

C-P142. Viscosity Variation During Addition of Ester and Ether Macrodiols to Isocyanates

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Polyurethane blends usually thicken up during the polymerization, but unexpected drop in viscosity could be occasionally observed [1]. In this study, an oligomeric ether-ester macro diol (EEMD of 2700 g/mol) [2] was diluted with polyethylene glycols (PEG of 200 g/mol or 400 g/mol). The polyols were mixed with a trifunctional adduct of hexamethylene -1,6- diisocyanate (HDI3, CAS 3779-63-3) at 1.4 mol excess to initiate addition reactions and assure eventual gelation.

Within 1 min of mixing dynamic viscosity η was measured using Anton Paar MCR 302 rheometer and a concentric cylinder system. The spindle was lowered leaving 1 mm gap between cylinders and assuring the absence of air bubbles. Viscosity was measured at 3 different shear rates: 1 s^{-1} , 10 s^{-1} , 100 s^{-1} , see fig 1.

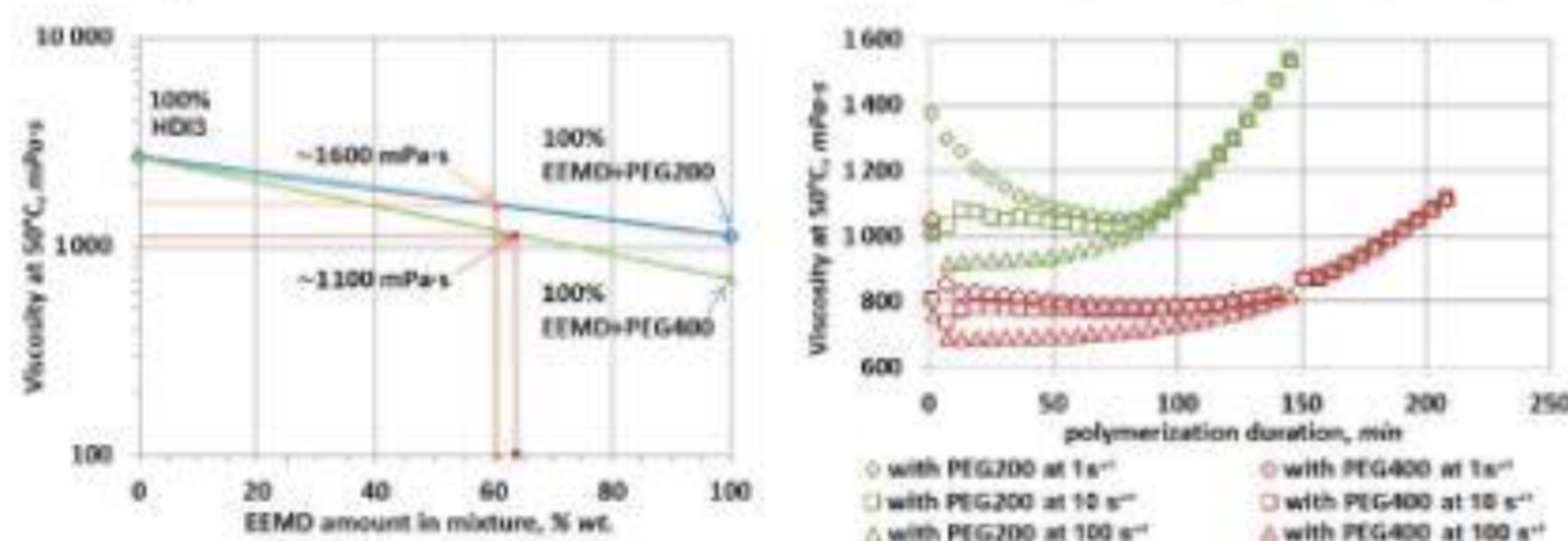


Fig. 1. Theoretically expected viscosities of polyol blends with HDI3 isocyanate (left) and viscosity increase during their polymerization at 50 °C (right).

The theoretically predicted viscosities are somewhat higher than measured. During early stages of polymerization the viscosity is highly dependent on shear, but later the trends become Newtonian-like [3]. Despite ongoing polymerization, viscosity seems to drop initially, or at least stagnate. It remains unclear what causes such unusual tendencies of viscosity dependence on polymerization.

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Keywords: adhesive, rheology, viscosity, polyurethane.

References:

1. P. Nemaniūtė et al. *Open Readings* p. 400 (2021)
2. D. Bražinskienė et al. *Advanced Materials and Technologies* p. 128 (2020)
3. R. P. Chhabra *Rheology of Complex Fluids* p. 3-34 (2010)

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- 8:30 – 9:00 **Registration**
- 9:00 – 9:45 **Witold Brostow** (University of North Texas, United States of America)
Fire Resistance of Materials
- 9:45 – 10:15 **Rynno Lohmus** (University of Tartu, Estonia)
How to Use Wood as a Material More Efficiently?
- 10:15 – 10:30 **Coffee break**
- 10:30 – 11:15 **Ashok Vaseashta** (International Clean Water Institute, United States of America)
Nanofibers of High-Performance Electret Polymers for Tactile Sensing and Wearable Electronics
- 11:15 – 12:00 **Azhar Ariffin** (University Malaya, Malaysia)
Carbazole-Based Organic Compounds in Organic Light Emitting Diodes, OLED, Applications
- 12:00 – 12:15 **Coffee Break**
- 12:15 – 13:15 **Morten Madsen** (University of Southern Denmark, Denmark)
Metal Oxide Interlayers for Scalable Organic and Perovskite Solar Cells
- 13:15 – 15:00 **Break**
- 15:00 – 18:30 **Poster Sessions Chairperson – Tomas Tamulevičius**
15:00 – 15:45 Poster Session A
15:55 – 16:40 Poster Session B
16:50 – 17:35 Poster Session C
17:45 – 18:30 Online Poster Session
- 18:45 – 19:15 **Best Poster Awards and Conference photo**

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Viscosity Variation During Addition of Ester and Ether Macrodiols to Isocyanates

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INTRODUCTION

Polyurethanes (PU) exist in various forms and can be used in a broad range of applications such as coatings, adhesives, foams, etc. [1] Two-component PU systems are formed by the reaction between various types of isocyanates and polyols to get different properties. Initial viscosity is important, especially when using PU adhesives in laminated packaging. Blends usually thicken up during the polymerization, but unexpected drop in viscosity could be occasionally observed [2]. In this study viscosity changes during polymerization are investigated for typical PU mixtures. Oligomeric ether – ester macrodiol (EEMD) was used as the main polyol. Its viscosity was quite high, therefore, it was diluted with polyethylene glycols PEG, see Scheme A for the molecular structures.

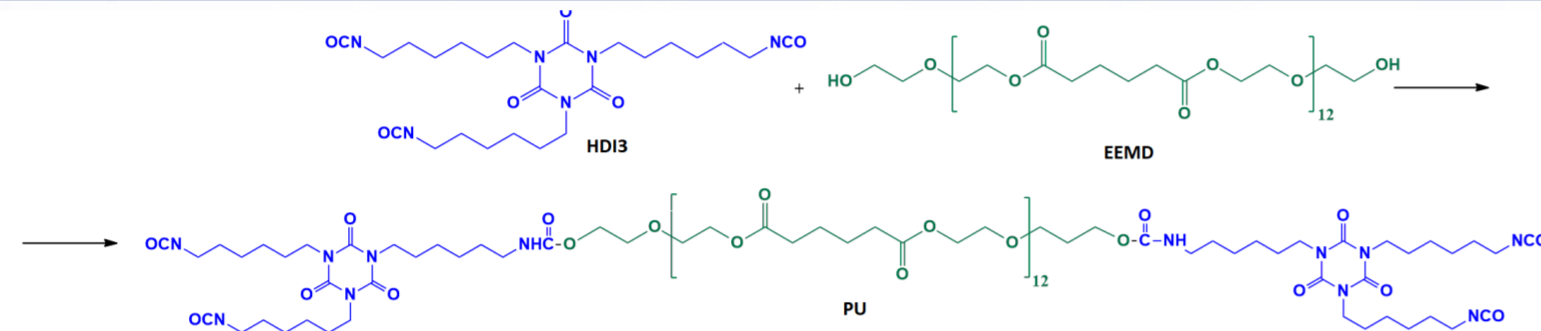


Fig. 1 Rotary rheometer Lamy CP-2000 (left) and Anton Paar MCR 302 rheometer (right)

MATERIALS

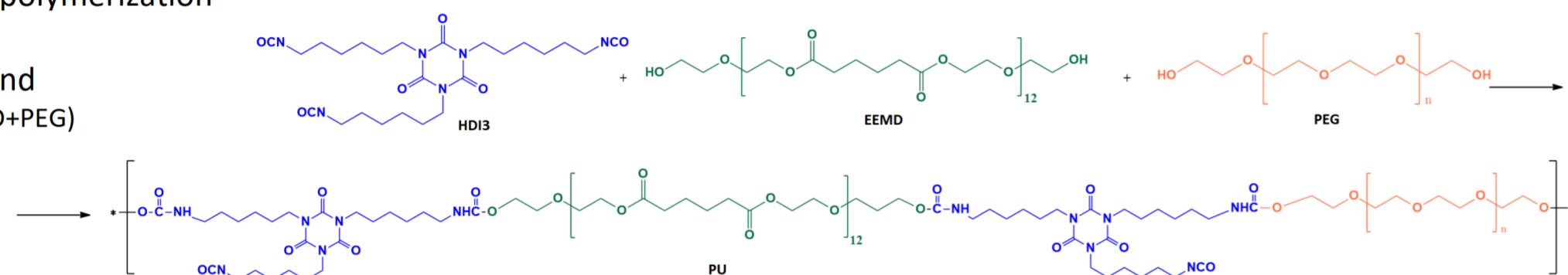
The oligomeric ether-ester macro diol (EEMD of 2700 g/mol) [3] was diluted with polyethylene glycols (PEG of 200 g/mol or 400 g/mol) at 4/1 or 65/35 w/w ratio respectively. The premixed polyols were reacted with a trifunctional adduct of hexamethylene -1,6- diisocyanate (HDI3, CAS 3779-63-3) at 1.4 mol excess to assure addition polymerization. Three polymerization mixtures were investigated: "Viscous Blend" w/o PEG (EEMD at 83.25% + HDI3 at 16.75% wt/wt) and "Thin Blends" with PEG 200 (at 12.1% + EEMD at 48.5% + HDI3 at 39.4%) and with PEG 400 (at 22.3% + EEMD at 41.4% + HDI3 at 36.3%).

Viscous Blend (HDI3+EEMD)



Early stages of polymerization

Thin Blend (HDI3+EEMD+PEG)



Scheme A Molecular structures of PU components and likely polymerization products during initial stages.

EXPERIMENTAL

Before polymerization, EEMD was premixed with PEG. The polyols and HDI3 were preheated separately at 50°C or 70°C for 15 minutes. At first their individual dynamic viscosities η were measured using Lamy CP-2000 with cone-plate or Anton Paar MCR 302 rheometer with a concentric cylinder system, Fig. 1. The spindle was lowered leaving 1 mm gap between cylinders and assuring the absence of air bubbles and the temperature was retained within $\pm 0.5^\circ\text{C}$. The latter instrument was used in viscosity monitoring during polymerization under three different shear rates (1 s^{-1} , 10 s^{-1} , 100 s^{-1}) at 50°C or 70°C.

RESULTS

The theoretical values of initial viscosity of PU blends before polymerization at 50°C were calculated assuming semilog relationship after measuring the viscosity of separate components, Fig. 2. Coincidentally, individual viscosities of HDI3 and EEMD are quite similar, 2630 and 2800 mPa·s at 50°C respectively, so their mixture, i.e. "Viscous Blend" should remain around 2700 mPa·s. The measurements show, Fig. 3, that the very initial viscosity is close to predictions. However, quite rapidly the Viscous Blend begins to thin down despite ongoing polymerization. Viscosity of the Viscous Blend seems not affected by shear rate variation between 1 s^{-1} and 100 s^{-1} . Such viscosity reduction with ongoing polymerization is very counter-intuitive. This puzzling tendency can also be clearly observed at 70°C, when it takes 70-80 min of polymerization for the Viscous Blend to reach its initial viscosity.

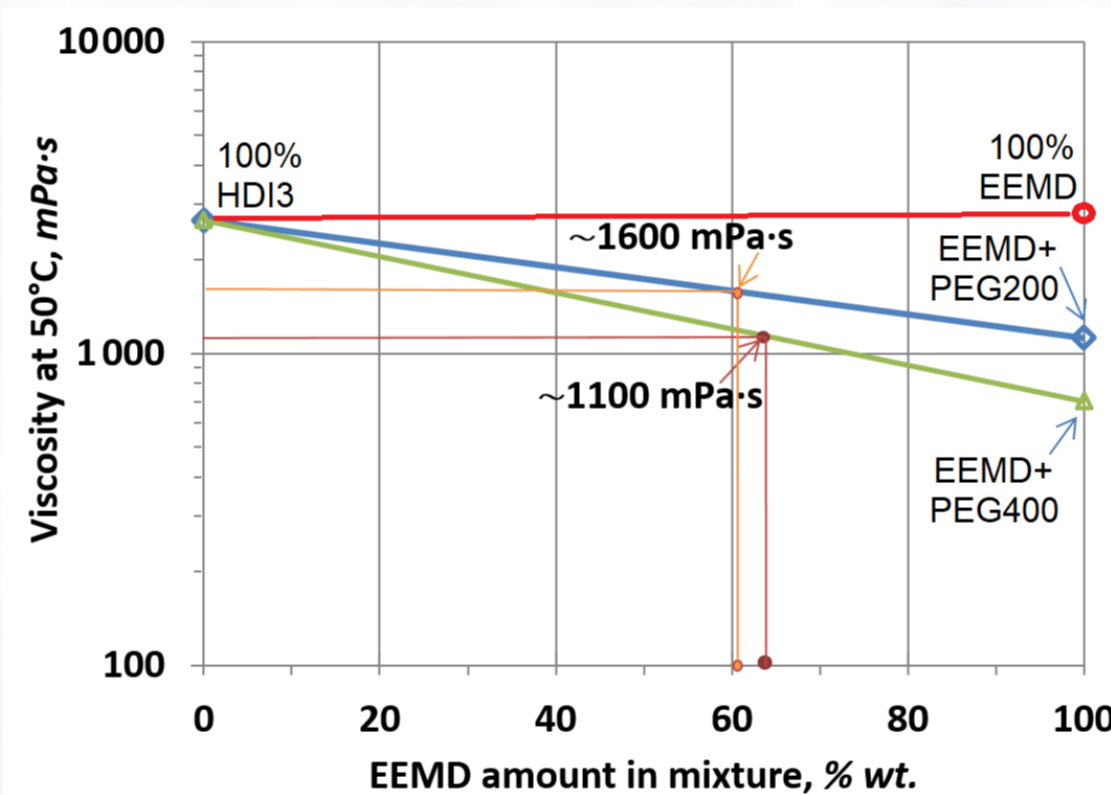


Fig. 2 Theoretically expected viscosities of polyol blends with HDI3 isocyanate at 50°C, assuming no polymerization.

Thin Blends were expected to show the initial viscosity with PEG200 around $\sim 1600\text{ mPa}\cdot\text{s}$ and that with PEG400 around $\sim 1100\text{ mPa}\cdot\text{s}$ at 50°C, Fig. 2. The respective values of 1400 and 1050 mPa·s were recorded immediately after blending at 1 s^{-1} shear rate, Fig. 4, i.e. not too far away from the predictions. But almost immediately the viscosity dropped sharply until stagnating despite ongoing polymerization. In addition, higher shear resulted in much lower viscosities. At low shear it took longer for viscosity to stop stagnating and begin increasing due to polymerization.

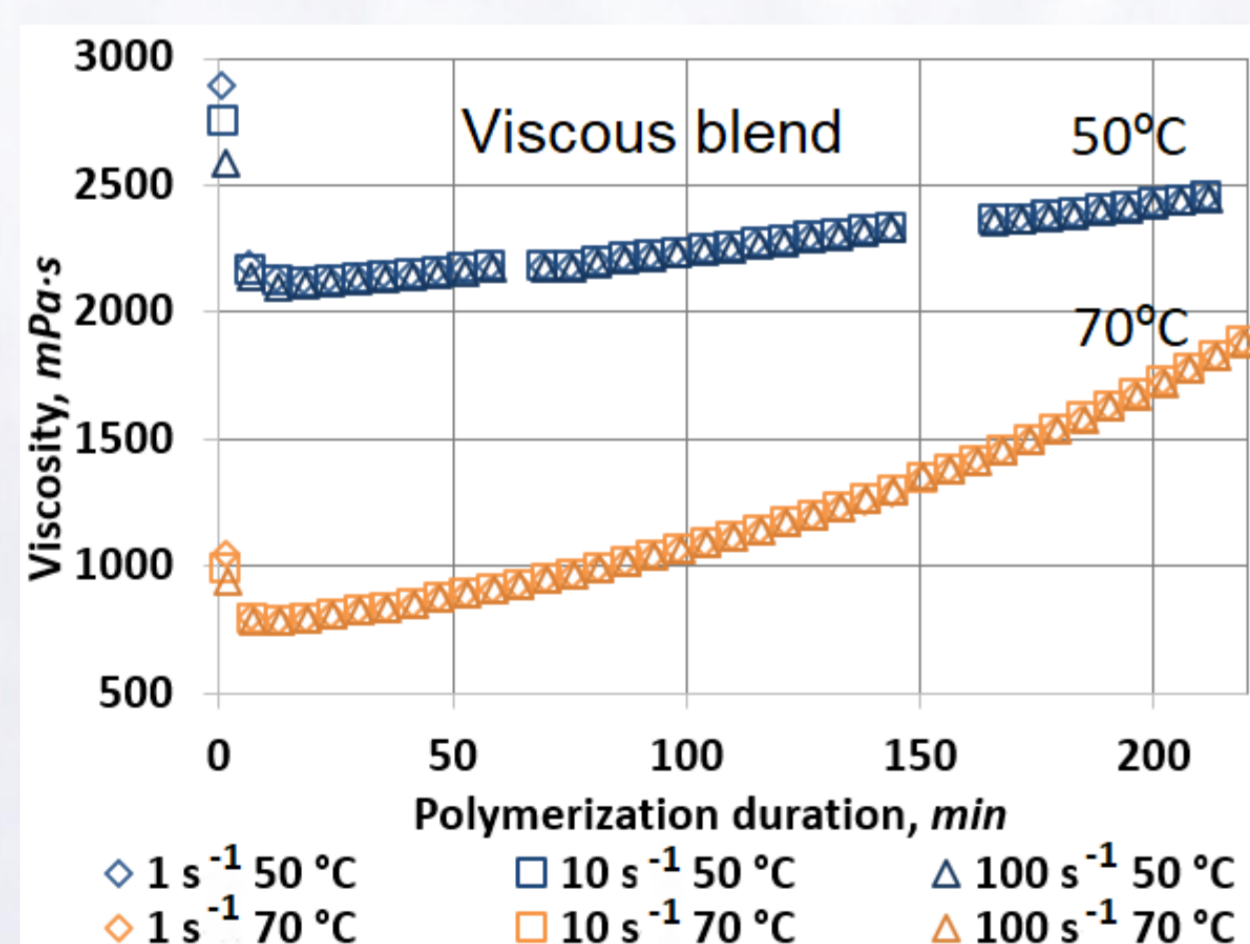


Fig. 3 Viscosity changes of the Viscous Blend at different shear rates during polymerization at 50°C and 70°C.

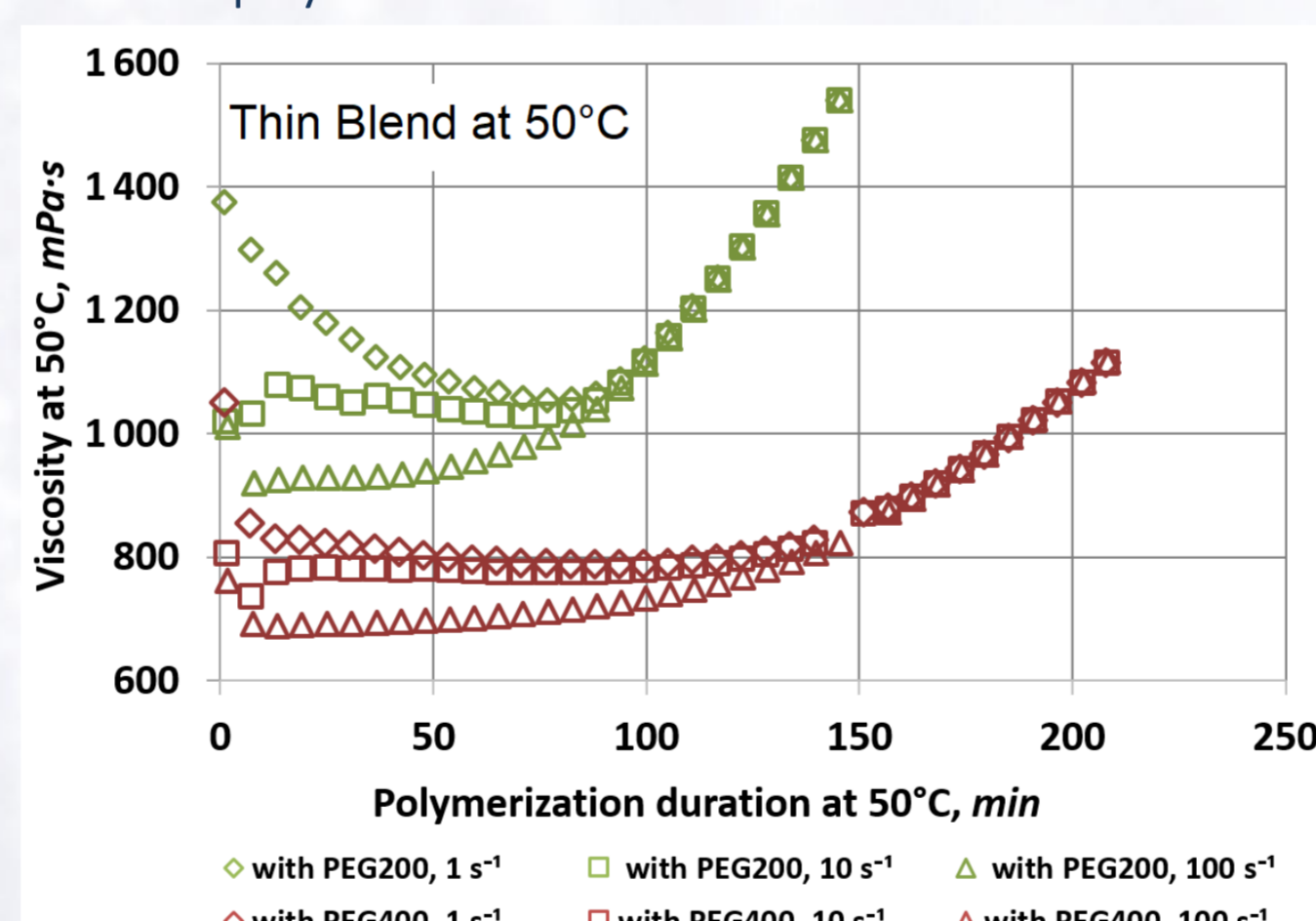


Fig. 4 Viscosity changes of Thin Blends under different shear rates during polymerization at 50°C.

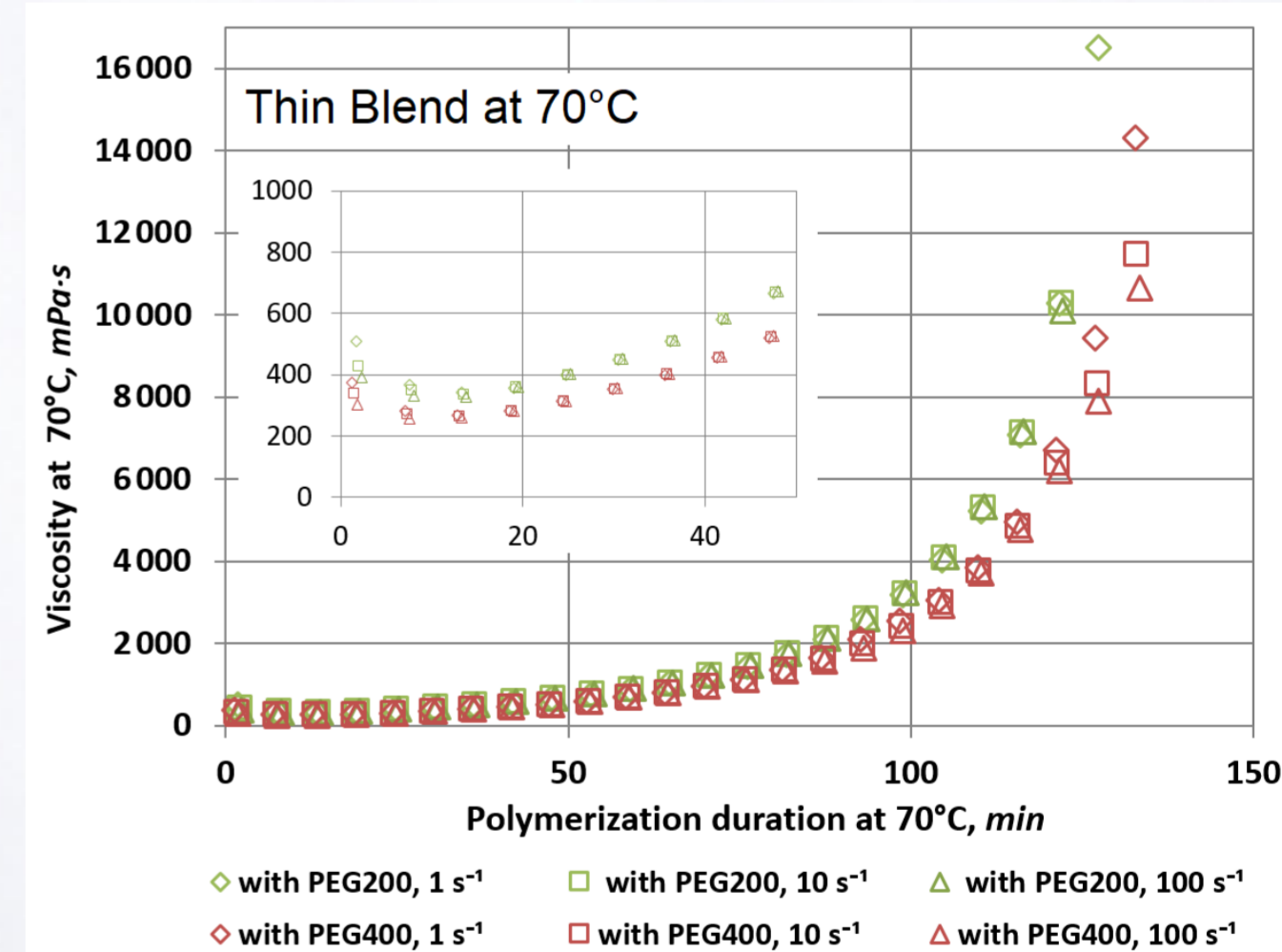


Fig. 5 Viscosity changes of Thin Blends under different shear rates during polymerization at 70°C. Inset: magnified scale of the initial stage.

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CONCLUSIONS

- The semilog relationship can predict approximate PU viscosity.
- During early stages of polymerization the viscosity is highly dependent on shear, which is more evident at lower temperatures [4].
- Despite ongoing polymerization, viscosity seems to drop initially and then stagnate.
- It remains unclear what causes such unusual tendencies of viscosity dependence on polymerization and shear.

REFERENCES

1. D. Abhijit, M. Prakash, "A brief discussion on advances in polyurethane applications", Adv. Ind. Eng. Polym. Res., 3 (2020), pp. 93-101
2. P. Nemaniūtė, D. Bražinskienė, S. J. Asadauskas, "Induction of viscosity increase during polyglycol addition to isocyanates", Open Readings, pg 400, Vilnius, 2021 DOI: 10.5281/zenodo.4778505
3. S. Mačiulytė, P. Nemaniūtė, D. Bražinskienė et al., "Influence of ester diluents and chain extension on polyurethane viscosities", Proc. of 22nd Conf. Advanced Materials and Technologies, ISSN 1822-7759, pg 128, Palanga, DOI: 10.5281/zenodo.4064006
4. Rajendra P. Chhabra, "Non-Newtonian Fluids: An Introduction", Rheology of Complex Fluids, pg 3-34, 2010 DOI: https://doi.org/10.1007/978-1-4419-6494-6_1

