

B-P98. Effects of Isocyanate Addition on Viscosity of Ester-Based Polyurethanes

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Polyurethanes are widely used in high performance adhesives, where their viscosity and curing trends are very important. In this study, several ester-based polyols were mixed with a trifunctional adduct of hexamethylene -1,6-diisocyanate (HDI3, CAS 3779-63-3) in 1.4 mol excess and it was monitored how viscosity varies with the course of polymerization. The reaction procedure and measurements using titration and a rotary viscometer were described previously [1]. FTIR spectrometer Frontier™ with ATR (Perkin-Elmer) was used to follow the depletion of NCO functional groups by determining the area under the peak from 2150 to 2400 cm⁻¹ and normalizing it to the CH₂ vibrational stretch at 2936 cm⁻¹. The results of castor oil polymerization with HDI3 are shown in Fig 1.

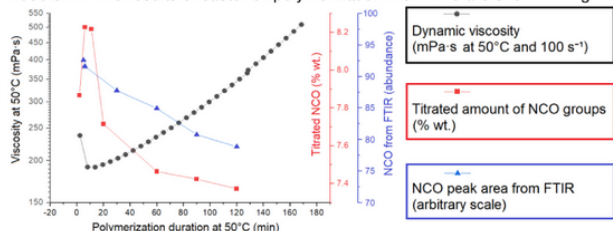


Fig. 1. Polymerization kinetics of castor oil after HDI3 addition at 5:4 w/w, as monitored by measuring viscosity, recording FTIR spectra and titrating NCO contents

During the early stages of polymerization, viscosity goes down while NCO contents seem to increase. This is in contrast with the expectation that polymerization should begin immediately. It is possible that initially the NCO groups are linked between each other by intermolecular forces, but such linkages are eventually disrupted by progressing polymerization. More experiments are needed to resolve this uncertainty.

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Keywords: polymerization, kinetics, spectroscopy.

References:

1. D. Bražinskienė et al. *Proc. Adv. Mat. Tech.* p. 128 (2020)



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August 25, Thursday

Chairperson Arnaud Spangenberg

8:30 – 9:00	Registration
9:00 – 9:45	Gediminas Juzėliūnas (Vilnius University, Lithuania) Topology for Electrons in Solids, Photons and Ultracold Atoms
9:45 – 10:30	Hubert Halbritter (ams-OSRAM International GmbH, Germany) Photons for the World Around Us
10:30 – 10:50	Coffee Break
10:50 – 11:35	Gerald Gerlach (Technische Universität Dresden, Germany) How To Bridge the Gap Between Academic and Industry-Oriented Sensor Research
11:35 – 12:20	Renata Butkutė (Center for Physical Sciences and Technology, Lithuania) Bandgap Engineering in Bismuth-Containing Semiconductors
12:20 – 12:50	Lina Grinevičiūtė (Center for Physical Sciences and Technology, Lithuania) The Evolution of Optical Coatings: From 1D to 3D Periodic Structures
12:50 – 13:10	Coffee Break
13:10 – 14:10	Yoshihiro Koide (Kanagawa University, Japan) Blue Light Emitting Facial Isomer of Tris (8-Hydroxyquinoline) Aluminum: Facile Synthesis and Formation Mechanism of Thermodynamically Unstable Isomer
14:10 – 14:55	Longin Lisetski (Institute for Scintillation Materials, Ukraine) Effects of Nanostructuring in Liquid Crystalline Systems: Physico-Chemical Studies and Molecular Models
14:55 – 16:00	Break
16:00 – 18:00	Poster Sessions with Voting for the Best Poster (Chairperson Tomas Tamulevičius) 16:00 – 16:50 Poster Session A 17:00 – 17:50 Poster Session B
16:00 – 18:00	Parallel event: Meeting of Project SPINMULTIFILM: "Physical principles of the creation of novel SPINtronic materials on the base of MULTILayered metal-oxide FILMs for magnetic sensors and MRAM" (Grant Agreement 778308, H2020-MSCA-RISE-2017 Marie Skłodowska-Curie Action: Research and Innovation Staff Exchange) (online)
18:00 – 18:30	Best Poster Awards and Conference Photo

Effects of isocyanate addition on viscosity of ester-based polyurethanes

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INTRODUCTION

Polyurethane (PU) is widely used in high performance adhesives, where viscosity and curing trends are very important. Bonab and others [1] described PU viscosity changes during polymerization (fig. 1). They argued that due to competing effects of heat transfer, which tends to lower viscosity, and polymerization reaction, which tends to increase viscosity, in the first stage, viscosity is constant or it can slightly drop. In this work viscosity changes during polymerization were investigated as well as NCO groups changes during the polymerization between industrially widespread isocyanate and polyols.

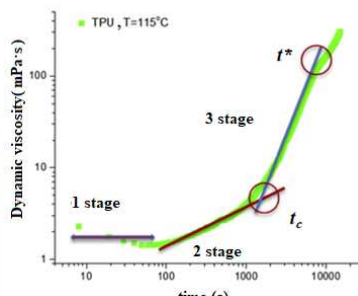


Fig. 1 Generalization of PU viscosity variation during polymerization [1]

MATERIALS

In this study, a polyol, either polydiethylene glycoladipate (PDEA of 2700 g/mol, CAS 25036-49-1) or castor oil (of approx. 933 g/mol), was mixed with a trifunctional adduct of hexamethylene -1,6- diisocyanate (HDI3, CAS 3779-63-3) (Fig. 2). Two PU blends were prepared at 1.4 mol excess of the isocyanate to assure the conversion of most OH groups:

- PDEA at 83% wt + HDI3 at 17% wt,
- Castor oil at 56% wt + HDI3 at 44% wt.

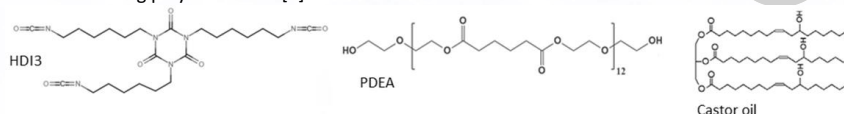


Fig. 2 Structures of the isocyanate (left) and polyols (center and right) used in this work

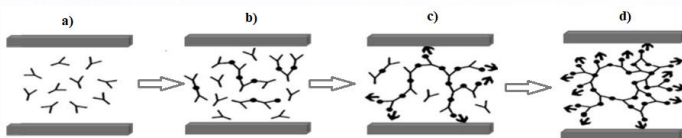


Fig. 3 Schematic diagram of the formation of a polymeric network during curing of a liquid bicomponent system [3]

RESULTS

1. VISCOSITY

The viscosity variation during the reaction of HDI3 blends with either castor oil (left) or PDEA (right) are shown in Fig. 4. In both cases a viscosity drop was detected during early stages of polymerization (Fig. 4 black curve). The initial viscosity of castor-based PU blend was 237.6 mPa·s and after 14 min viscosity dropped to 191 mPa·s. Similar trends, just of lower magnitude, were observed with PDEA-based PU blend. From the initial viscosity of 2137 mPa·s after 13 min it dropped to 2101 mPa·s. Eventually in both reactions the viscosity started going up, but such trend still contradicts to the assumption that viscosity should always increase with polyaddition, as molecules combine to form larger compounds without releasing any components of lower molecular weight. Early drop in viscosity might be related to the predominance of hydrogen bonding among OH groups of PDEA or castor oil. They might restrict intermolecular movement and cause higher viscosity. With ongoing polyaddition the density of OH groups goes down, which might have more effect on the viscosity than gradual increase in average molecular weight due to polymerization. Consequently, viscosity drops initially and recovers only after the increase in average molecular weight becomes more significant. Additional techniques would be needed to investigate this possibility.

2. TITRIMETRIC DATA

In the PU formation reaction, the NCO groups combine with the OH groups to form larger compounds. The depletion of the NCO groups by titration was therefore investigated to check whether the addition reaction starts right after mixing PU components. Counterintuitively, for both PU blends 2 min after the start of the reaction, the reaction mixtures were found to contain higher amounts of isocyanate groups than at the beginning of the reaction. This does not agree with the expectation that NCO should be depleted. As the reaction time increases, the content of isocyanate groups in the mixture decreases and the titration trend begins to agree with polyaddition kinetics. It is puzzling why NCO contents seem to increase during the early stages of polyaddition and start dropping only afterwards. Such paradox could be caused by a possible interaction between isocyanate groups, which might involve van-der-Waals linkages, as shown in Fig. 5. Such agglomerates of isocyanate groups might not readily react with dibutyl amine, which is used for determination of NCO contents. The agglomerates could be more abundant during the beginning of the polymerization, but with progressing reaction their intermolecular linkages should be broken down. Then it becomes easier for the isocyanates react with dibutyl amine and NCO titration might produce higher values.

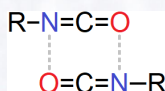


Fig. 5 Possibility of intermolecular linkages between isocyanate groups

EXPERIMENTAL

An ester-based polyol was mixed with HDI3 and it was monitored how viscosity varies with the course of polymerization. The reaction procedure and measurements using titration and viscometry were described previously in detail [2]. The reaction was performed within the concentric cylinder compartment of the rotary MCR302 viscometer. The same reaction was carried out separately for titrimetric and spectroscopic measurements. Small samples were periodically withdrawn from the latter mixture. They were reacted with dibutyl amine, whose excess was titrated with HCl using bromophenol blue to establish NCO contents. Another series of samples were withdrawn and evaluated using FTIR spectrometer Frontier™ with ATR (Perkin-Elmer) to follow the depletion of NCO functional groups by determining the area under the peak from 2150 to 2400 cm⁻¹ and normalizing it to the CH₂ vibrational stretch at 2936 cm⁻¹.

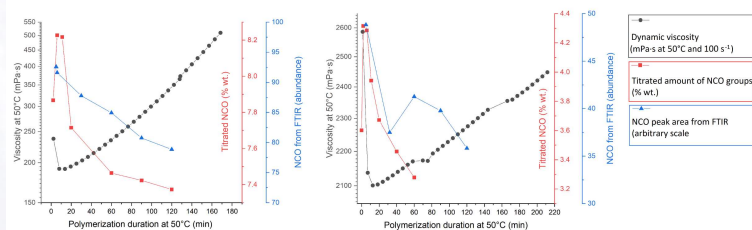


Fig. 4 Polymerization kinetics of castor oil (left) and PDEA (right) after HDI3 addition, as monitored by measuring viscosity, recording FTIR spectra and titrating NCO contents.

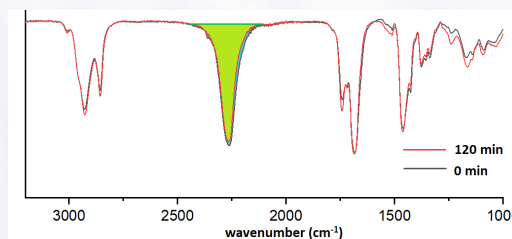


Fig. 6 Reduction of the FTIR peak at 2270 cm⁻¹ in 120 min of polyaddition reaction between castor oil and HDI3.

3. FTIR SPECTROSCOPY

FTIR was also used to follow the depletion of NCO functional groups by determining the normalized areas under the NCO peak at 2270 cm⁻¹, as illustrated in Fig. 6. The obtained areas under this peak in arbitrary units are plotted Fig. 4 (blue curve). For PU blend with castor oil (Fig. 4 left) these areas decreased from 9257 to 7884 and for the mixture with PDEA (Fig. 4 right) from 4883 to 3582 within 2 hours of the reaction. This data confirms that the addition reaction is ongoing continuously despite unusual trends of viscometric and titrimetric data.

CONCLUSIONS

- The drop in viscosity can be observed despite ongoing polyaddition. This might be related to a gradual depletion of hydroxyl groups and weakening hydrogen bonding.
- It is possible that initially the NCO groups are linked between each other by intermolecular forces, but such linkages are eventually disrupted by progressing polymerization.

ACKNOWLEDGMENTS

This study was carried out under project TERMINUS, funded by the European Union under Horizon 2020. Call: H2020-NMBP-ST-IND-2018. Grant Agreement: 814400.



1. V. Solouki Bonab et al. Polym. J., pg 513-520, 2016, doi: 10.1016/j.polymer.2016.07.043
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