Measuring viscosity of polyethylene blends using a rotational rheometer

Dorottya Nagy and Károly Belina

Department of Materials Technology, GAMF Faculty of Engineering and Computer Science, John von Neumann University, Kecskemét, Hungary

E-mail: nagy.dorottya@gamf.uni-neumann.hu

Abstract. Polyethylene (PE) is one of the most important and widely used polymer in packaging industry, film and tube forming technology [1]. Knowing the properties of polymer blends and the characterization of their rheological behavior is useful for industrial processes. For that very reason in our research PE blends were prepared and characterized by rheological method to find out the differences between the blends and the base materials. The base materials were TIPELIN FA 381-10 (high-density polyethylene, HDPE) and TIPOLEN FB 243-51 (low-density polyethylene, LDPE). The PE blends were made in the following proportions: 80/20, 60/40, 40/60 and 20/80. The first numbers mean the FA content percentage in the blend, while the second numbers mean the FB content percentage. Viscosity of the polymer melts were measured by rotational rheometer at low shear rate and the effect of temperature on viscosity were also measured. The structure viscous behavior of the polymer melt was confirmed, as the physical structure of the polymeric chain changes in flow. The fact that the number and the structure of the branches influence viscosity was revealed. FA material (HDPE) has the highest viscosity, while FB (LDPE) has the least. The blends show a good correlation between the two limits, although the complex viscosity does not show linear behavior in FA material content. The least viscosity was measured at 20% FA content. The modulus values plummet with temperature. The polydispersity index is 2.2 for FA material at 230°C. The temperature dependence of viscosity was revealed for blend (40-60). Moreover the activation energy was calculated at three frequencies. The fact that the activation energy decreases in function of angular frequency was demonstrated.

1. Introduction

Polyethylene (PE) is one of the most important and widely used polymers in packaging industry, film and tube forming technology [1]. Different types of PE are known according to the chain structure and the manufacturing technologies. Polyethylene with few branches is capable to reach high amount of crystalline, it is called high-density polyethylene (HDPE). Branched polyethylene is hardly form into crystalline fractions, so it is called low-density polyethylene (LDPE). The density influences the properties of the polymer. Hence polyethylene blends having different branches are worth to investigate [2].

Because of the polymer forming process, rheology of thermoplastic polymers is essential. Polymer forming is usually done in molten state, then the polymer melt becomes solid and is used in many fields of our life. The properties of the solid product depend on the forming process and the properties of the melt. Viscosity is generally measured to characterize the flow of polymer melts. The viscoelastic behavior of the polymer melt is known, but it depends on the structure of material. As
viscosity is not a constant value namely it depends on deformation rate, it is worth to investigate materials at different ranges of flow. A novel measuring method examine materials at low shear rate range, so the beginning of the flow can be observed. There are some reports, where polymer melt is examined in oscillation mode, so even storage and loss modulus can be determined besides complex viscosity [3-10]. Since the characteristic values are temperature depending ones, measurements must be done at least three different temperatures above the melting temperature of the polymer. Temperature dependence of the viscosity of polymeric materials can be characterized by the activation energy of flow at a given frequency [11-12]. In our research PE blends were prepared and characterized by oscillation rheological method to find out the differences between the blends and the base materials. Moreover, our aim is to determine the flow activation energy for one chosen blend in function of frequency.

2. Materials and Experimental Procedure
The base materials were TIPELIN FA 381-10 (high-density polyethylene, HDPE) and TIPOLEN FB 243-51 (low-density polyethylene, LDPE). They were purchased by MOL Group, manufactured by TVK Nyrt. in Hungary. HDPE is a copolymer with hexen-1 comonomer [13]. LDPE does not contain any additives [14]. Both are appropriate for film blowing and can be processed by conventional extruder. The PE blends were made in the following proportions: 80/20, 60/40, 40/60 and 20/80. The first numbers mean the FA content percentage in the blend, while the second numbers mean the FB content percentage.

Polyethylene blends were made by a Collin Teach-line conventional extrusion line with an E20T single-screw extruder, as shown in Figure 1. The zone temperatures were 190-190-200-210°C. The extruder speed was 80 turn/min.

![Figure 1. Extruder with standard screw](image)

The blends and the extruded materials were investigated by a rotational rheometer, ARES G2 in oscillation mode with cone-plate geometry, as shown in Figure 2. ARES G2 contains SMT system, which means Separated Motor Transducer, and has a Forced Convention Oven (FCO).
3. Results and Discussions
Complex viscosity is shown in function of angular frequency in Figure 3. The blends and the extruded materials were examined at 230°C. The viscosity is decreasing with frequency, because polymer melts show non-Newtonian behavior. The physical structure of the macromolecules changes during the flow, therefore the internal resistance is not constant. In low frequency range, the viscosity is almost constant, due to the mechanism of flow (deformation of the physical network). FA material (HDPE) has the highest viscosity, while FB (LDPE) has the least. The number and the structure of the branches influence the viscosity. HDPE (copolymer) has the most branches therefore the inner resistance of the polymer melt is the highest. The viscosities of the materials show a good correlation with the ratio of the materials in the blend.
Figure 4. Complex viscosity (Pas) in function of FA content

The complex viscosity in function of FA material content at constant angular frequency (at 6.28 rad/s), does not show linear behavior, as shown in Figure 4. The viscosity change shows negative deviation from the linear. It is assumed, that this deviation due to the change of the free volume in the melt.

Figure 5. Modulus values of FA material

The storage and loss modulus values were measured for FA material at 230 and at 250°C, as shown in Figure 5. The modulus values plummet with temperature, because of the softening, and the steepness of the curves decreases in small extent. The intersection of the storage and loss modulus curves shows the polydispersity-index of the material, giving 2.2 for the FA material at 230°C.
One blend (40-60) was chosen to measure at three temperatures: at 220°C, at 230°C and at 240°C, as shown in Figure 6. In this way the temperature dependence of viscosity can be investigated. At higher temperature, complex viscosity is lower, the inner resistance against flow of the material decreases.
This blend (40/60) was appropriate to present the complex viscosity in function of 1/temperature at constant angular frequency (6.28; 62.8 and 471 rad/s), as shown in Figure 7. These curves are linear in logarithmic scale, which means that the viscosity change follows the Arrhenius law.

From the slope of the linear lines, activation energy can be calculated at different frequencies. The activation energy decreases with frequency, as shown in Figure 8. This result also emphasizes the structural change of the polymeric melt.

4. Conclusion
In our study, polyethylene blends were prepared and investigated by rheological method. The results of extruded materials and blends were compared. Complex viscosity, loss and storage modulus, polydispersity index and the activation energy were determined.

The structure viscous behavior of the polymer melt was confirmed, as the physical structure of the polymeric chain changes in flow. The fact that the number and the structure of the branches influence viscosity was revealed. FA material (HDPE) has the highest viscosity, while FB (LDPE) has the least. The blends show a good correlation between the two limits, although the complex viscosity does not show linear behavior in FA material content. The least viscosity was measured at 20% FA content. The modulus values plummet with temperature. The polydispersity index is 2.2 for FA material at 230°C. The temperature dependence of viscosity was revealed for blend (40-60). Moreover the activation energy was calculated at three frequencies. The fact that the activation energy decreases in function of angular frequency was demonstrated.

Acknowledgement
This research is supported by EFOP-3.6.1-16-2016-00006 "The development and enhancement of the research potential at John von Neumann University" project. The Project is supported by the Hungarian Government and co-financed by the European Social Fund.

5. References
[1] Elvers B, Hawkins S, Schulz G 1992 Ullman’s Encyclopedia of Industrial Chemistry 5th ed. 487.
[2] Litvinov V M, Ries M E, Baughman T W, Henke A, Matloka P P 2013 Macromolecules 46 541 http://dx.doi.org/10.1021/ma302394j
[3] MohammadiM, Yousefi A A, Ehsani M 2012 J Polym Res. 19 9798 http://dx.doi.org/10.1007/s10965-011-9798-9
[4] Stadler F J, Piel C, Kaschta J, Rulhoff S, Kaminsky W, Münstedt H 2006 RheolActa 45 755 http://dx.doi.org/10.1007/s00397-005-0042-6
[5] Byutner O, Smith G D 2001 J. of Polym Sci. Part B: Polym Phys. 39 3067
[6] Raju V R, Smith G G, marin G, Knox J R, Graessley W W 1979 J. of Polym Sci.: Polym Phys 17 1183
[7] Lee J H, Archer L A 2002 Macromolecules 35 6687 http://dx.doi.org/10.1021/ma020398e
[8] Mead D W 2013 J. of Non-Newtonian Fluid Mechanics 195 99 http://dx.doi.org/10.1016/j.jnnfm.2013.02.001
[9] Mavridis H, Shroff R N 1992 Polym Eng. and Sci .32 (23) 1778
[10] Shen H-W, Xie B-H, Yang W, Yang M-B 2013 J. of Appl Polym Sci http://dx.doi.org/10.1002/app.38850
[11] Ye Z, AObaidi F, Zhu S 2004 Macromol. Chem. Phys. 205 897 http://dx.doi.org/10.1002/macp.200300128
[12] Gu S-Y, Zhang K, Ren J, Zhan H 2008 Carbohydrate Polymers 74 79 http://dx.doi.org/10.1016/j.carbpol.2008.01.017
[13] https://mol.hu/images/pdf/.../polimer.../hdpe.../fa-381-10_eng.pdf
[14] https://www.granulat.com.pl/media/.../tipolen%20fb%2043%2051.pl...
[15] https://polymerinnovationblog.com/rheology-thermosets-part-2-rheometers/