Miscibility and interactions of rheology improvers based on functional polymethacrylate in toluene solutions

Kornelije Kraguljac, Ivana Šoljić, Elvira Vidović and Ante Jukić
Faculty of Chemical Engineering and Technology, University of Zagreb
Marulićev trg 19, HR-10000 Zagreb, CROATIA

In this work, miscibility and molecular interactions of poly(dimethylaminoethyl methacrylate) (PDMAEMA) and series of homologous poly(n-alkyl methacrylates), namely: poly(methyl methacrylate), poly(hexyl methacrylate), poly(dodecyl methacrylate) and poly(octadecyl methacrylate), as well as between PDMAEMA and poly(ethylene-co-propylene) (EPC) or polystyrene (PS), were investigated by the dilute solution viscometry, in toluene as a model solvent for mineral base oil at 30 °C. The specific, reduced and intrinsic viscosities as well as viscometric interaction parameters were determined for binary, polymer / toluene, and ternary, PDMAEMA / (PAMA or EPC or PS) / toluene systems. The PDMAEMA / (PMMA or PHMA or PODMA or EPC) investigated polymer / polymer pairs showed the negative viscometric interaction parameter values ($\Delta b_{12} < 0$), calculated applying the Catsiff-Hewett and Krigbaum-Wall theoretical equations. Therefore, these polymer mixtures were found to be immiscible. The observed repulsive molecular interactions originate from the differences in polymer composition and structure. This conclusion was supported by calculations employing the group contribution approach of Coleman, Graf and Painter, where the interaction parameter values $\Lambda_{12} > 0$. Investigated polymers are widely used as lubricating mineral oil rheology modifiers, that is viscosity index improvers, dispersants and pour point depressants. Thus, interaction and miscibility of the corresponding polymer mixture additives are important factors for the formulation of lubricants, such as motor oils.

1. Introduction

Rheological properties of mineral lubricating oils, particularly their viscosity and temperature dependence, viscosity index, are considerably improving by the addition of certain polymers in low concentrations having controlled and defined structural characteristics (Mortier and Orszulik, 1997). From a large number of polymeric systems prepared and tested as modifiers of the lubricating oil rheological properties, many long-chained, linear or branched homopolymers, and statistic, block or grafted copolymers characterized by good solubility and high hydrodynamic volume in hydrocarbons are in use. The most efficient and the most commonly used polymers as lubricating oil rheology modifiers are statistical olefins, namely ethylene / propylene copolymers, hydrogenated styrene / butadiene and styrene / isoprene block copolymers, copolymers and terpolymers of long-chained methacrylic acid esters (C_1, C_{10} ... C_{18}),

methacrylic ester copolymers with maleic acid anhydride, styrene and other vinyl monomers, alkylated polystyrene, esterified styrene / maleic acid anhydride copolymers and poly (alkyl-vinyl ether). Recently, due to their practical importance, exploration of polymeric additive mixtures as rheology modifiers has intensified since they have shown some complementary and even synergetic effects (Mortier and Orszulik, 1997; Jukić et al., 2005). However, due to physico-chemical differences most polymers are rarely miscible; they generate separate phases readily, particularly in solutions. Polymer-polymer miscibility is investigated by several techniques such as differential scanning calorimetry, microscopic methods, light and neutron scattering, dynamic mechanical measurements and others. The specific technique for miscibility estimation is dilute solution viscosity method. It was found particularly useful in cases where polymeric blends are applied directly in the form of a solution, as is the case of a mineral oil mixed polymer additives.

In this paper, the miscibility and intermolecular interactions were studied by the dilute solution viscometry method, in mixed additive systems consisting of poly(dimethyl-aminoethyl methacrylate) (PDMAEMA) and series of homologous poly(n-alkyl metha-crylates), namely: poly(methyl methacrylate) (PMMA), poly(hexyl methacrylate) (PHMA), poly(dodecyl methacrylate) (PDDMA) and poly(octadecyl methacrylate) (PODMA), as well as between PDMAEMA and poly (ethylene-co-propylene) (EPC) or polystyrene (PS). The toluene solutions at 30 °C were investigated.

2. Theory

The application of dilute solution viscometry method for the study of interactions and miscibility phenomena in dilute multicomponent polymer solutions has been described in more details elsewhere (Rogošić and Mencer, 1997). The most important features will be given here. The concentration dependence of viscosity of ideal ternary polymer solutions of the polymer 1 + polymer 2 + solvent type is usually described by equations like that of Krigbaum and Wall (1950):

$$\frac{\eta_{\text{sp}}}{\gamma_1+\gamma_2} = [\eta]_1\, w_1 + [\eta]_2\, w_2 + (k_{\text{H1}}[\eta]_1^2\, w_1^2 + k_{\text{H2}}[\eta]_2^2\, w_2^2 + 2b_{12}^{*}\, w_1 w_2)(\gamma_1+\gamma_2) \qquad (1)$$

or that of Catsiff and Hewett (1962):

$$\frac{\eta_{\text{sp}}}{\gamma_1+\gamma_2} = [\eta]_1\, w_1 + [\eta]_2\, w_2 + (k_{\text{H1}}[\eta]_1^2\, w_1^2 + k_{\text{H2}}[\eta]_2^2\, w_2^2 + 2b_{12}^{**}\, w_1 w_2)(\gamma_1+\gamma_2) \qquad (2)$$

Here η_{sp} denotes the specific viscosity, $[\eta]$ is the intrinsic viscosity (limiting viscosity number), γ is the mass concentration of polymer and k_{H} is Huggins' constant, which may be related to the thermodynamic quality of solvent. The composition dependence of viscosity in ternary systems is described by relative mass fractions of dissolved polymers, w_i. Both of these equations reduce to empirical Huggins's equation for binary polymer solutions in absence of the second polymeric component ($\gamma_2 = 0$):

$$\frac{\eta_{\text{sp}}}{\gamma} = [\eta] + k_{\text{H}}[\eta]^2 \gamma = [\eta] + b\gamma . \tag{3}$$

The slope of Huggins' equation, b, is defined in previous equation. It serves for the description of ideal behavior of ternary polymer solutions; "ideal" quantities $b_{12}{}^*$ and $b_{12}{}^{**}$ are calculated by:

$$b_{12}^* = \sqrt{b_1 \times b_2} \quad \text{and} \quad b_{12}^{**} = \frac{b_1 + b_2}{2} , \tag{4}$$

respectively.

In the infinite dilution limit, both Krigbaum-Wall's and Catsiff-Hewett's expression reduce to the miscibility rule of Philippoff (1937):

$$[\eta]_{12} = [\eta]_1 w_1 + [\eta]_2 w_2 \tag{5}$$

It is possible to replace the "ideal" terms $b_{12}{}^*$ and $b_{12}{}^{**}$ in equations (1) and (2) by an empirically defined quantity, b_{12}. A purely empirical relation is then obtained that may be used to the fit the linear dependence of specific viscosity on total polymer concentration in the low-concentration range, observed in non-ideal ternary solutions. The obtained relation may be formally identified with Huggins' expression (3):

$$\frac{\eta_{\text{sp}}}{\gamma_1 + \gamma_2} = [\eta] + k_{\text{H}}[\eta]^2 (\gamma_1 + \gamma_2) = [\eta] + b_{\text{M}}(\gamma_1 + \gamma_2) \tag{6}$$

The extent of the deviation of experimental from "ideal" b-values may be used to quantify the interactions between polymeric components of a system under consideration. The quantities of interest (miscibility criterion variables, relative form) are defined as (Rogošić and Mencer, 1997):

$$\Delta b_{\text{rel}}^* = \frac{b_{12} - b_{12}^*}{b_{12}^*} \quad \text{and} \quad \Delta b_{\text{rel}}^{**} = \frac{b_{12} - b_{12}^{**}}{b_{12}^{**}} \tag{7}$$

respectively. The negative values of miscibility criterion variables imply repulsive interactions (immiscibility of polymers); positive values imply attractive interactions (miscibility).

3. Experimental

3.1 Materials

In this investigation, seven different polymers were used. Poly(ethylene-*co*-propylene) (EPC) was a commercial product (Lubrizol 7067) of Lubrizol Chem. Co. Polystyrene, PDMAEMA and poly(*n*-alkyl methacrylates) were synthesized by the free radical polymerization of corresponding monomers using peroxide initiators (Trigonox 21&29, Akzo Nobel). Toluene of high purity (Kemika, reagent grade) was used as received.

3.2 Methods

Binary polymer solutions were prepared by dissolving the appropriate mass of polymers in toluene, 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 the 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 ($\eta_{rel} = \eta / \eta_0 = t / t_0$). The experiments were performed in the range of $1.05 < \eta_{rel} < 1.5$ to provide typically five data points. 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 ^{1}H NMR spectrum of EPC copolymer was recorded on the 90 MHz Varian EM-360 spectrometer at room temperature, in deuterated chloroform with TMS as an internal standard. 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 and toluene were used as solvents.

4. Results and discussion

The miscibility, namely interaction in binary polymer system of PDMAEMA and poly (alkyl-methacrylate) homopolymers, PS or EPC in toluene was investigated by dilute solution viscosity measurements (Bohdanecký and Kovář, 1982). The principle of using dilute solution viscosity to measure the polymer miscibility is based on the fact that the repulsive or attractive intermolecular interaction between two different polymers in solution should make a different contribution to the viscosity of the polymer mixture solution. It also has been assumed that polymer-polymer interactions usually dominate over polymer-solvent ones. Attraction between two component molecules may cause a swell of macro-molecular coils, resulting in an increase in viscosity and a positive deviation from additivity, or otherwise, repulsion may cause shrinkage of the macromolecular coils giving a negative deviation from viscosity additivity. As a result, the viscosity of ternary system may be either lower or higher than the one calculated from viscosities of both pure blend components assumed on the additivity law. Experimentally determined reduced viscosities ($\eta_{red} = \eta_{sp} / \gamma = (\eta_{rel}-1) / \gamma$) are shown in Fig. 1 and Fig. 2 for the PDMAEMA/EPC/toluene and PDMAEMA/PDDMA/toluene systems, respectively, as functions of total polymer concentration, $\gamma = \gamma_1 + \gamma_2$. Huggins' extrapolation lines (linear regression coefficients higher than 0.96) are depicted, as well. One may observe that all the investigated systems follow the linear concentration dependence proposed by Huggins. Viscometric parameters obtained from the equations from (1) to (7) are given in Table 1. In the PDMAEMA / PMMA / toluene, PDMAEMA / PHMA / toluene, PDMAEMA / PODMA / toluene and PDMAEMA / EPC / toluene systems negative deviations of Huggins' slopes are observed, producing negative Δb^{*}_{rel} and Δb^{**}_{rel} values, implaying the immiscibility (repulsive interaction) of investigated polymer pairs.

For the systems PDMAEMA / PDDMA / toluene and PDMAEMA / PS / toluene positive Δb^*_{rel} and Δb^{**}_{rel} values were found indicating the miscibility of these polymer pairs in toluene. The specific, attractive interactions between PDMAEMA and PS or PDDMA are not likely to occur. Hence, in the PDMAEMA / PS / toluene system positive values of viscosity interaction parameters probably have the origin in the compatibilizing effect of the solvent, due to great similarity in the chemical structure of toluene and PS. In the PDMAEMA / PDDMA / toluene system, the influence of the self-association of polymeric molecules on the solution viscosity is reflected in the experimental values of miscibility criterion variables (Bohdanecký and Kovář, 1982; Jukić et al., 2004). These findings are supported by the interaction parameters for binary polymer blends calculated using the group contribution approach of the Coleman, Graf and Painter (Coleman et al., 1991), given in Table 2. All the investigated polymer pairs were predicted to be immiscible, due to the positive interaction parameter values.
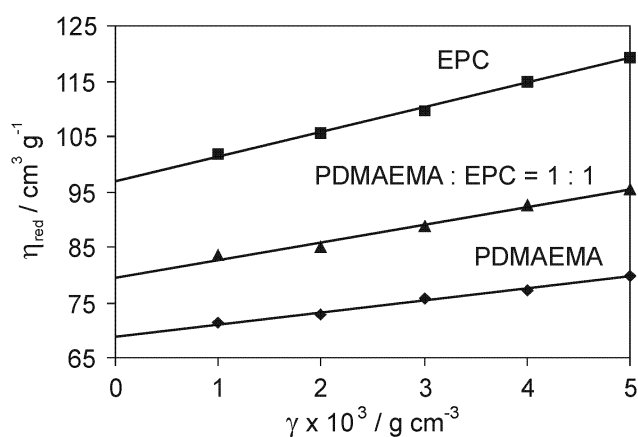

Figure 1. Reduced viscosity dependence on total polymer concentration of PDMAEMA and EPC mixture, in toluene solution at 30 °C.
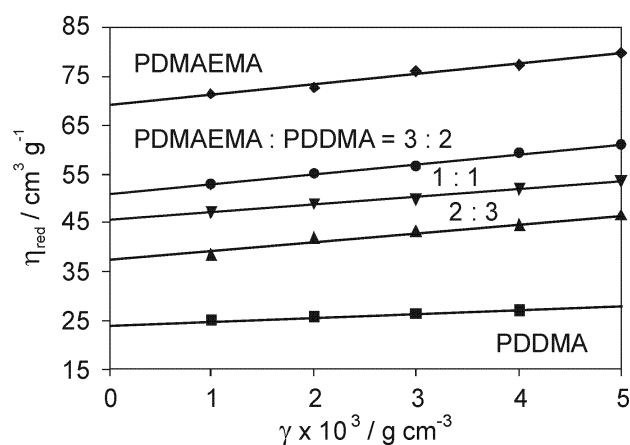

Figure 2. Reduced viscosity dependence on total polymer concentration and composition of PDMAEMA and PDDMA mixture, in toluene solution at 30 °C.

Table 1. Viscometric interaction parameters for binary polymer mixtures in toluene solution at 30 °C.

System	$w_{PDMAEMA}$	b_m / cm^6 g^{-2}	$[\eta]$ / cm^3 g^{-1}	$b_{12,exp}$ / cm^6 g^{-2}	Δb_{rel}*	Δb_{rel}**
PDMAEMA / PMMA	0.5	991	39.3	639	-0.40	-0,52
PDMAEMA / PHMA	0.5	2633	79.3	2582	-0.02	-0.04
	0.4	1851	37.4	2569	1.01	0.76
PDMAEMA / PDDMA	0.5	1712	45.1	1967	0.54	0.35
	0.6	1968	51.0	2230	0.75	0.53
PDMAEMA / PODMA	0.5	1822	42.5	1611	-0.21	-0.21
PDMAEMA / PS	0.5	2314	74.6	2770	0.51	0.49
PDMAEMA / EPC	0.5	3183	79.5	3071	-0.01	-0.07

Table 2. Thermodynamic interaction parameters, Λ_{12}, for binary polymer mixtures as solid blends, based on the group contribution approach of the Coleman, Graf and Painter (1991).

System	Λ_{12} / J cm^{-3}	System	Λ_{12} / J cm^{-3}
PDMAEMA / PMMA	0.79	PDMAEMA / PODMA	0.62
PDMAEMA / PHMA	0.034	PDMAEMA / EPC	3.50
PDMAEMA / PDDMA	0.35	PDMAEMA / PS	2.99

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