**Ante Jukić, Kornelije Kraguljac, Ivana Šoljić Jerbić, Elvira Vidović,
Ankica Barišić**

ISSN 0350-350X
GOMABN 49, 3, 229-249
Izvorni znanstveni rad/ Original scientific paper
UDK 665.765.035.6:621.892.2:532.13:678.744.33.04:678.021.18

VISCOSITY AND RHEOLOGICAL PROPERTIES OF MINERAL LUBRICATING OILS CONTAINING DISPERSIVE POLYMETHACRYLATE ADDITIVES

Abstract

The viscometric and rheological behavior of solutions of the polymeric additives of lubricating oils that display dispersive properties was investigated. Additives are synthesized by radical copolymerization of styrene, dodecyl methacrylate, octadecyl methacrylate and dimethylaminoethyl methacrylate (DMAEMA, 2 and 4 mol. % share) in base mineral oil. All solutions of copolymers in basic oil displayed high values of kinematic viscosity and viscosity index (> 150). By embedding of DMAEMA into macromolecules the interactions between polymeric additives and oil change significantly. As a result, much larger hydrodynamic volume of polymeric molecules compared to the conventional methacrylate additives occurs. The viscosity increases due to the hydrodynamic volume increase, oppositely shear stability of solutions decreases while pour points are comparable. Relative, specific and reduced viscosities of diluted solutions of homopolymeric constituents of investigated additives: poly(alkyl methacrylate) (methyl-, PMMA; dodecyl-, PDDMA; octadecyl-, PODMA) and polystyrene (PS), as well as other most commonly used additives, ethylene-propylene (EPC) copolymes as well as styrene and hydrogenated butadiene (SHB) were determined, where following ranking was obtained: EPC ≥ SHB > PDMAEMA ≥ PS >> PDDMA > PMMA ≥ PODMA. Huggins' equation describes concentration dependence of viscosity where limiting viscosity number and Huggins' constants are determined as well. The obtained relationships between polymer composition and rheological properties of their solutions in oil, knowing of molecular interactions between polymers and solvents (base oil), enable formulating of lubricating oils of advanced application properties.

Introduction

Rheological properties of liquids such as lubricating oils can be influenced significantly by adding even small quantities of certain polymers.[1-3] Molecules of polymers in solutions assume a shape of statistical coil.[4] The hydrodynamic volume of a coil is influenced by the interactions between polymeric and molecules of the solvent, as well as between the same kind of molecules and diverse molecules of polymers in solutions, apart from the basic structure of polymeric molecules (chain length, branching). Type and intensity of interactions depend on the temperature, polymer concentration and, again, structure of polymeric macromolecules.[5,6] An adequate choice of polymeric additive, its macromolecular dimensions and structure allow control of rheological properties such as solution viscosity and viscosity dependence on temperature. Among numerous examples it is worth to underline application of amorphous poly(ethylene-*co*-propylene), poly(alkyl methacrylates), or hydrogenated block and star poly(styrene-*co*-butadiene) and poly(styrene-*co*-isoprene) as mineral lubricating oil additives, where they act as viscosity index improvers.[1-3,7]

Alkyl methacrylate copolymers (PAMA) of specific composition and structure are well known and widely used improvers of rheological properties of mineral lubricating oils, [1-3,7] especially viscosity index and pour point of the engine and transmition oils where they are added in relatively high concentrations. Recently, development of the PAMA additives is oriented towards copolymers that display detergent-dispersive properties apart from improving shear and oxidation stability.[8] Desired effect can be reached via polymerization by incorporating in macromolecules comonomers containing functional groups that include oxygen or nitrogen.[9-12] Regulations regarding emission of harmful gases being more stringent each day have helped that process. By implementation of exhaust gas recirculation (EGR) system in diesel engines the emission of NO_x gases in air reduces successfully, but at the same time increases the amount of resulting sludge in engine oils.[13] The duty of functional group in polymeric additive is to disperse sludge in oil and/or to prevent deposition of the combustion products that form a thin surface layer on the vital parts of an engine. This enables better efficiency of the engine, reduces friction, requirement on energy and fuel consumption.

The viscosity and rheological properties of the dispersive polymethacrylic additives of lubricating oils are investigated in this paper. Polymeric additives are synthesized by copolymerization of styrene, long-chain alkyl methacrylates and a functional comonomer that contributes to the dispersive properties,[1,2,8] dimethylaminoethyl methacrylate, in mineral base oil. Free-radical mechanism was handed in isothermal reactions where peroxy initiator was used. Viscosity of diluted solutions of homopolymeric constituents of investigated additives in a modal solvent, toluene, was investigated in detail, in order to assess polymer / solvent molecular interactions, and, thereby a more detailed description of rheological properties.

Experimental part

Polymeric additives based on the copolymers of styrene (St), *n*-dodecyl methacrylate (DDMA), *n*-octadecyl methacrylate (ODMA) and dimethylaminoethyl methacrylate (DMAEMA) are produced by polymerization of the monomers mixture in solution of the mineral base oil SN-150, using peroxide as an initiator under isothermal conditions.[14] The ratio of polymer in base oil is equal to the monomers ratio since the total conversions are accomplished and amount 50 wt. %. Homopolymers poly(dimethylaminoethyl methacrylate) (PDMAEMA), polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(dodecyl methacrylate) (PDDMA) and poly(octadecyl methacrylate) (PODMA) are prepared by radical polymerization of corresponding monomers in xylene solution at 90 ºC, using *tert*-butyl peroxy-2-ethylhexanoate (Akzo Chemicals) as an initiator. Solvents, toluene and xylene of high purity (p.a.), and base oils SN-150 and SN-200 are used without further purification. Polydispersity and molar mass averages of polymers are determined by the size exclusion chromatography (SEC) on the GPC-20 Polymer Laboratories instrument fitted with RI detector. Tetrahydrofuran was used as a solvent and eluent. Molar masses were determined as polystyrene equivalents. Results are shown in table 1. The copolymers composition was identify with the assistance of ^{1}H NMR spectroscopy, on the Bruker Avance NMR 300 instrument. Measurements are performed at the room temperature in deuterated chlorform ($CDCl_3$) using tetramethylsilane as an internal standard. The viscosimetric and rheological properties of the polymers in oil solutions are determined by normed methods: kinematic viscosity according HRN EN ISO 3104, viscosity index according HRN ISO 2909, shear stability according DIN 51382 and pour point according HRN ISO 3016. Viscometric measuremetns of diluted solutions of polymers are performed at 30 ± 0.02 ºC, using the capillary viscometer Cannon-Fenske 50 K immersed in a constat temperature bath. Relative viscosities are calculated by dividing the flow times of polymer solutions by that of the pure solvent ($\eta_{rel} = \eta / \eta_o = t / t_o$). The experiments were performed in the range of $1.05 < \eta_{rel} < 1.5$ with provided (typically) five different concetrations. The reproducibility of results was tested by repeating experimets using newly prepared solutions.

Table 1: Number, weight and *z*-average molar masses (M_n, M_w, and M_z), and polydispersity index of studied polymers ($D = M_w / M_n$); PMMA – poly(methyl methacrylate), PDDMA – poly(dodecyl methacrylate), PODMA – poly(octadecyl methacrylate), EPC – poly(ethylene-*co*-propylene), SHB – poly(styrene-*co*-hydrogenated butadiene), PS – polystyrene.

Polymer	M_n / kg mol^{-1}	M_w / kg mol^{-1}	M_z / kg mol^{-1}	D
PMMA	46.9	77.1	120.7	1.64
PDDMA	34.2	73.0	135.1	2.13
PODMA	33.4	71.3	130.4	2.13
EPC	65.1	112.2	178.6	1.72
SHB	76.4	122.2	216.0	1.60
PS	108.5	213.4	379.6	1.97

Results and discussion

Concentrated and semiconcentrated solutions

Viscosity is a major property of lubricating oils. Figure 1 shows viscosities of polymeric batches, i.e. of concentrated solutions of polymers in the base oil SN-150 at 100 °C. Concentration of polymer in oil was 50 wt. %. Examined polymers contain 0, 2 and 4 mol. % of dispersive functional component DMAEMA and are assigned as PSAMA, dispersive PSAMA-1 and dispersive PSAMA-2. A detailed composition of polymers is shown in table 2. In all three polymers, the amount of styrene was kept constant and amounts 15 wt. %, as well as mass ratio between long-chain alkyl methacrylates, DDMA : ODMA = 1 : 1. Former examinations have shown that such composition results in excellent viscosity properties and shear stability, simultaneously keeping good low-temperature properties.[15,16]

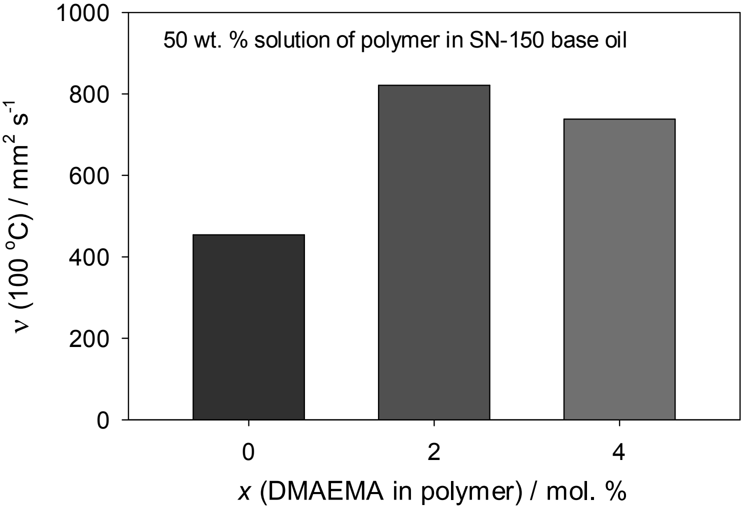

Figure 1: Dependence of kinematic viscosity of polymeric additive on molar ratio of dispersive component DMAEMA in styrene, dodecyl methacrylate and octadecyl methacrylate copolymer.

As it can be seen from figure 1, there is a big influence of copolymers composition on viscosity of solutions. Even a very small ratio of the DMAEMA of 2 mol. % (1.4 wt. %) and 4 mol. % (2.8 wt. %) causes almost a twofold increase of solution viscosity compared to the additives without DMAEMA. In table 2 are given the general structural properties of polymers: weight and number average molar masses, and polydispersity index. Weight average molar masses of polymers, that are the nearest to the viscometric average molar masses, show relatively uniform values. Therefore, the abrupt increase of viscosity of dispersive additives with the DMAEMA is not consequence of the differences in molar masses of polymers, but of the alternation of solvent / polymer molecular interactions.[5,17] Obviously, under the conditions of examination, base oil is thermodynamically a better solvent for dispersive PSAMA compared to the PSAMA, and, thereby, the volume of hydrodynamic coil of polymeric molecules in the solutions is larger which results in the viscosity increase. These speculations will be described in more detail and broadly quantify within the study of viscometric behavior of diluted solutions of homopolymeric constituents of investigated additives.

Table 2: Composition and structural properties of polymers, viscosity and rheological properties of polymeric additives (concentrated, semiconcentrated and diluted solutions of polymers in base oil): molar ratio of monomer in polymer, x, number average molar masses, M_n, weight average molar masses, M_w, polydispersity index, D, kinematic viscosity, v, viscosity loss, Δv, viscosity index, IV, and pour point, ϑ.

Additive			PSAMA	dispersive PSAMA-1	dispersive PSAMA-2
x / mol. % (polymer)	DMAEM		0.0	2.0	4.0
	Styrene		33.0	32.7	32.4
	DDMA		38.2	37.3	36.4
	ODMA		28.8	28.0	27.2
M_n / kg mol^{-1}			68.4	57.0	44.8
M_w / kg mol^{-1}			119.2	108.2	105.8
$D = M_\mathrm{w} / M_\mathrm{n}$			1.74	1.90	2.36
ν (100 °C) / mm^2 s^{-1} (polymer ratio 50 wt. %)			453.99	820.98	738.27
Shear stability test (polymer ratio 5 wt. %)	ν (40 °C) / mm^2 s^{-1}	before	84.64	100.46	94.49
		after	79.48	86.97	84.72
		$\Delta\nu$ / %	11.60	22.37	17.98
	ν (100 °C) / mm^2 s^{-1}	before	12.65	15.11	14.22
		after	11.87	13.06	12.70
		$\Delta\nu$ / %	11.96	22.80	18.79
	IV before		147	158	155
	IV after		143	150	148
Pour point, ϑ / °C (polymer ratio 0.5 wt. %)			-18	-18	-18

A semiconcentrated, 5 wt. % solution of polymer was prepared by diluting of the 50 wt. % solution with the mineral base oil SN-200. Table 2 shows values of kinematic viscosity at 40 and 100 °C, viscosity index, and change of viscosity caused by the implementation of the shear stability test, performed on the semiconcentrated solutions. Viscosity of additives of polymers that contain 2 and 4 mol. % DMAEMA at 40 and 100 °C are higher than those of additives without DMAEMA, despite of somewhat lower values of molar masses. Polymer solution with 4 mol. % of the DMAEMA displays slightly lower values of viscosity due to the smaller molar masses and broader molar mass distribution that is expressed with the higher polydispersity index. The shear stability of additives is described by the relative decline of viscosity that is result of breakdown of polymer molecules because of the shear stress in the test of shear stability. Due to the large hydrodynamic volume of polymeric molecules, additives with the DMAEMA display an inferior stability, which can be improved by reducing molar mass of polymers. Furthermore, the dispersive additives show also high values of viscosity index, IV ~ 150. Pour point values, measured for the 0.5 wt. % polymer solutions in base oil that are prepared by additional diluting, are equal for all additives and amount -18 °C. Low pour point values chiefly depend on the content and ratio of long-chain alkyl methacrylate in polymer, respectively, as well as their mutual ratio.[16] Since the polymeric dispersive additives still contain high ratio of dodecyl methacrylate and octadecyl methacrylate, higher than 60 mol. % (> 80 wt. %), good low temperature properties are retained that are characteristic for the improvers of rheological properties of lubricating oils based on alkyl methacrylate copolymers.

Diluted solutions

Aiming at the more detailed description and insight in viscometric behavior of investigated systems, the viscosity of diluted solutions of homopolymeric constituents of polymeric additives of lubricating oils: poly(dimethylaminoethyl methacrylate) (PDMAEMA), constituent that contributes to the detergent-dispersive properties of additives, furthermore, poly(methyl methacrylate) (PMMA), poly(dodecyl methacrylate) (PDDMA) and poly(octadecyl methacrylate) (PODMA) was investigated. For the comparison reasons, viscosity of the diluted solution of polyolefinic additive poly(ethylene-co-propylene) (EPC) of amorphous structure, poly(styrene-co-hydrogenated butadiene) (SHB) copolymers and polystyrene (PS), was inspected. Toluene was used as a model solvent, due to the properties similar to the mineral base oil. In table 3 are listed values of relative, η_{rel}, and specific viscosity, η_{sp}, depending on the polymer concentration in solution. Figure 2 shows reduced viscosities of the PDMAEMA solution and other methacrylate polymers, PMMA, PDDMA and PODMA. In figure 3 are shown reduced viscosities of the PDMAEMA solution and the non-methacrylate polymers, EPC, SHB and PS.

Table 3: Dependence of relative, η_{rel}, and specific viscosity, η_{sp}, on the polymer concentration in toluene solution at 30 °C.

γ / g cm^{-3}	0.001	0.002	0.003	0.004	0.005
PDMAEMA / poly(dimethylaminoethyl methacrylate)					
η_{rel}	1.079	1.161	1.249	1.348	1.444
η_{sp}	0.079	0.161	0.249	0.348	0.444
η_{red} / cm^3 g^{-1}	78.93	80.49	82.94	86.89	88.74
PMMA / poly(methyl methacrylate)					
η_{rel}	1.018	1.037	1.056	1.075	1.094
η_{sp}	0.018	0.037	0.056	0.075	0.094
η_{red} / cm^3 g^{-1}	17.87	18.25	18.50	18.65	18.80
PDDMA / poly(dodecyl methacrylate)					
η_{rel}	1.025	1,051	1.079	1.109	1.137
η_{sp}	0.025	0,051	0.079	0.109	0.137
η_{red} / cm^3 g^{-1}	24.93	25,63	26.44	27.19	27.40
PODMA / poly(octadecyl methacrylate)					
η_{rel}	1.017	1.033	1.051	1,073	1.092
η_{sp}	0.017	0.033	0.051	0,073	0.092
η_{red} / cm^3 g^{-1}	17.00	16.34	17.05	18,30	18.30
EPC / poly(ethylene-*co*-propylene)					
η_{rel}	1.097	1.205	1.328	1.450	1.588
η_{sp}	0.097	0.205	0.328	0.450	0.588
η_{red} / cm^3 g^{-1}	97.31	102.30	109.25	112.42	117.50
SHB / poly(styrene-*co*-hydrogenated butadiene)					
η_{rel}	1.097	1.205	1.317	1.436	1.567
η_{sp}	0.097	0.205	0.317	0.436	0.567
η_{red} / cm^3 g^{-1}	97,05	102.68	105.65	108.92	113.39
PS / polystyrene					
η_{rel}	1.077	1.156	1.238	1.325	1.416
η_{sp}	0.077	0.156	0.238	0.325	0.416
η_{red} / cm^3 g^{-1}	76.46	78.20	79.23	81.21	83.16

According to the shown values one can conclude that viscosities of the all investigated systems increase with the polymer concentration increase. Among methacrylate the highest viscosity display the DMAEMA solutions, significantly higher than solutions of the short- and long-chain poly(alkyl methacrylates). This behavior is in line with the viscosity results obtained for polymer solutions in base oil.

Solutions of the EPC and SHB have higher viscosities compared to the DMAEMA solution, while viscosity of the PS solution is slightly lower. The viscosities of all investigated systems decrease in the following order:

EPC ≥ SHB > PDMAEMA ≥ PS >> PDDMA > PMMA ≥ PODMA.

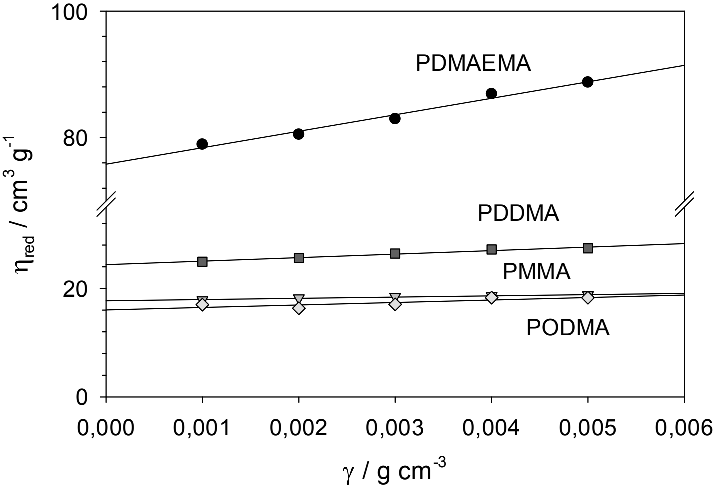

Figure 2: Dependence of reduced viscosity on weight concentration of diluted polymer solutions PDMAEMA, PMMA, PDDMA and PODMA in toluene at 30 °C.

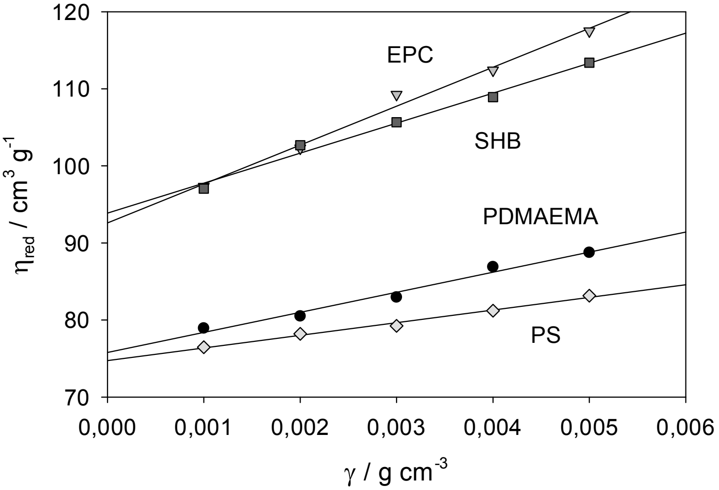

Figure 3: Dependence of reduced viscosity on weight concentration of diluted polymer solutions PDMAEMA, EPC, SHB and PS in toluene at 30 °C.

Viscosity of the polymer solutions in the range of polymer low concentration usually is described by Huggins' equation:

$$\frac{\eta_{\mathrm{sp}}}{\gamma} = [\eta] + k_{\mathrm{H}}[\eta]^2 \gamma = [\eta] + b\,\gamma$$

where η_{sp} refers to the specific viscosity, $[\eta]$ is the limiting viscosity number, γ is the weight concentration of polymer, and k_H is the Huggins' constant, that is empirically related to the thermodynamical quality of solvent. Experimentally determined dependence of reduced viscosity on concentration (figures 2 and 3) can be described by Huggins' extrapolation straight lines regarding all investigated systems, with coefficient of linear regression higher than 0.9. Corresponding Huggins' constants and limiting viscosity numbers are listed in table 4. Systems of the PS, SHB, PDMAEMA / toluene give k_H-values between 0.29 and 0.45 that are characteristic for a polymer in a good solvent, while value of the EPC is slightly higher and corresponds to the values of a polymer in thermodynamically poor solvent. Toluene is, in particular a poor solvent for the PMMA, where $k_H \approx 0.7$. In case of PDDMA and PODMA solutions k_H-values above 1 are noticed, characteristic for the poly(alkyl methacrylates) solutions as systems prone to the associations of polymeric molecules.[5,18] Values of limiting viscosity numbers, that are measure of polymer / solvent interactions and directly proportional to the size of hydrodynamic coil of the polymer molecules in solution, support these findings. The limiting viscosity numbers, as well as the slope of Huggins' straight line, *b*, that is a measure of polymer / polymer interaction, have maximal values for the EPC and SHB solutions, followed with the PDMAEMA and PS, and finally lowest values have solutions of alkyl methacrylate polymers.

Table 4: Experimental values of limiting viscosity numbers, $[\eta]$, and Huggins' constants, k_H, of investigated diluted solutions of polymers in toluene at 30 °C; PDMAEMA - poly(dimethylaminoethyl methacrylate), PMMA - poly(methyl methacrylate), PDDMA - poly(dodecyl methacrylate), PODMA - poly(octadecyl methacrylate), EPC - poly(ethylene-*co*-propylene), SHB - poly(styrene-*co*-hydrogenated butadiene), PS – polystyrene.

Polymer	b / cm^6 g^{-2}	$[\eta]$ / cm^3 g^{-1}	k_H	r^2
PDMAEMA	2601	75.8	0.45	0.98
PMMA	225	17.7	0.72	0.95
PDDMA	757	24.2	1.30	0.99
PODMA	714	15.0	3.17	0.90
EPC	5050	92.6	0.59	0.99
SHB	3891	93.9	0.44	0.99
PS	1641	74.7	0.29	0.99

Conclusion

Performed investigations show that even a small ratio of the DMAEMA functional comonomer in the styrene / alkyl methacrylate copolymer has a significant influence on the viscometric behavior and rheological properties of the solutions in oil. Embedding of the DMAEMA in macromolecules changes considerably molecular interactions between polymeric additive and oil, which results in an essentially larger hydrodynamic volume of polymeric molecules in comparison to the conventional methacrylate additives. With the increase of the coil volume viscosity increases and the shear stability of solutions decreases. The viscosity index values of the dispersive PSAMA solutions are slightly higher compared to the conventional PAMA additive, while the pour points are comparable. The obtained interdependences between polymer composition and rheological properties of their solutions in oil, as well as knowing of molecular interactions between polymers and solvents (base oil), enable formulating of lubricating oils of advanced properties in use.

References

1. Mortier, R. M., Orszulik S. T. (Eds.), *Chemistry and technology of lubricants*, 2nd Ed., Blackie, London (1997).
2. Braun, J., Omeis, J., *Additives*. In: *Lubricants and lubrication*, Mang, T. and Dresel, W. (Eds.), New York: Wiley-VCH (2007) p. 85.
3. Janović, Z., *Naftno petrokemijski procesi i proizvodi*, Hrvatsko društvo za goriva i maziva, Zagreb (2005).
4. Janović, Z., Polimerizacije i polimeri, Hrvatsko društvo kemijskih inženjera i tehnologa, Zagreb (1997).
5. Bohdanecký, M., Kovář, J., *Viscosity of polymer solutions*, Elsevier, Amsterdam (1982).
6. Matusinović, Z., Rogošić, M., Mencer, H. J., Eur. Polym. J., 41 (2005) 2934.
7. Stambaugh, R. L., *Viscosity index improvers and thickeners*. In: *Chemistry and technology of lubricants*, Mortier, R. M., Orszulik, S. T. (Eds.), Blackie, London (1997), p. 144.
8. Rudnick, L. R., *Lubricant additives*, CRC Press, Wilmington (2003), p. 329.
9. Akhmedov, A. I., Chem. Tech. Fuels Oils, 23 (1987) 147.
10. Jukić, A., Vidović, E., Janović, Z., Chem. Tech. Fuels Oils, 43 (2007) 386.
11. Fan, J. Y., Muller, M., Spikes, H., Technische Akademie Esslingen International Tribology Colloquium Proceedings 15 (2006) p. 295.
12. Šoljić, I., Jukić, A., Janović, Z., Polym. Eng. Sci., 50 (2010) 577.
13. Aldajah, S., Ajayi, O. O., Fenske, G. R., Goldblatt, I. L., Wear, 263 (2007) 93.
14. Jukić, A., Rogošić, M., Janović, Z., Ind. Eng. Chem. Res., 46 (2007) 3321.
15. Jukić, A., *Disertation*, University of Zagreb, Zagreb (2004).
16. Janović, Z. et al., Goriva i maziva, 45 (2006) 143.
17. Jukić, A., Tomašek, Lj., Janović, Z., Lubr. Sci., 17 (2004) 431.
18. Jukić, A., Rogošić, M., Bolarić, I., Tomašek, Lj., Janović, Z., J. Mol. Liq., 112 (2004) 161.

Ključne riječi	Keywords
Mineralna maziva ulja	Mineral lubricating oils
Viskoznost	Viscosity
Reološka svojstva	Rheological properties
Disperzantni polimetakrilatni aditivi	Dispersant polymethacrylate additives

Authors
prof. dr. sc. Ante Jukić (e-mail: ajukic@fkit.hr), Kornelije Kraguljac, dipl. ing.,
dr. sc. Ivana Šoljić Jerbić, doc. dr. sc. Elvira Vidović
University of Zagreb, Faculty of Chemical Engineering and Technology
Ankica Barišić, dipl. ing.
Maziva - Zagreb Ltd., member of INA group

Received
1.6.2010.

Accepted
21.6.2010.