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Effect of Fluoropolymer Antidripping Agent on Rheological Behavior of LLDPE

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Abstract. In this work, high molecular weight polytetrafluoroethylene based antidripping agent was blended with Ziegler-Natta based LLDPE in different concentrations. Rheological characterization was consequently performed for all the blends and the obtained results were compared with the pure LLDPE. It has been found that high molecular weight PTFE based melt modifier MM 5935 EF significantly enhancing the shear viscosity/elasticity and especially the extensional viscosity of the LLDPE melt.

Keywords: Fluoropolymer, Antidripping, Polymer melts, Rheological properties.
PACS: 47.50.Ef, 47.57.Ng, 47.57.Qk, 83.80.Tc, 83.85.Rx, 83.85.Vb

INTRODUCTION

Flame retardants are additives which deter or extinguish flame propagation which improves the safety of plastics used in consumer goods [1]. Due to the fact that flow properties of molten thermoplastics during ignition or flaming can play a large part in flame retardant modes of action, it is desirable to combine flame retardant additives together with polytetrafluoroethylene (PTFE) based drip suppressant additives (melt modifier). In more detail, the superfine fluorine-containing polymer particles together with halogenated flame retardants have been claimed to control the meltdripping behavior for numerous polymers including polyester in the concentration ranges of 0.01-1 phr (part per hundred) due to fibrillation [1-7]. Unfortunately, there is only a little information in the open literature about the effect of antidripping agent on basic rheological characteristics of the polymer melts [7]. In order to extend the knowledge in this field, the main aim of this work is to investigate the effect of the antidripping agent on the shear as well as extensional rheological characteristics for Ziegler-Natta based LLDPE.

Novel Trends in Rheology IV
AIP Conf. Proc. 1375, 248-252 (2011); doi: 10.1063/1.3604485
© 2011 American Institute of Physics 978-0-7354-0935-4/$30.00

Experimental Analysis

In this work, Dyneon^{TM} high molecular weight PTFE based melt modifier MM 5935 EF was used as the antidripping agent whereas Ziegler-Natta based LLDPE (ExxonMobile LL1002) as the basic polymer for the experimental research. 0.5%, 1%, 1%, 1.5% and 2% MM 5935 EF were blended with LLDPE. SEM images for pure LLDPE sample and LLDPE+2% MM 5935 EF blend is provided in Figure 1.

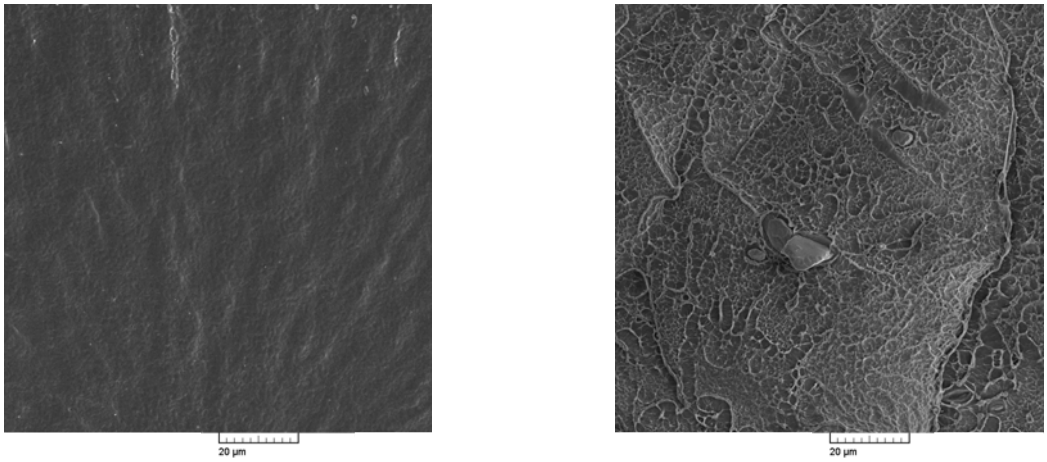

FIGURE 1. SEM images of the LLDPE (left) and the LLDPE with 2% MM 5935 EF (right).

For all polymer samples, the linear viscoleastic properties (storage modulus *G'*, loss modulus *G"*, complex viscosity η^*) were measured with use of the Advanced Rheometric Expansion System (ARES 2000) Rheometrics rheometer. Considering the Cox-Merz rule [8] and the similarity between $N_1/2$ and storage modulus *G'* [9], the recoverable shear, *Sr* - the measure of the shear elasticity, has been evaluated in this work according to the following equation:

$$Sr = \frac{G'}{\eta^* \omega} \tag{1}$$

Steady state shear and uniaxial extensional viscosities at high deformation rates have been determined by RH7-2 control speed capillary rheometer. In order to determine uniaxial extensional viscosities at very high extensional strain rates, the Cogswell model [10] has been utilized. In order to measure entrance pressure drop correctly, recently proposed zero length die has been used [11].

Transient uniaxial extensional viscosity was measured using the ARES 2000 rheometer equipped with the SER Universal Testing Platform (SER-HV-A01 model) from Xpansion Instruments [12–13] at two different extensional strain rates (1 s^{-1} and 10 s^{-1}).

All the measured rheological data are provided in Figures 2-7. It is clearly visible that with increased amount of antidripping agent, Newtonian viscosity, shear elasticity

and extensional viscosity of the LLDPE melt is increasing. On the other hand, steady shear viscosity at very high shear rates (above 10 s^{-1} for a given temperature) is not influenced by the antidripping agent. Interestingly, with increased amount of antidripping agent (up to 1%), the strain at break decreases and then increases (1.5%-2%).

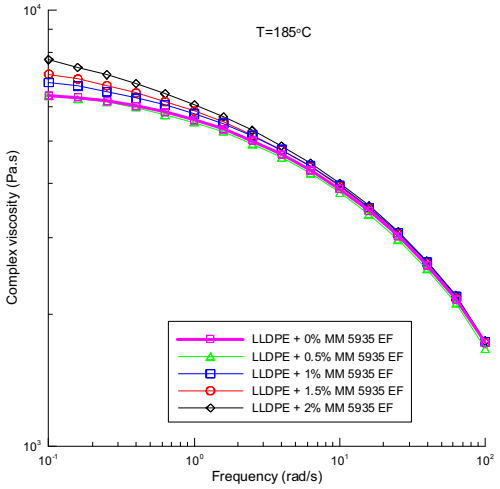

FIGURE 2. The effect of the flow modifier on the LLDPE complex viscosity.

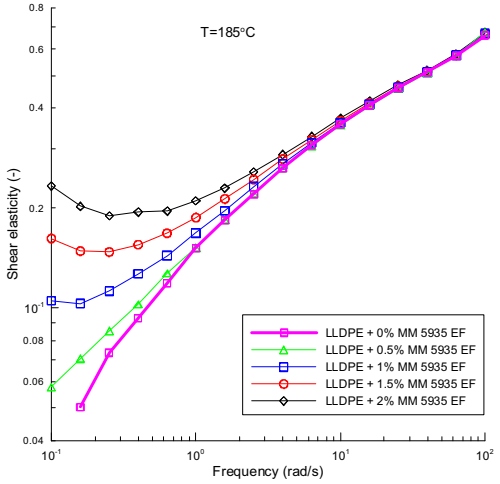

FIGURE 3. The effect of the flow modifier on the LLDPE shear elasticity.

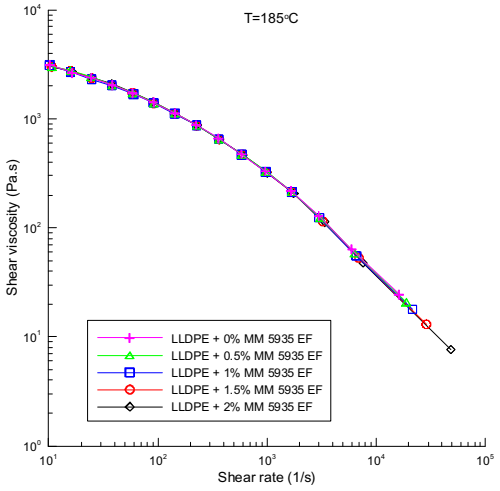

FIGURE 4. The effect of the flow modifier on the LLDPE steady shear viscosity.

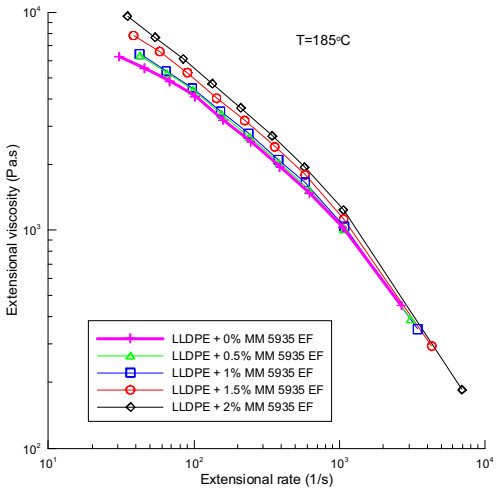

FIGURE 5. The effect of the flow modifier on the LLDPE steady uniaxial extensional viscosity.

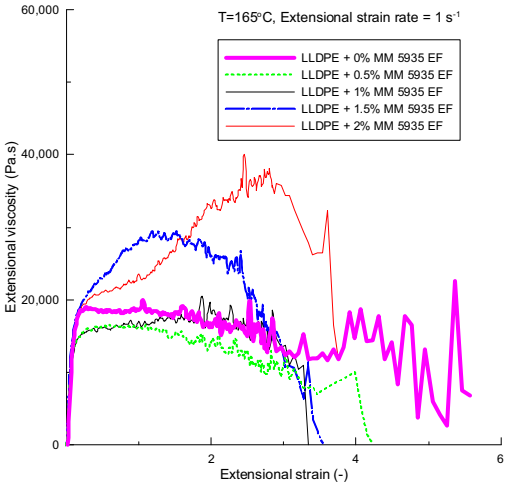

FIGURE 6. The effect of the flow modifier on the LLDPE transient uniaxial extensional viscosity; extensional strain rate = 1 s^{-1}.

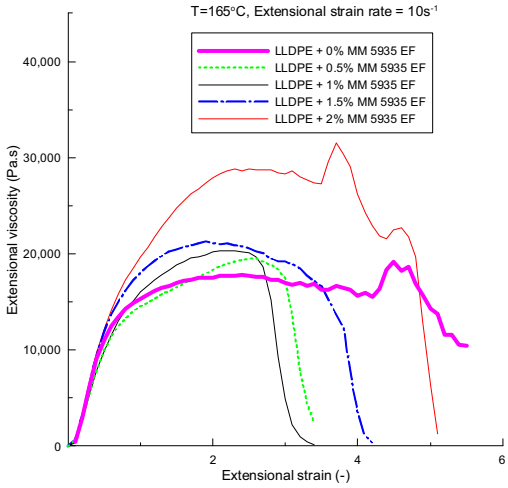

FIGURE 7. The effect of the flow modifier on the LLDPE transient uniaxial extensional viscosity; extensional strain rate = 10 s^{-1}.

CONCLUSION

It has been found that high molecular weight PTFE based melt modifier MM 5935 EF significantly enhancing shear viscosity/elasticity and especially extensional viscosity of the LLDPE melt. It has been revealed that the effect of the flow modifier on the extension strain at break has non-monotonic character.

ACKNOWLEDGMENTS

The support of the projects GA AS CR (Grant No. A200600703). This article was written with support of Operational Program Research and Development for Innovations co-funded by the European Regional Development Fund (ERDF) and national budget of Czech Republic, within the framework of project Centre of Polymer Systems (reg. number: CZ.1.05/2.1.00/03.0111).

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