RHEOLOGICAL INVESTIGATIONS OF POLY(HYDROXYBUTYRATE) AND POLY(ETHYLENE OXIDE) SOLUTIONS AND THEIR MIXTURES

Agnessa Nikolova[1], Rainer Schnabel[2]

[1] *University of Chemical Technology and Metallurgy*
 8 Kl. Ohridski, 1756 Sofia, Bulgaria
 E-mail: agnessan@mail.bg

[2] *Martin-Luther Universität Halle-Wittenberg,*
 06099 Halle, Germany

ABSTRACT

Rheological investigations were carried out of poly (hydroxybutyrate) and poly (ethylene oxide) solutions in chloroform as well as of their mixtures in different ratios. It was established that all solutions (pure polymers and their mixtures) exhibit non-Newtonian (shear thinning) behaviour which is described by the Ostwald-de Waele model. The value of the activation energy for the solutions can be a measure for the influence of the temperature on their rheological behaviour.

Keywords: poly (hydroxybutyrate), poly (ethylene oxide), rheological investigations, shear thinning liquids, apparent viscosity, activation energy.

INTRODUCTION

Owing to improved mechanical properties and easy processability thermoplastics have been widely used in various fields of daily commodities, medical materials and so forth. However, much attention has been paid on pollution problems caused by plastic waste. As a result, biodegradable polymers have attracted wide attention.

Poly (hydroxybutyrate), (PHB), is aliphatic polyester synthesised by bacterial fermentation [1]. In 1925 Lemogine [2] discovered PHB formed by Bacillus megaterium. In general, PHB is produced by different bacterial strains of microorganisms [3] from renewable resources in the form of an intracellular storage material. The chemical structure of PHB is - (O-CH (CH$_3$) - CH$_2$ - CO-)$_n$ - . This truly biodegradable polymer has been widely investigated in order to replace conventional plastics, which cause environmental pollution due to difficult biodegradability [4].

PHB exhibits thermoplastic behaviour and can be processed by traditional processing such as extrusion or injection moulding [5]. However, due to its very narrow processing window, relatively low impact resistance,

and high cost, its application is now limited. These shortcomings could be overcome by blending PHB with other polymers. A number of investigations have been published on the compatibility of PHB blends [6 - 8].

It is of interest from practical point of view to find a polymer compatible with PHB, which when blended together [9, 10] may lower the melting temperature of PHB without any deterioration of its end-use properties.

Poly (ethylene oxide) (PEO), -(CH$_2$-CH$_2$-O-)$_n$-, ("Polyox"), was chosen as blending material since it is known to be miscible with PHB. Avella and Martuscelli [6, 7] have observed that PHB/PEO blends exhibit a single glass transition temperature T_g and a depression of the equilibrium melting temperature T_m of PHB.

In the present work, the rheological characteristic of poly(hydroxybutyrate) and poly(ethylene oxide) solutions as well as their mixtures are reported.

EXPERIMENTAL

Materials

PHB was supplied by Biomer, Krailling, Germany. It has been obtained by fermentation of sugar utilising

mutant of Alcaligenes eutrophus. The polymer is a white powder with a molecular mass of 230000 g/mol. It has melting point of about 175°C and crystallinity of activation energy about 60 % [9].

PEO was obtained from Union Carbide Corporation (Polyox WSR N-750). It is a white powder with molecular mass of 300000 g/mol and with crystalline melting point of about 65°C.

Mixtures with different PHB/ PEO ratio were prepared by mixing 2 % PHB and PEO solutions in chloroform. PEO was dissolved in chloroform (p.a., Carl Roth GmbH, Karlsruhe) at room temperature by magnetic stirring at 300 rpm for 3 hours.

Since PHB is insoluble in chloroform at room temperature [6, 7, 11] its solution was prepared by the similar way, but at 60° C and with 5 hours stirring. The corresponding mixtures were prepared by mixing PHB and PEO solutions with magnetic stirring for 1 hour at 300 rpm and room temperature.

Rheometry

Rheological measurements were carried out using a rheometer with concentric cylinders (Rheotest RV2.1, VEB Pruefgeraetewerk, Medingen, Germany), at 20 ± 0,1°C and 30 ± 0,1°C. The relationship between the shear stress, τ, and the shear rate, $\dot{\gamma}$, was described mathematically by the Ostwald-de Waele model [12, 13]:

$$\tau = k\dot{\gamma}^n \tag{1}$$

The apparent viscosity, η, of the solutions examined decreases with the increase of the shear rate (shear-thinning fluids, n < 1):

$$\eta = \frac{\tau}{\dot{\gamma}} = k\dot{\gamma}^{n-1} \tag{2}$$

According to the eq. 2, the dependence of η on PHB content in the solutions of its mixtures with PEO was determined at a constant shear rate equal to 243 s^{-1}. In order to calculate the activation energy of the viscous flow, E, by means of eq. 3 the flow curves of the polymer solutions were determined at two different temperatures T_1 and T_2. η_1 and η_2 are the apparent viscosities measured at the temperatures T_1 and T_2, respectively.

$$E = \frac{RT_1T_2}{T_2 - T_1} \ln\frac{\eta_1}{\eta_2} \tag{3}$$

RESULTS AND DISCUSSION

The flow curves for the solutions of each polymer and their mixtures (shear stress, τ, versus shear rate, $\dot{\gamma}$), are presented in Figs. 1 and 2. The PHB and PEO solutions, as well as their mixed solutions show pseudoplastic non-Newtonian behaviour, which is described by the rheological model of Ostwald-de Waele- eq. (1). The values of the parameters, k and n, obtained, are listed in Tables 1 and 2. There is a good correlation ($\pm \varepsilon = 5,3$ %) between the results obtained and the predicted ones by Ostwald-de Waele model.

It is obvious from the results shown in Tables 1 and 2 that the decrease of the PHB content in the mixed PHB/ PEO solutions causes small changes in the value of the rheological n-parameter, while the value of the consist-
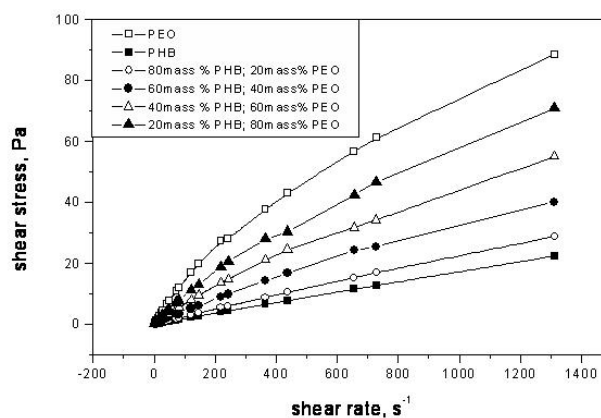

Fig. 1.   Flow curves of the PHB, PEO solutions and their mixtures, 20°C.
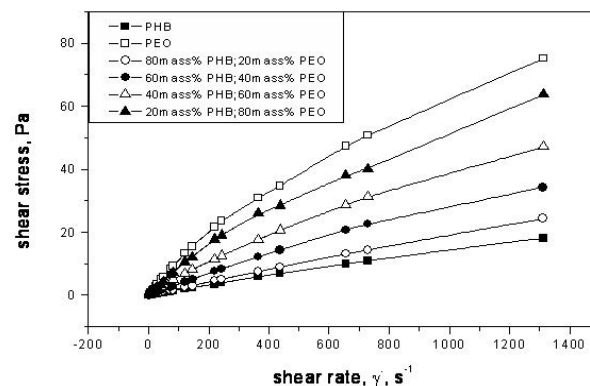

Fig. 2. Flow curves of the PHB, PEO solutions and their mixtures at 30°C.

Table 1. k and n values in the Ostwald-de Waele equation for the PHB, PEO solutions and their mixtures at 20°C.

Nr	Solution	Flow index, n	Coefficient of consistency, k, Pa.s^n
1.	PHB	0,948	0,0242
2.	80% mass PHB, 20% mass PEO	0,920	0,0320
3.	60% mass PHB, 40% mass PEO	0,903	0,0674
4.	40% mass PHB, 60% mass PEO	0,852	0,1320
5.	20% mass PHB, 80% mass PEO	0,823	0,209
6.	PEO	0,766	0,405

Table 2. k and n values in the Ostwald-de Waele equation for the PHB, PEO solutions and their mixtures at 30°C.

Nr	Solution	Flow index, n	Coefficient of consistency, k, Pa.s^n
1.	PHB	0,937	0,02268
2.	80% mass PHB, 20% mass PEO	0,929	0,0301
3.	60% mass PHB, 40% mass PEO	0,917	0,0528
4.	40% mass PHB, 60% mass PEO	0,840	0,1310
5.	20% mass PHB, 80% mass PEO	0,828	0,1851
6.	PEO	0,759	0,342

ency coefficient, k, grows considerably. The rheological behaviour of the PHB/PEO mixtures is controlled by PHB /PEO ratio. This is illustrated by the viscosity curves, Fig. 3 and 4, as well as by the dependence of the apparent viscosity, η, (determined at a constant shear rate $\dot{\gamma} = 243$ s^{-1}) on PHB content in its mixtures (Fig. 5).

As seen from Figs 3, 4 and 5 the η values decrease with the increase of the shear rate and with the increase of PHB content by $\dot{\gamma}$ = const. It is noteworthy to mention that the observed dependence (Fig. 5) is not linear.
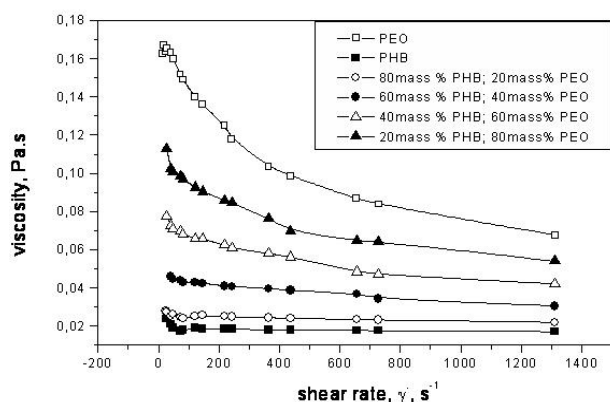
It can be described by the following expression [10, 13]:

$$\lg\eta_{mixture} = x_{PHB} \cdot \lg\eta_{PHB} + x_{PEO} \cdot \lg\eta_{PEO}$$

where: $\eta_{mixture}$ is the apparent viscosity of the mixtures; x_{PHB}, x_{PEO} are the volumetric content of PHB and PEO; η_{PHB}, η_{PEO} are PHB and PEO apparent viscosity. The correlation between the experimental and calculated results at 30°C is shown on Fig. 6.

The activation energy, E, (Eq. 3) at τ = const [14] was evaluated in order to estimate the effect of the

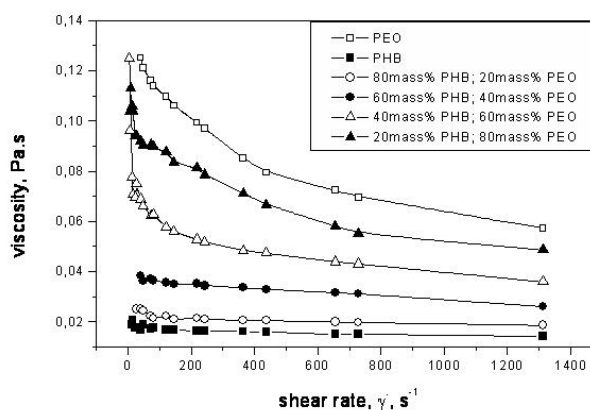Fig. 3. Viscosity curves of the PHB, PEO solutions and their mixtures at 20°C.

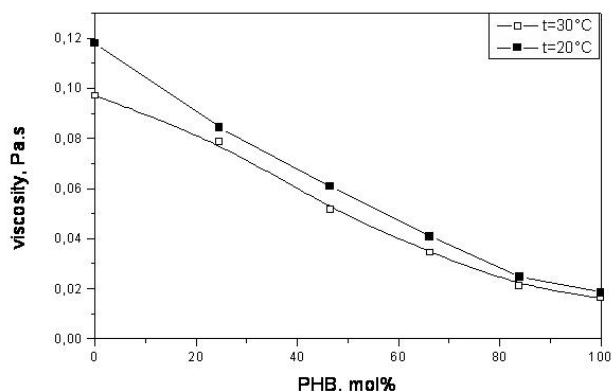Fig. 4. Viscosity curves of the PHB, PEO solutions and their mixtures at 30°C.

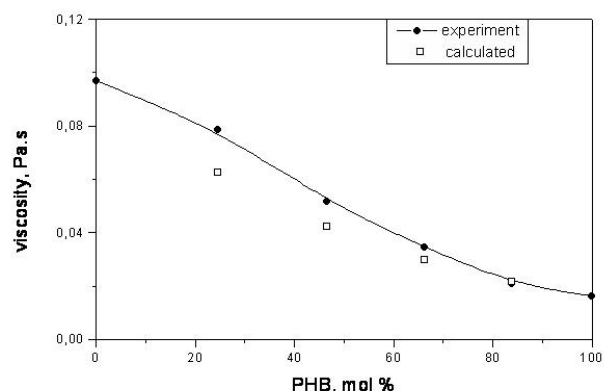Fig. 5. Apparent viscosity versus PHB content, mol %, for PHB, PEO solutions and their mixtures.

Fig. 6. Experimental and calculated apparent viscosity versus PHB content, mol %, for PHB, PEO solutions and their mixtures.

Fig. 7. Activation energy versus PHB content, mol %, for the PHB, PEO solutions and mixtures of them.

CONCLUSIONS

From the present study it may be concluded that the rheological behaviour of the PHB and PEO solutions as well as their mixtures exhibit non-Newtonian (shear thinning) behaviour which is described by the Ostwald-de Waele model. The value of the activation energy for PHB, PEO solutions and their mixtures can be a measure for the influence of the temperature on their rheological behaviour.

Table 3. Activation energy for PHB, PEO solutions and their mixtures.

Nr	Solution	Activation energy, E, kJ/mol
1.	PHB	12,03
2.	80% mass PHB, 20% mass PEO	12,76
3.	60% mass PHB, 40% mass PEO	13,56
4.	40% mass PHB, 60% mass PEO	15,14
5.	20% mass PHB, 80% mass PEO	15,5
6	PEO	21,5

temperature on the rheological behaviour of PHB, PEO solutions and their mixtures. The results are shown in Table 3.

From the results shown in Table 3 and Fig. 7 we can conclude that the activation energy increases with the decrease of the PHB content in the mixtures. The high value obtained for PEO explains the considerable decrease of the apparent viscosity with the increased temperature observed for the PEO solutions. This tendency is less pronounced for the PHB solution because of the lower E value.
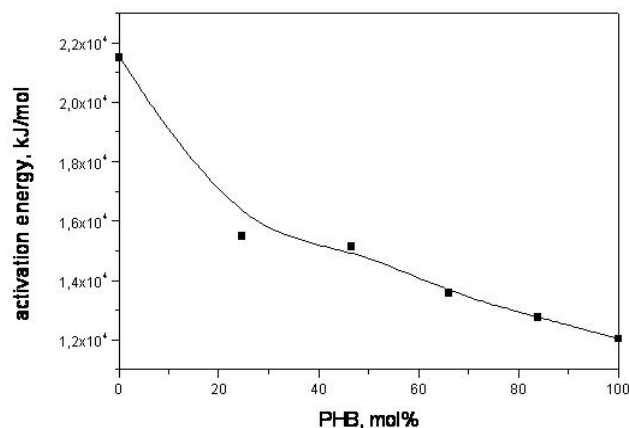
REFERENCES

1. Y. Doi, Microbial Polyesters, VCH Publishers, New York, 1990, p.17.
2. M. Lemogine, Ann. Inst. Pasteur, 39, 1925, 144.
3. A. Steinbüchel, H. Valentin, FEMS Micro Lett., 128, 1995, 219.

4. J. Peanasky, J. Long, R. Wool, J. Polym. Sci., Part B-Polym. Phys., 29, 1991, 565.
5. J. Ruge, H. Wohlfahrt, Technologie der Werkstoffe, Vieweg Verlag, Wiesbaden, 2001, p. 268.
6. M. Avella, E. Martuscelli, Polymer, 29, 1988, 1738.
7. M. Avella, E. Martuscelli, P. Greco, Polymer, 32,1991, 1047.
8. P. Xing, L. Dong, Y. An, Z. Feng, M. Avella, E. Martuscelli, Macromolecules, 30, 1997, 2726.
9. G. El-Hadi, Dissertation, Martin-Luther Universitaet Halle-Wittenberg, 2002.
10. L. Utracki, Polymer Alloys and Blends, Thermodynamics and Rheology, Carl Hanser, Munich, 1989, p.12.
11. H. Choi, S. Park, J. Yoon, H. Lee, S. Choi, Polym. Eng. Sci., 20, 1995, 12.
12. M. Pahl , W. Gleißle, H. Laun, Praktische Rheologie der Kunststoffe und Elastomere, VDI-Verlag, Düsseldorf, 1995, p. 34.
13. W. M. Kulicke, Fliessverhalten von Stoffen und Stoffgemischen, Hüthig&Wepf Verlag, New York-Basel-Heidelberg, 1992, p. 44.
14. A. Leonov, N. Bassov, U. Kazankov, Basics of reactivity plastics and resins processing by injection molding, Ed. Chemistry, Moscow, 1977, p.72, (in Russian).