrylate	61
Perfluoroalkyl (N = 8.2)methacrylate	68
Perfluoroalkyl (N = 9.0)methacrylate	62
Perfluorobutyl-1,1,2-tri-H-n-1-hexene	45

metric excess of perfluoroalkyl (N = 8.2)-1,1,2,2-tetra-H-ethanol (Zonyl BA).

8. Preparation of OCP-g-[(3-(perfluoroalkoxy (N = 9.0)-1,1,2,2-tetra-H)-2-hydroxyl-n-propyl)methacrylate

The experimental condensation protocol from Example 6 is again utilized substituting 50% stoichometric excess of perfluoroalkyl (N = 9.0)-1,1,2,2-tetra-H-ethanol (Zonyl BA-N).

9. Preparation of OCP-g-(2-isocyanoethyl)methacrylate

The aforementioned grafting procedure illustrated in Example 1 is again utilized substituting 8 g of 2-isocyanoethyl methacrylate.

10. Preparation of OCP-g-[(2-perfluoroalkyl (N = 7.2)urethane)ethyl]methacrylate

OCP-g-(2-isocyanoethyl)methacrylate is condensed with 50% stoichometric of perfluoroalkyl (N = 7.2)-1,1,2,2-tetra-H-ethanol (Zonyl BA-L) and purified according to the procedure outlined in Example 6.

11. Preparation of OCP-g-[(2-perfluoroalkyl (N = 8.2)urethane)ethyl]methacrylate

The aforementioned experimental procedure outlined in Example 10 is again utilized using perfluoroalkyl (N = 8.2)-1,1,2,2-tetra-H-ethanol (Zonyl BA).

12. Preparation of OCP-g-[(2-perfluoroalkyl (N = 9.0)urethane)ethyl]methacrylate

The aforementioned experimental procedure outlined in Example 10 is again utilized using perfluoroalkyl (N = 9.0)-1,1,2,2-tetra-H-ethanol (Zonyl BA-N).

TESTING AND MATERIAL EVALUATION

To evaluate wear resistance of OCP rubbers containing perfluoro grafts, the experimental materials were subjected to the Four Ball Wear Test, ASTM Test No. MS 82-79. In this test, oil containing the experimental material is heated to 167°F for 60 min at 600 rpm under a load of 40 kg and antiwear properties assessed on the basis of the resulting scar di-

Table VI   Scar Diameters for Unmodified Graft Copolymers, and Perfluoroalkyl and Perfluoroalkylpolyether Graft Copolymers Using the Four Ball Wear Test at 167°F for 1.0 h at 600 rpm with a 40 kg Load

Polymer	Average Scar Diameter (mm)
OCP (unmodified)	0.67
OCP-g-GM	0.69
OCP-g-FGM (N = 7.2)	0.57
OCP-g-FGM (N = 8.2)	0.59
OCP-g-FGM (N = 9.0)	0.46
OCP-g-FEGM (M_n = 2500)	0.55
OCP-g-FEGM (M_n = 3750)	0.48
OCPg-FM (N = 7.2)	0.60
OCP-g-FM (N = 8.2)	0.57
OCP-g-FM (N = 9.0)	0.63
OCP-g-IEM	0.73
OCP-g-FPU (N = 7.2)	0.39
OCP-g-FPU (N = 8.2)	0.43
OCP-g-FPU (N = 9.0)	0.45
OCP-g-Rf	0.54

ameter. Reference oil samples containing unmodified poly(ethylene-co-propylene) were initially evaluated so that a comparison with chemically modified polymeric materials is possible. Components in a typical blend is provided in Table IV. In this mixture, Oil A has a specific gravity at 60/60°F of 0.858–0.868; viscosity at 11°F is 123–133 cPs; and pour point is 0°F. Oil B has a specific gravity at 60/60°F of 0.871–0.880; viscosity at 100°F is 325–350 cPS; and pour point is 10°F. Additionally, antiwear properties were also assessed using Sequence VI gasoline engine oil testing. This ASTM Sequence VI dynamometer test is used to qualify engine lubricants for the Energy Conserving Tier's I and II using a 1982 Buick 3.8L V-6 engine equipped with an electronically controlled carburetor. It provides a comparison for experimental additives against an ASTM 20W-30 HR reference oil and reflects the difference as Equivalent Fuel Economy Index (EFEI).

RESULTS AND DISCUSSION

Representative infrared and thermal gravimetric spectra are provided in Figures 1 and 2, respectively. Free-radical grafting efficiencies for IEM, GM, perfluorobutyl-1,1,2-tri-H-1-hexene, and perfluoroalkyl

Table VII   Sequence VI Engine Testing for Two Experimental Materials Generating Minimum Scar Formation in the Four Ball Wear Test, OCP-g-perfluoroalkyl (N = 7.2)- and Perfluoroalkyl (N = 8.2)Urethanes

Polymer	EFEI
OCP-g-FPU (N = 7.2)	4.27
OCP-g-FPU (N = 8.2)	4.33

methacrylate using dicumyl peroxide as the free-radical initiator are summarized in Table V. Vigorous reaction conditions and a stoichometric excess of perfluoro nucleophiles quantatatively converted pendant epoxide and isocyano functions into the corresponding ether–alcohol and urea, respectively. Four Ball Wear Test results for unmodified, graft copolymers, and perfluoroalkyl and perfluoropoly-ether graft copolymers are summarized in Table VI. These data indicate that optimum scar reduction is achieved using OCP graft perfluoroalkyl urethane copolymers. Subsequent Sequence VI engine testing results of OCP-g-[(perfluoroalkyl(N = 7.2)- and (N = 8.2)urethane)ethyl)]methacrylate are summarized in Table VII. The myriad of bearing surfaces in an engine prevented us from determining whether the friction modification entailed hydrodynamic, elastohydrodynamic, or boundary conditions.[4] Thermal decomposition of perfluoro monomers,

however, indicated that perfluoroalkyl aliphatic urethanes have the least stability, while perfluoroalkenes the greatest. Table VIII provides a summary of perfluoro monomer thermal stability. These thermal test results are consistent with the observations of investigators who correlated additive thermal instability with antiwear efficacy[5]; surfaces modified by additive decomposition were recently characterized by Palacious using SEM.[6] Moreover, enhanced surface anticorrosive properties provided evidence of perfluoropolyoxyalkyl adsorbion or chemisorbion on metallic surfaces by the polar carboxylic acid portion of the molecule.[7] Chemisorption onto metallic surfaces of urethane pyrolysis products[8] is especially favored since the decomposition occurs smoothly at relatively low temperatures and a perfluoroalkyl alcohol is generated. Pyrolysis of the identical material at higher temperatures generates the corresponding alkene through alcohol dehydration. Both the absence of any distinctly polar features and the spatial alignment requirements for alkene preclude appreciable amounts becoming adsorbed to a metallic surface. In addition to generating the corresponding perfluoropolyether acid upon ester pyrolysis, a competing acid or ester decarboxylation reaction becomes favored at elevated temperatures. Although reactive alkyl ketenes may be generated, acid decarboxylation more routinely generate nonpolar products, most notably alkanes,[9] with its concurrent limited surface adsorption.

Table VIII   Thermogravimetric Analyses of Single- and Two-step Perfluoroalkyl Monomers Using a Heating Rate of 20°C min^{-1} Under a Nitrogen Atmosphere

Monomer	5% Wt. Loss Temperature (°C)	50% Wt. Loss Temperature (°C)
Perfluoroalkyl (N = 7.2) methacrylate	—	147.9
Perfluoroalkyl (N = 8.2) methacrylate	—	152.2
Perfluoroalkyl (N = 9.0) methacrylate	—	155.2
Perfluoroalkyl (N = 7.2) urethane	127.9	141.1
Perfluoroalkyl (N = 8.2) urethane	112.5	144.9
Perfluoroalkyl (N = 9.0) urethane	124.9	139.0
Poly(perfluoroalkyl ether)carboxylic acid (M_n ~ 2500 amu)	240.0	369.5
Poly(perfluoroalkyl ether)carboxylic acid (M_n ~ 3750 amu)	257.0	377.8
Perfluoroalkyl (N = 7.2) glycidyl methacrylate	135.2	143.7
Perfluoroalkyl (N = 8.2) glycidyl methacrylate	128.8	154.8
Perfluoroalkyl (N = 9.0) glycidyl methacrylate	134.9	148.0
Perfluoroalkyl-1,1,2-tri-H-n-hexane	151.0	238.4

CONCLUSIONS

Dissolution of viscosity index improvers containing perfluoroalkyl esters, ethers, or urethanes in lubricating oils enhances the overall friction-reducing properties of the oil. This effect is broadly attributable to the thermal instability of the perfluoroalkyl-linking chemical moiety.

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