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Molecular interaction in some polymeric additive solutions containing styrene-hydrogenated butadiene copolymer

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ABSTRACT

The miscibility of styrene-hydrogenated butadiene copolymer (SHB) with different constituents of polymer additives for lubricating mineral oils was studied in dilute solution regime, using xylene as model solvent, at 30 °C, in a wide range of polymer blend compositions. The systems studied were SHB/poly(ethylene-*co*-propylene) (EPC), SHB/poly(methyl methacrylate) (PMMA), SHB/poly(dodecyl methacrylate) (PDDMA) and SHB/polystyrene (PS). The viscometric interaction parameters were calculated according to the Krigbaum–Wall and Catsiff–Hewett models of ideal viscometric behavior. Strong repulsive interactions were found in SHB/PMMA and SHB/PDDMA systems pointing to immiscibility. SHB/EPC and SHB/PS deviated much less from ideality. The results were compared to the theoretical estimation of interaction in polymer blends in the absence of solvent, using the Coleman–Graf–Painter approach. No correlation was observed between the interaction in the bulk and in solution.

1. Introduction

Styrene-hydrogenated butadiene (SHB) copolymers belong to the class of hydrogenated styrene–diene viscosity index improvers. This class comprises several subclasses, according to the diene unit incorporated (butadiene or isoprene), or according to the different molecular architecture (random, block, star-shaped polymers) [1,2]. Viscosity index (VI) is a number that characterizes the temperature changes in oil viscosity, and is used, for example, in the field of automotive lubricants. Lubricating oil must reduce friction between engine components both in start regime (temperature of environment) as well as in the fully developed working regime (temperatures up to 200 °C). The best oils (with the highest VI) will not vary much in viscosity – they will perform well in the whole temperature range. The chemistry and performance features of SHB viscosity index improvers have been reviewed in details in books, technical and scientific papers [1–7]. The viscosity loss of base mineral oil is compensated with the viscosity increase due to association of copolymer molecules promoted at elevated temperatures. The basic member of the group is random copolymer with about 50–60 wt.% styrene. It would be desirable for butadiene to polymerize with a high content of 1,4-configuration, for solubility reasons. However, to prevent formation of linear polyethylene-like blocks prone to crystallization at low temperatures, some butadiene in the products has to be of 1,2-configuration. The final copolymers are obtained by hydrogenation using a technique which gives very high conversion on the butadiene-derived unsaturation, while hydrogenating little or none of styrene [1]. Also, these studies show that polymer behavior depends highly on solvent nature (paraffinic *vs.* napthenic oil) and temperature.

Beside SHB, the following classes of polymers are most commonly used as viscosity index improvers of lubricated mineral oils: olefine copolymers (OCP), such as amorphous poly(ethylene-*co*-propylene) (EPC) and poly(alkyl methacrylates) (PAMA) [1]. Often, these copolymer classes are functionalized with certain comonomers to improve particular properties, such as solubility, dispersivity, etc.

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In practice, polymeric additives are very often combined for the reasons of economy, but also in a desire for optimal properties. A textbook example is a mixture of OCP/PAMA [1,8]; OCP is a component of much lower price, while PAMA significantly improves low-temperature properties. One immediately meets the problems of miscibility and compatibility in ternary polymer solutions. Namely, polymers of different chemical structures are generally immiscible in the absence of specific interactions, due to the extremely low entropy of mixing. This effect was quantified by the well-known Flory–Huggins theory, and it is observed commonly even in dilute solution range. It is of utmost importance to study the molecular interactions to formulate the product of good lubricating properties. In this work we studied molecular interactions and miscibility of SHB with other polymer classes used as components of VI improvers: poly(ethylene-*co*-propylene) (EPC), poly(methyl methacrylate) (PMMA), poly(dodecyl methacrylate) (PDDMA) and polystyrene (PS). The method of choice for such studies was dilute solution viscometry – solution properties are studied directly. Model solvent – xylene was used to mimic the mineral base oil.

2. Experimental

2.1. Materials

Four binary polymer systems were investigated with respect to miscibility, formed by five polymers. Styrene-hydrogenated butadiene copolymer (SHB) and poly(ethylene-*co*-propylene) (EPC) were commercial products (Lubrizol 7440 and 7067, respectively) of Lubrizol Chem. Co. Polystyrene (PS) of general purpose was commercial product of DIOKI Organic Petrochemistry, Zagreb. Poly(methyl methacrylate) (PMMA) and poly(dodecyl methacrylate) (PODMA) were synthesized by the free radical polymerization of corresponding monomers in xylene solution at 90 °C, using *tert*-butyl peroxy-2-ethylhexanoate (Akzo Chemicals) as an initiator. The detailed procedure was described in the previous paper [9]. Xylene of high purity (Kemika, Zagreb, p.a.) was used as received.

2.2. Methods

Binary polymer solutions were prepared by dissolving the appropriate mass of polymers in xylene, followed by dilution to a measured volume. Ternary polymer solutions were prepared by mixing the two corresponding binary solutions. Viscometric measurements were carried out at 30 ± 0.02 °C, using a Cannon–Fenske 50 K capillary viscometer immersed in a constant temperature bath. Relative viscosities of polymer solutions were calculated by dividing the flow times of solutions by that of the pure solvent ($\eta_{rel} = \eta/\eta_o = t/t_o$). The experiments were performed in the range of $1.05 < \eta_{rel} < 1.5$ to provide typically five data points. The full range of polymer mixture compositions was investigated. No kinetic energy corrections were made due to the observed high value of solvent flow time. The reproducibility of experiments was ensured by measurement replication. For that purpose, ternary polymer solutions were made from newly prepared binary polymer solutions. No significant difference between replicated measurements was observed.

The ^1H NMR spectrum of SHB was recorded on the 300 MHz Bruker Avance spectrometer at room temperature, in deuterated chloroform with TMS as an internal standard (Fig. 1). The molar fraction of styrene was calculated to be 30 mol.%. Ethylene fraction in EPC was determined previously [8] to be 60 mol.%. The molar mass distributions of investigated polymers were determined by the size exclusion chromatography (SEC) carried out on the GPC-20 Polymer Laboratories instrument fitted with RI detector. Tetrahydrofuran (Kemika, Zagreb, p.a.) was used as a solvent. Molar masses were calculated as polystyrene equivalents and their average values are listed in Table 1.

3. Results and discussion

Interactions in dilute solutions of two or more polymers in common solvent are usually studied by capillary viscometry [4,8,10–15]. The principle will be described on the basis of Fig. 2. Reduced viscosity, calculated as the ratio of specific viscosity, η_{sp}, and mass concentration of polymer, γ, is plotted *vs.* polymer mass concentration. For a two-component system (a polymer in a solvent), this concentration dependence is described as a linear Huggins' function:

$$\eta_{red} = [\eta] + k_H[\eta]^2\gamma, \tag{1}$$

that is valid only in a limited range of concentrations in the dilute region. k_H denotes so-called Huggins constant, that is dependent on the thermodynamic quality of solvent, but may include effects such as shape of the solute molecules and self-association of macromolecules [4,10,16]. Intrinsic viscosity, $[\eta]$, depends primarily on the molar mass of solute (polymer), temperature, etc. [10,17]. The slope of the Huggins' line is:

$$b = k_H[\eta]^2. \tag{2}$$

For a three-component system, Huggins' equation may be written as:

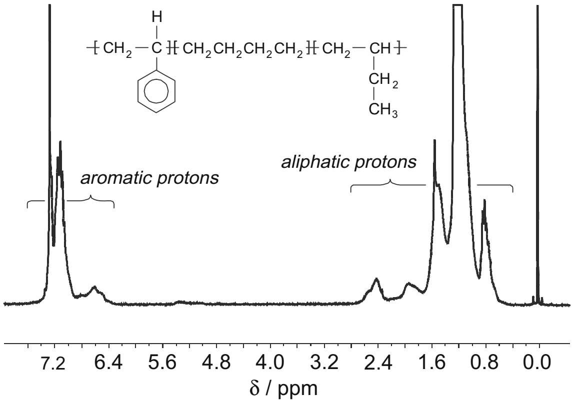

Fig. 1. ^1H NMR spectrum of styrene-hydrogenated butadiene copolymer.

Table 1
Number and weight average molar masses of SHB, EPC, PS and synthesized poly(alkyl methacrylates), PMMA and PDDMA.

	M_n/kg mol^{-1}	M_w/kg mol^{-1}	M_w/M_n
SHB	76.4	122.2	1.6
EPC	59.1	108.9	1.8
PS	108.5	213.4	2.0
PMMA	32.5	70.8	2.2
PDDMA	34.2	73.0	2.1

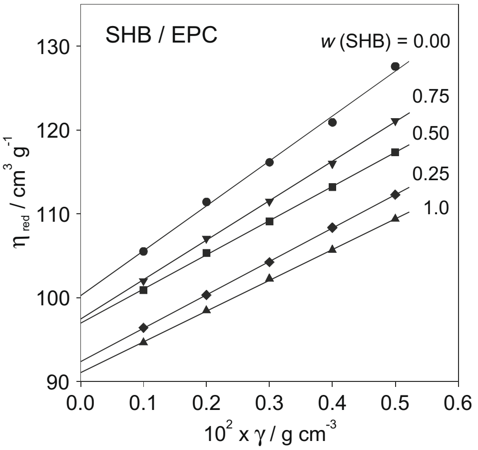

Fig. 2. Reduced viscosity *vs.* total polymer concentration in the SHB/EPC system; xylene solution at 30 °C.

$$\eta_{\mathrm{M,red}} = [\eta]_{\mathrm{M}} + b_{\mathrm{M}}\gamma_{\mathrm{M}}. \tag{3}$$

Here, M, denotes mixture. Upon replacing γ with the sum of component concentrations, and intrinsic viscosity by an appropriate mixing rule, one obtains:

$$\frac{\eta_{\mathrm{sp}}}{\gamma_1+\gamma_2} = [\eta]_1 w_1 + [\eta]_2 w_2 + b_{\mathrm{M}}(\gamma_1+\gamma_2). \tag{4}$$

In theory, b_{M}, may be related to the component Huggins lines by:

$$b_{\mathrm{M}} = k_{\mathrm{H1}}[\eta]_1^2 w_1^2 + k_{\mathrm{H2}}[\eta]_2^2 w_2^2 + 2b_{12}w_1w_2. \tag{5}$$

b_{12} is interaction coefficient and may be calculated from experimental slope, b_{M}. For "ideal" solutions, it may be compared either to a geometric average (Krigbaum–Wall, [18]):

$$b_{12}^{*} = \sqrt{b_1 \times b_2}, \tag{6}$$

or to an arithmetic average (Catsiff and Hewett [19]):

$$b_{12}^{**} = \frac{b_1+b_2}{2} \tag{7}$$

Negative deviations:

$$\Delta b_{\mathrm{rel}}^{*} = \frac{b_{12}-b_{12}^{*}}{b_{12}^{*}} < 0, \tag{8}$$

$$\Delta b_{\mathrm{rel}}^{**} = \frac{b_{12}-b_{12}^{**}}{b_{12}^{**}} < 0, \tag{9}$$

point to immiscibility (or incompatibility) of polymeric components in the solution. Positive deviations refer to miscibility. Figs. 2–5 show all the relevant data needed to calculate interactions in the four investigated polymer pairs.

In all the investigated systems and for all investigated polymer mixture compositions, the viscosity of solution increase with the increase of (total) polymer concentration. For all the investigated mixtures, the viscosities of ternary solutions (two polymers in xylene) lie between the viscosities of corresponding binary solutions (one polymer in xylene). Considering only the binary solutions, the highest viscosity is observed for EPC in xylene, followed by SHB, PS, PDDMA and PMMA. This ordering is a result of somewhat different molar masses (and molar mass distributions) of investigated polymers. One has to keep in mind that molar masses of different polymers cannot be directly compared without universal calibration [20], and even then interactions between stationary phase and solute may complicate the interpretation. Large effect on the viscosity of a polymer solution is commonly ascribed to polymer–solvent interactions. Huggins' constant is the measurable viscometric property that is related to the thermodynamic quality of solvent for a given polymer; k_{H}-values are 0.33, 0.44, 0.53, 1.58, 1.94 for PS, SHB, EPC, PDDMA and PMMA, respectively (Figs. 6–9). According to literature [10], values ranging from 0.3 to 0.4 are characteristic for good solvents; xylene as an aromatic compound is a good solvent for aromatic PS, somewhat poorer for semi-aromatic SHB and poor for aliphatic EPC. Exceptionally high values for PDDMA and PMMA are due to self-association of polymethacrylate molecules in solution [16].

Figs. 6–9 show intrinsic viscosities and Huggins constants for solutions of investigated polymer pairs. For the polymethacrylate-containing systems, the shape of k_{H} *vs.* w(SHB) curve show that even a small quantity of SHB may disrupt the self-association pattern of PMMA and PDDMA (Figs. 7 and 8), pushing k_{H}-values into range (0.4–0.5) characteristic to "near-to-good" solvents. Regarding the $[\eta]$-values, they practically follow the characteristic linear $[\eta]$ *vs.* w(SHB) relationships posed by Philippoff [21]. In the SHB/EPC and SHB/PS systems (Figs. 6 and 9), the

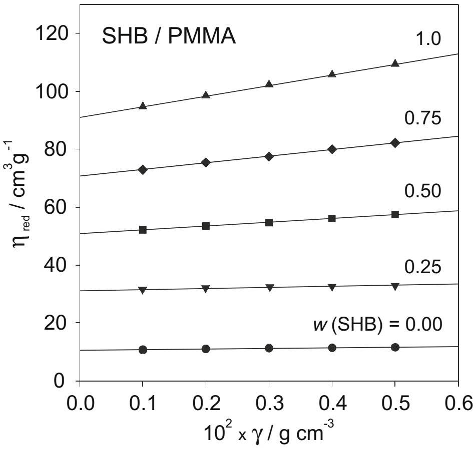

Fig. 3. Reduced viscosity *vs.* total polymer concentration in the SHB/PMMA system; xylene solution at 30 °C.

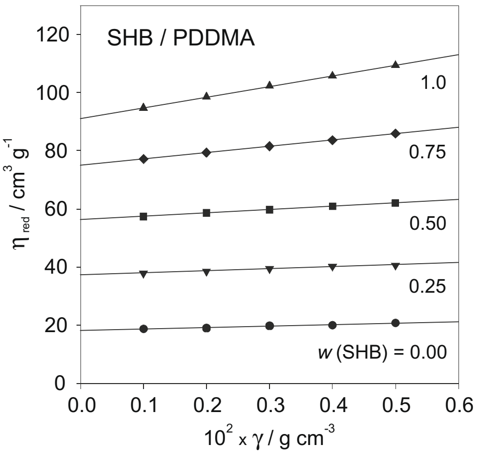

Fig. 4. Reduced viscosity *vs.* total polymer concentration in the SHB/PDDMA system; xylene solution at 30 °C.

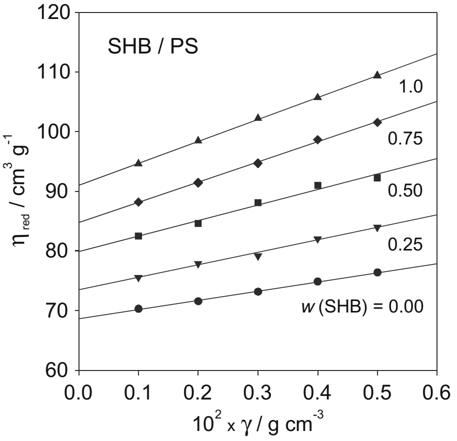

Fig. 5. Reduced viscosity *vs.* total polymer concentration in the SHB/PS system; xylene solution at 30 °C.

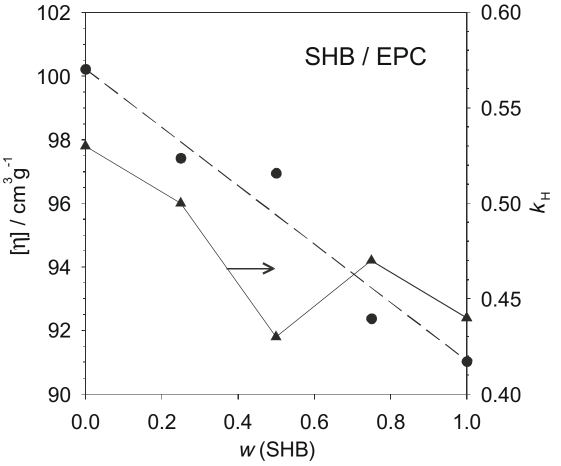

Fig. 6. Intrinsic viscosity and Huggins constant *vs.* mass fraction of SHB in total polymer for the SHB/EPC system; xylene solution at 30 °C.

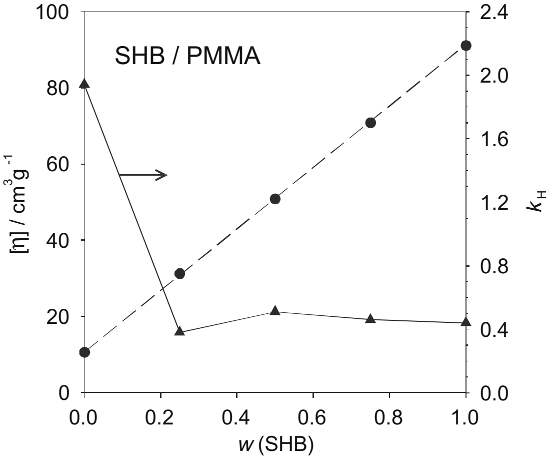

Fig. 7. Intrinsic viscosity and Huggins constant *vs.* mass fraction of SHB in total polymer for the SHB/PMMA system; xylene solution at 30 °C.

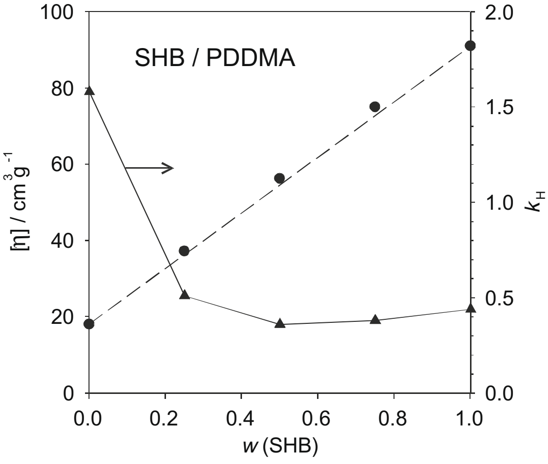

Fig. 8. Intrinsic viscosity and Huggins constant *vs.* mass fraction of SHB in total polymer for the SHB/PDDMA system; xylene solution at 30 °C.

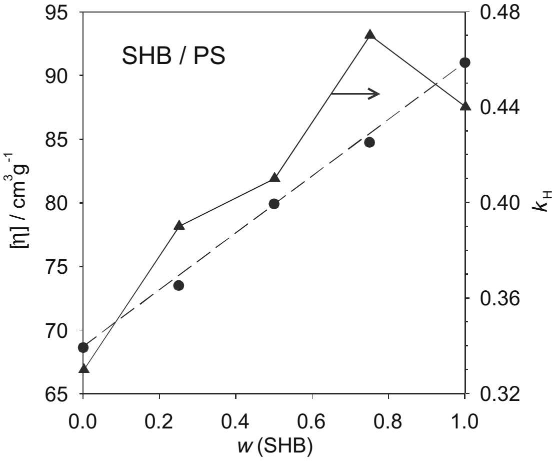

Fig. 9. Intrinsic viscosity and Huggins constant *vs.* mass fraction of SHB in total polymer for the SHB/PS system; xylene solution at 30 °C.

range of k_H-values is rather narrow; generally, intermediate values (within experimental error limits) are observed for ternary solutions. Philippoff's mixing rule is obeyed as well, within the experimental error limit.

In Table 2, the calculated viscometric miscibility criterion variables are shown for investigated systems. For methacrylate-containing systems, all the calculated interaction parameters (Δb^*_{rel} and Δb^{**}_{rel}) are large and negative, which points to immiscibility of the polymeric components. This is not surprising, due to large differences in their chemical structure. The behavior of methacrylate units is dominantly characterized by polar ester groups; these groups are responsible for self-association, observed both in long- and short-chain alkyl methacrylates. On the other hand, the behavior of SHB is characterized by aromatic styrene part in combination with saturated aliphatic butyl part; those molecules are not prone to self-association and the viscosity of the solutions is dominated by the solvent–solute interactions. In the investigated systems where polymeric components are more similar, the situation is somewhat different. In the SHB/EPC system, negative values of criterion variables are still found, but significantly lower values are observed – yet pointing to immiscibility. In the SHB/PS systems, practically zero interaction is observed for the samples with 50 and 75 wt.% PS; for mixtures with 25 wt.% PS, positive interaction is found. This is the system where no specific interactions between polymeric components exist. It seems that the addition of small quantities of PS may relax the intramolecular repulsion between styrene and hydrogenated butadiene sequences in the SHB copolymer, which is then observed as the viscosity increase due to polymer coil expansion [22].

Although we are dealing with miscibility in solution, we applied the Coleman–Graf–Painter approach [23,24] for the calculation of interaction in polymer blends, for the sake of quantitative comparison. The general interaction parameter for the mixing of two copolymers (SHB + EPC) is:

$$\begin{aligned}\Lambda_{12} = {} & \Lambda_{AC}\varphi_{A1}\varphi_{C2} + \Lambda_{AD}\varphi_{A1}\varphi_{D2} + \Lambda_{BC}\varphi_{B1}\varphi_{C2} \\ & + \Lambda_{BD}\varphi_{B1}\varphi_{D2} - \Lambda_{AB}\varphi_{A1}\varphi_{B1} - \Lambda_{CD}\varphi_{C2}\varphi_{D2}\end{aligned} \tag{10}$$

The equation is easily reduced for the more simple case of a mixture of a homopolymer with copolymer (SHB + PS or PMMA or PDDMA):

$$\Lambda_{12} = \Lambda_{AC}\varphi_{A1}\varphi_{C2} + \Lambda_{BC}\varphi_{B1}\varphi_{C2} - \Lambda_{AB}\varphi_{A1}\varphi_{B1}. \tag{11}$$

Here, Λ_{KL} denotes the interaction between comonomer segments K and L, and φ_{Kj} denotes the volume fraction of comonomer segment K in the copolymer j. Λ_{KL} are calculated according to the group contribution approach, from the group interaction parameters F_i^* listed in Table 3. The corresponding formulas are:

Table 3
Relevant Coleman–Graf–Painter group contribution parameters.

Structure unit	V_i^*/cm^3 mol^{-1}	F_i^*/cal$^{0.5}$ cm$^{1.5}$ mol^{-1}	M_i^*/g mol^{-1}
$-CH_3$	31.8	445.9	15
$-CH_2-$	16.5	270.0	14
>CH–	1.9	47.05	13
>C<	−14.8	−198.4	12
–OCO–	19.6	609.6	44
$-C_6H_5$	75.5	1503	77

$$\delta_K = \frac{\sum_{i=1}^{g} \nu_{i,K} F_i^*}{\sum_{i=1}^{g} \nu_{i,K} V_i^*}, \tag{12}$$

$$\Lambda_{JK} = (\delta_J - \delta_K)^2. \tag{13}$$

$\nu_{i,K}$ is the number of groups i in the comonomer segment K and δ_K is the so-called non-hydrogen-bonding solubility parameter of the comonomer segment K. The Gibbs energy of mixing may then be calculated as:

$$\Delta G_M = RT\left(\frac{\phi_1}{\upsilon_1}\ln\phi_1 + \frac{\phi_2}{\upsilon_2}\ln\phi_2\right) + \Lambda_{12}\phi_1\phi_2 \tag{14}$$

Both volume fractions of comonomer segments, φ_{Kj}, and volume fractions of copolymers in the blend may be calculated from the tabulated volume group contribution parameters, V_i^*, that are summed up for corresponding structure units, e.g.:

$$\upsilon_K = \sum_{i=1}^{g} \nu_{i,K} V_i^*, \tag{15}$$

$$\varphi_K = \frac{x_K \upsilon_K}{\sum x_L \upsilon_L}. \tag{16}$$

Necessary volume parameters are listed in Table 3 as well. Comonomer segments and number of corresponding structural groups are defined in Table 4. The results of calculation are shown in Table 5. There is no direct correspondence between the calculated data and measured viscometric interaction parameters. For example, the Coleman–Graf–Painter approach predicts the borderline bulk miscibility in the SHB/PDDMA system. Obviously, the mean-field approximation inherent to Coleman–Graf–Painter is quite unsatisfactory for extrapolation to the

Table 2
Miscibility criterion variables for investigated ternary systems.

w (HSB)	SHB/EPC			SHB/PS			SHB/PMMA			SHB/PDMMA		
	b_{12}	Δb^*_{rel}	Δb^{**}_{rel}	b_{12}	Δb^*_{rel}	Δb^{**}_{rel}	b_{12}	Δb^*_{rel}	Δb^{**}_{rel}	b_{12}	Δb^*_{rel}	Δb^{**}_{rel}
0.25	3920.9	−0.12	−0.13	2673.8	0.12	0.02	63.84	−0.93	−0.97	516.7	−0.62	−0.75
0.50	3634.5	−0.18	−0.20	2581.5	0.08	−0.01	713.5	−0.20	−0.63	202.0	−0.85	−0.90
0.75	4212.8	−0.05	−0.07	3277.8	0.37	0.26	593.2	−0.33	−0.70	175.3	−0.87	−0.92
	b_{12}^* = 4438			b_{12}^* = 2384			b_{12}^* = 891			b_{12}^* = 1375		
	b_{12}^{**} = 4518			b_{12}^{**} = 2611			b_{12}^{**} = 1945			b_{12}^{**} = 2094		

Table 4
Relevant Coleman–Graf–Painter group contribution parameters.

	MMA (in PMMA)	DDMA (in PDDMA)	S (in PS and SHB)	E (in EPC)	P (in EPC)	HB* (in SHB)
$-CH_3$	2	2	–	–	1	0.2
$-CH_2-$	1	12	1	2	1	3.6
$>CH-$	–	–	1	–	1	0.2
$>C<$	1	1	–	–	–	–
$-OCO-$	1	1	–	–	–	–
$-C_6H_5$	–	–	1	–	–	–

* Here, 20% of 1,2-configuration of hydrogenated butadiene is assumed.

Table 5
Calculated copolymer segment interaction parameters, Λ_{12}, and Gibbs energy of mixing at equivolume polymer blend composition, ΔG_M.

System	Λ_{12}/J cm^{-3}	ΔG_M/J cm^{-3}
SHB/EPC	5.78	1.40
SHB/PS	3.96	0.949
SHB/PMMA	1.28	0.268
SHB/PDDMA	0.119	−0.0182

dilute polymer solution range, where strong solvent effects may be expected. In the dilute range, each polymer molecule behaves as a more-or-less isolated solvated coil with strong polymer–solvent interactions. The contribution of intermolecular contacts, though measurable, is not dominant. Basically, the miscibility of the solvated molecules is investigated by the dilute solution viscometry. In addition, the approach of Coleman–Graf–Painter cannot account for the effects such as self-association of methacrylate molecules, which is found to be very important in some of the systems investigated.

4. Conclusions

The miscibility of SHB with different constituents of polymer additives for lubricating mineral oils was studied in dilute solution regime, using xylene as model solvent. The type and intensity of interactions were deduced from the calculated values of viscometric interaction parameters. The methacrylate-containing systems (SHB/PMMA, SHB/DDMA) were found to be immiscible. The interactions in the other two systems (SHB/EPC, SHB/PS) were found to be significantly less pronounced; the systems were much closer to ideal viscometric behavior. The intensity of interactions was estimated for the studied polymer blends in the absence of solvent, using the Coleman–Graf–Painter approach. No correlation was observed between the interaction in the bulk and in solution.

Acknowledgement

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References

[1] Stambaugh RL. Viscosity index improvers and thickeners. In: Mortier RM, Orszulik ST, editors. London: Blackie Academic & Professional; 1997. p. 144–80.

[2] Braun J, Omeis J. Additives. In: Mang T, Dresel W, editors. New York: Wiley-VCH; 2007. p. 85–114.

[3] Dementev AV, Medzhibovskii AS, Nemsadze GG, Tonkonogov BP. Behavior of viscous additives in oils during thermomechanical action. Chem Tech Fuels Oils 2008;44(6):425–9.

[4] Bezot P, Hesse-Bezot C, Elmakoudi B, Constans B, Faure D, Hoornaert P. Comparison of hydrodynamic and rheological properties of dilute solutions of a styrene-hydrogenated butadiene copolymer in aliphatic solvents by light scattering and viscometric techniques. J Appl Polym Sci 1994;51:1715–25.

[5] Natov M, Pavlov D. Rheological properties of mineral oil with hydrogenated butadiene-styrene copolymer. Chem Tech Fuels Oils 1985;21(10):541–3.

[6] Struglinski MJ, VerStrate GW, Fetters LJ. Viscosity modifier polybutadiene polymers. US Patent 5703171, 1997. US Patent 5945485, 1999.

[7] Briggs S, Chu C. Viscosity index improvers for lubricating oil compositions. US Patent 7163913, 2007.

[8] Jukić A, Tomašek LJ, Janović Z. Polyolefin and poly(alkyl methacrylate) mixed additives as mineral lubricating oil rheology modifiers. Lubr Sci 2005;17(4):431–49.

[9] Jukić A, Rogošić M, Janović Z. Optimization of alkyl methacrylate terpolymer properties as lubricating oil rheology modifier. Ind Eng Chem Res 2007;46(10):3321–7.

[10] Bohdanecký M, Kovář J. Viscosity of polymer solutions. Amsterdam: Elsevier; 1982.

[11] Aroguz AZ, Kismir Y. Viscometric study on the miscibility of polystyrene/brominated polystyrene blends. Eur Polym J 2007;43: 410–5.

[12] Wanchoo RK, Thakur A, Sweta D. Viscometric and rheological behaviour of chitosan-hydrophilic polymer blends. Chem Biochem Eng Q 2008;22(1):15–24.

[13] Lewandowska K. The miscibility of poly(vinyl alcohol)/poly(*N*-viniylpyrrolidone) blends investigated in dilute solutions and solids. Eur Polym J 2005;41:55–64.

[14] Imren D, Boztug A, Yilmaz E, Zengin HB. Viscometric investigation of compatibilization of the poly(vinyl chloride)/poly(ethylene-co-vinyl acetate) blends by terpolymer of maleic anhydride-styrene-vinyl acetate. J Mol Struct 2008;891:329–32.

[15] García R, Melad O, Gómez CM, Figueruelo JE, Campos A. Viscometric study on the compatibility of polymer–polymer mixtures in solution. Eur Polym J 1999;35(1):47–55.

[16] Jukić A, Rogošić M, Bolarić I, Tomašek LJ, Janović Z. Viscometric study of miscibility and interactions of some polyolefin and PAMA in dilute xylene solutions. J Mol Liq 2004;112(3):161–9.

[17] Matusinović Z, Rogošić M, Mencer HJ. A correlation of the limiting viscosity number, molecular mass and composition of statistical linear styrene–methyl methacrylate copolymers. Eur Polym J 2005;41(12):2934–44.

[18] Krigbaum WR, Wall FT. Viscosities of binary polymeric mixtures. J Polym Sci 1950;5(4):505–14.

[19] Catsiff EH, Hewett WA. The interaction of two dissimilar polymers in solution. J Appl Polym Sci 1962;6(23):S30–2.

[20] Rudin A, Hoegy HLW. Universal calibration in GPC. J Polym Sci A Polym Chem 1972;10(1):217–35.

[21] Philippoff WE. Über Mischungsversuche und Einfluß der Heterodispersität auf die Fließkurve bei organischen Hochpolymeren. Ber. 1937;70:827–38.

[22] Ten Brinke G, Karasz FE, MacKnight WJ. Phase behavior in copolymer blends: poly(2,6-dimethyl-1,4-phenylene oxide) and halogen-substituted styrene copolymers. Macromolecules 1983;16(12): 1827–32.

[23] Coleman MM, Graf JF, Painter PC. Specific interactions and miscibility of polymer blends. Lancaster: Technomic; 1991.

[24] Jukić A, Rogošić M, Janović Z. Miscibility and interactions of polystyrene/polyolefine and polystyrene/poly(n-alkyl methacrylate) mixtures in dilute xylene solutions. Eur Polym J 2006;42(5):1105–12.