

# VISCOSITY VARIATION DURING ADDITION OF POLYGLYCOLS TO TRIFUNCTIONAL ISOCYANATE

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Polyurethanes (PUR) are among the most widely used polymers due to the versatility of their properties. In order to perform pouring, filling, curing and other manufacturing operations properly, viscosity of the polymer blend has to be carefully controlled, especially when the polymer mixture is being exposed to the new surfaces. It might be expected for the viscosity to increase during polyaddition reaction, but previously, when an ether-ester macrodiol had been mixed with polyglycols and reacted with an isocyanate, a highly unusual drop in viscosity had been observed during early stages of polymerization [1]. In this study, instead of complex mixtures, two simple polyalkylene glycols were investigated for their viscosity variation during the addition reaction with a trifunctional isocyanate. Polyethylene glycol (PEG) of 400 g/mol and polypropylene glycol (PPG) of 2000 g/mol were reacted with a trifunctional adduct of hexamethylene -1,6-diisocyanate (HDI3, CAS 3779-63-3). The isocyanate was used at 1.4 mol excess, therefore HDI3 contents were higher than those of PEG. Before blending, the components were preheated to 50°C and their viscosities measured under different shear rates using Anton Paar MCR 302 rheometer with a concentric cylinder system [1]. Individually, PPG and HDI3 did not show much dependence on shear, recording 102.9, 102.2 and 102.1 mPa·s at 50°C under 1 s<sup>-1</sup>, 10 s<sup>-1</sup> and 100 s<sup>-1</sup> for PPG and 481.9, 481.7 and 481.4 for HDI3 respectively. PEG was thinning much faster with higher shear, resulting in 34.7, 30.2 and 29.5 mPa·s respectively. With both polyglycol and isocyanate preheated separately, they were blended together and the viscosity measurements were started within 1 min. Two mixtures were tested:

- “PPG+HDI3” (containing 78.7% wt. PPG plus 21.3% wt. HDI3), and
- “PEG+HDI3” (containing 42% wt. PEG plus 58% wt. HDI3).

Theoretically, the initial values of the blend viscosity should have been quite similar for both PUR mixtures, assuming semilog dependence between the components and no polymerization, Fig. 1.

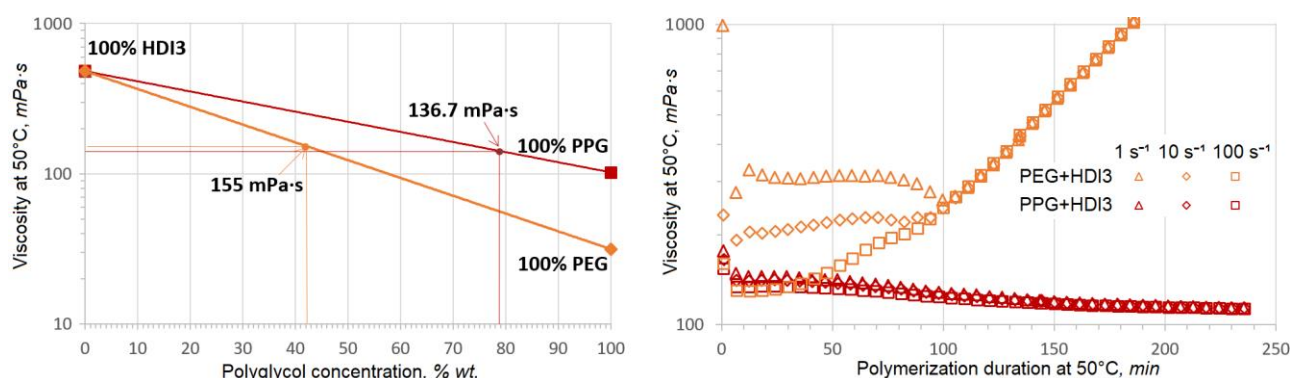


Fig. 1. Theoretically expected viscosities of the initial PUR mixtures at 50°C (left) and experimentally measured viscosities during their polyaddition reaction at 50°C (right).

Measured initial viscosities under 100 s<sup>-1</sup> shear rate nearly matched the predicted values. This suggests that semilog relationships might still be valid when predicting viscosities of non-reactive blends. However, viscosities of the PEG mixture appeared highly dependent on shear rate, showing many times higher magnitude than in case of individual components. When comparing the measurements of the same PEG mixture under 1 s<sup>-1</sup> and 10 s<sup>-1</sup>, the values barely fit within the same order. In contrast, the PPG mixture did not show much shear thinning. Nevertheless, both mixtures thinned down during early stages of polymerization. PEG mixture eventually rebounded and its viscosity started increasing, while that of PPG mixture did not increase within 4 hrs. This might imply that the PPG polymerization is much slower compared to PEG, in agreement with previous studies [2], but the absence of the viscosity increase alone cannot implicate that PPG doesn't react. With progressing polyaddition viscometric trends eventually become Newtonian-like. However, the initial stages, which often are extremely important during manufacturing, could be very perplexing.

**Conclusion.** Viscosity variation of polyglycol and isocyanate blends might be highly complex and demonstrate a reduction in viscosity despite ongoing polymerization. The drop in viscosity might be related to a gradual depletion of hydroxyl groups, but more testing is needed to assess this effect.

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[1] P. Nemaniūtė, M. Jurkūnas, D. Bražinskienė et al. Viscosity Variation During Addition of Ester and Ether Macrodiols to Isocyanates. Proc. of 22nd Conf. Advanced Materials and Technologies, ISSN 2669-1930, pg 175, Palanga, 26 August 2021  
[2] S. Mačiulytė, A. Strakšys, S. Asadauskas, Influence of aliphatic moieties in diisocyanates on chain extension kinetics of adipate macrodiols. Proc. Baltic Polymer Symp. pg 40, Vilnius (2019) DOI: 10.5281/zenodo.3813463

# Viscosity variation during addition of polyglycols to trifunctional isocyanate

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## INTRODUCTION

In the production of multilayer films, it is important to select most suitable adhesives. Often PU (polyurethane) adhesives, obtained by reacting polyols and isocyanates, are used, Fig. 1. In order to perform pouring, filling, curing and other manufacturing operations properly, viscosity of the polymer blend must be carefully controlled. Using different components the curing rate, degree of reticulation and other polymer properties can be manipulated [1]. In this study, viscosity changes with proceeding polymerization were investigated for several polyols.

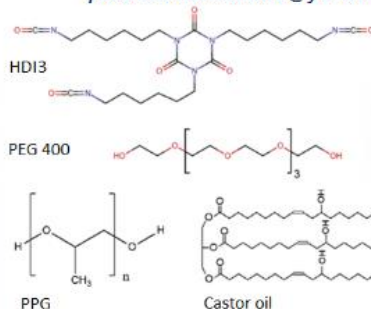


Fig. 2 Structures of components used in the tests

## MATERIALS

Polyethylene glycol (PEG of 400 g/mol), polypropylene glycol of 2000 g/mol (PPG) and castor oil of approx. 933 g/mol [2] were used as polyol components, Fig. 2. Trifunctional adduct of hexamethylene -1,6- diisocyanate (HDI3, CAS 3779-63-3) was employed as isocyanate. Three PUR mixtures were investigated at 1.4 mol excess of isocyanate to assure polyaddition:

- "with PEG400" (PEG400 at 42% + HDI3 at 58%),
- "with PPG" (PPG at 78.7% + HDI3 at 21.3%),
- "with castor oil" (Castor oil at 55.6% + HDI3 at 44.4%).

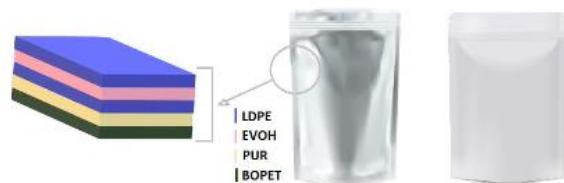


Fig. 1 Multilayer film (left) and example of multilayer packages for food (right)

## EXPERIMENTAL

Before blending, components were preheated separately at 50°C or 70°C for 15-20 min. Then viscosity was measured using Anton Paar MCR 302 rheometer with a concentric cylinder system using 1 mm gap. Dynamic viscosities were measured for individual components and for their mixtures during polyaddition reaction under three different shear rates: 1 s<sup>-1</sup>, 10 s<sup>-1</sup> and 100 s<sup>-1</sup> and two different temperatures (50°C or 70°C). With both polyol and isocyanate preheated separately, they were blended together and the viscosity measurements were started within 1 min.

Temperature	50°C			70°		
	1 s <sup>-1</sup>	10 s <sup>-1</sup>	100 s <sup>-1</sup>	1 s <sup>-1</sup>	10 s <sup>-1</sup>	100 s <sup>-1</sup>
HDI3	481.9	481.7	481.4	165.6	165.1	165.1
PPG	102.9	102.2	102.1	50.99	50.44	50.37
Castor oil	137.1	137.3	137.5	52.44	51.51	51.58
PEG400	34.68	30.16	29.49	17.74	15.73	15.49

Table 1 Viscosity values of individual components at 50°C and 70°C

## RESULTS (1)

Individually, PPG, castor oil and HDI3 did not show much dependence on shear, see Table 1. PEG 400 was thinning much faster with higher shear, resulting in 34.7, 30.2 and 29.5 mPa·s respectively. Theoretically, the initial values of the blend viscosity at 50°C temperature should have been quite similar for PUR mixtures "with PPG" 136.7 mPa·s and "with PEG400" 155 mPa·s with a slightly larger initial viscosity value for PUR mixture "with castor oil" – 233.8 mPa·s. This prediction assumes semilog dependence between the components and no polymerization, Fig. 3. Measured initial viscosities under 100 s<sup>-1</sup> shear rate nearly matched the predicted values, Fig 4. This suggests that semilog relationships might still be valid when predicting viscosities of non-reactive blends. However, viscosities of the PEG 400 mixtures appeared highly dependent on shear rate, showing many times higher magnitude than in case of individual components.

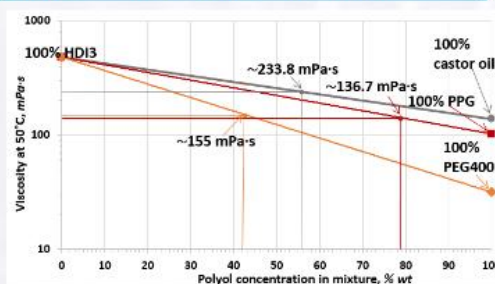


Fig. 3 Theoretically expected viscosities of PUR blends at 50°C

## RESULTS (2)

When comparing the measurements of the same PEG400 mixture under 1 s<sup>-1</sup> and 10 s<sup>-1</sup> at 50°C, the values barely fit within the same order. In contrast, the PPG and castor oil mixtures did not show much shear thinning. Nevertheless, all mixtures thinned down during early stages of polymerization. The mixtures of PEG400 and castor oil eventually rebounded and their viscosity started increasing. For the mixture with castor oil, the viscosity started increasing much earlier (after 19 minutes) than for the mixture with PEG400 (after 70 minutes). The viscosity of PPG mixture did not increase within 4 hrs. This might imply that the PPG polymerization is much slower compared to PEG400 or castor oil, in agreement with previous studies [3], but the absence of the viscosity increase alone cannot implicate that PPG doesn't react. At 70°C the viscosity of PPG mixture slowly started to increase after about 130 minutes (Fig. 5). For mixtures with PEG and castor oil, the viscosity thinned down at very early stages of polyaddition reaction at 70°C as well, just their viscosity started to increase a lot earlier than at 50°C (Fig. 5). Despite quite evident dependence of individual PEG400 on shear at 70°C, at this temperature PU mixture with PEG400 did not show any shear thinning, in contrast to expectations and the trends at 50°C. This further highlights how perplexing the viscosity variation could be during polymerization.

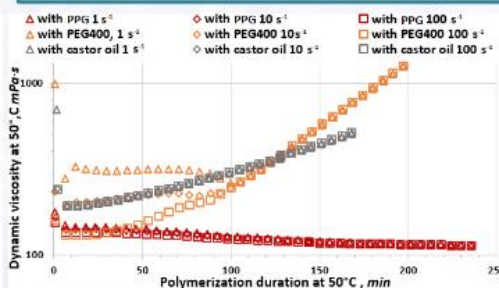


Fig. 4 Dynamic viscosity results during polyaddition reaction under different shear at 50°C

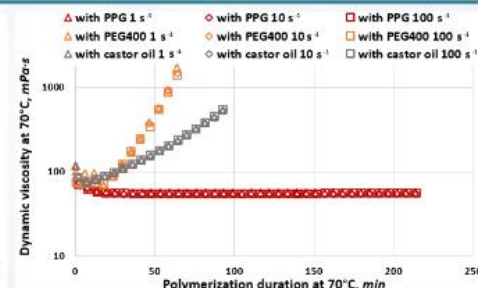


Fig. 5 Dynamic viscosity results during polyaddition reaction under different shear at 70°C

## CONCLUSIONS

- Viscosity variation of polyglycol and isocyanate blends might be highly complex and demonstrate a reduction in viscosity despite ongoing polymerization.
- The drop in viscosity might be related to a gradual depletion of hydroxyl groups, but more testing is needed to assess this effect.

## ACKNOWLEDGMENTS

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