

INFLUENCE OF LAYERED DOUBLE HYDROXIDE ON POLYADDITION OF AROMATIC ISOCYANATE AND MACRODIOL

Gytautė Sirgėdaitė, Paulina Nemaniūtė, Dalia Bražinskienė, Svajus J. Asadauskas

Department of Chemical Engineering and Technology, FTMC, Vilnius, Lithuania
gytaute.sirgedaite@ftmc.lt

Layered double hydroxides (LDH), hydrotalcites in particular, represent a major and versatile class of 2D materials, which can be used to encapsulate drugs, flavors and other functional components in various matrices [1]. Consequently, LDH finds innovative uses in diverse polymer applications. However, its usage in polyurethane (PUR) might be complicated, because LDH contains hydrated moieties, which might react with isocyanates and disrupt polymerization. In this study, hydrotalcite LDH as $Mg_x[Al_2(OH)_2]_{(2+x)}CO_3$ ($x=4-6$) with relatively low H_2O contents ($<0.5\%$ wt. loss in 2 hrs at $105^\circ C$) was incorporated into PUR by mixing it in a diluted OH-terminated prepolymer and curing with aromatic isocyanate. The prepolymer was produced in ethyl acetate by chain extending the ether-ester macrodiol of 2700 g/mol, synthesized from adipic acid and diethylene glycol, with hexamethylene diisocyanate at 1:0.3 mol. ratio [2]. Polymerization was carried out by mixing the prepolymer with a trifunctional aromatic isocyanate (prediluted with 25% wt. ethyl acetate with or without LDH) at 1.4 mol. excess. Three mixtures were studied at $50^\circ C$:

- no LDH (60% wt. prepolymer, 32.5% wt. ethyl acetate and 7.5% wt. isocyanate);
- 1.8% LDH (59% wt. prepolymer, 31.7% wt. ethyl acetate, 1.8% wt. LDH and 7.5% wt. isocyanate) and
- 6% LDH (56% wt. prepolymer, 31.5% wt. ethyl acetate, 6% wt. LDH and 7.5% wt. isocyanate).

In every mixture, the isocyanate was preheated and added as the last component immediately before testing. The mixtures were agitated for 0.5-1 min and poured into a capillary Cannon-Fenske viscometer of 500 size (orifice of 2 mm ID), equilibrated at $50^\circ C$. The rate of isocyanate polyaddition to the OH-terminated prepolymer was monitored by measuring kinematic viscosity using an adapted ASTM D445 procedure [3].

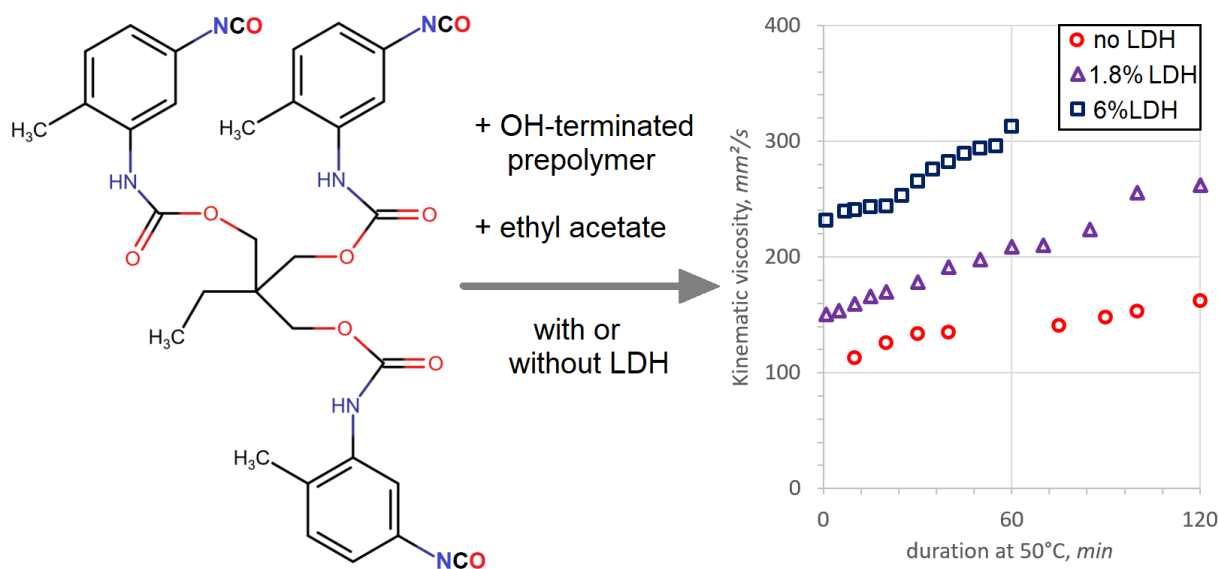


Fig. 1. Polyaddition of trifunctional aromatic isocyanate (left) to prepolymer, leading to viscosity increase and effects of LDH inclusion (right).

The results show, Fig. 1, that viscosity builds up gradually due to the ongoing polyaddition. Inclusion of 1.8% wt. LDH increases the viscosity by nearly 50%, retaining this ratio throughout the course of polyaddition. Higher amounts of LDH increase viscosity further, as in case of 6% wt. LDH. Nevertheless, the rate of thickening remains similar, which implies that LDH addition does not change polymerization mechanism significantly. However, H_2O concentration in LDH should be carefully considered, because the tested hydrotalcite had relatively low moisture levels.

Conclusion. Addition of hydrotalcite LDH into polyurethane matrix increases viscosity but should not significantly affect polymerization mechanisms. This could make it possible to develop PUR plastics with innovative functions.

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[1] N.B. Allou, P. Saikia, A. Borah et al., Hybrid nanocomposites of layered double hydroxides: an update of their biological applications and future prospects. *Colloid Polym Sci*, vol. 295, pp. 725–747 (2017) DOI 10.1007/s00396-017-4047-3

[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

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FTMC Department of Chemical Engineering and Technology, Saulėtekio 3, Vilnius, Lithuania
gytaute.sirgedaite@ftmc.lt



Introduction

Polyurethanes (PUR) represent a very versatile class of polymers due to the broad variety of polyols and macrodiols, which can be reacted with isocyanates. PUR is used in foams, coatings, insulation, adhesives and many other applications, Fig. 1. In order to impart some specialized properties, such as new odor or resistance to degradation, various components can be added into PUR.



Fig. 1. Examples of various polyurethane products with functional additives

In order to control the release of such components into the PUR matrix, layered double hydroxides (LDH) can be employed. LDH represent a major category of 2D materials, which can be used to encapsulate drugs, flavors and other functional components into various matrices [1]. Consequently, LDH finds innovative uses in diverse polymer applications. However, its usage in polyurethane (PUR) might be complicated, because LDH might affect polymerization trends. In this study, kinematic viscosity of PUR mixture in ethyl acetate solvent was monitored during the ongoing polymerization to evaluate the LDH effects on the reaction kinetics.

Materials

Two types of LDH were used: SML (small particles) and LRG (large particles). SML was represented by hydrotalcite LDH as $Mg_xAl_{2-x}(OH)_2[CO_3]_{(2-x)}$ ($x=4-6$) with relatively low water contents (<0.5% wt. loss in 2 hrs at 105°C). Individual SML particles were smaller than 100 nm. LRG particles were much larger, since they were obtained by sieving through 100 μm mesh and collecting the fine fraction. LDH particles were incorporated into PUR by mixing them with OH-terminated prepolymer, prediluted with ethyl acetate, and curing with aromatic isocyanate, Fig. 2. PUR was composed of 60% wt. prepolymer, 32.5% wt. ethyl acetate and 7.5% wt. isocyanate. LDH was added at 1.8% or 6% w/w

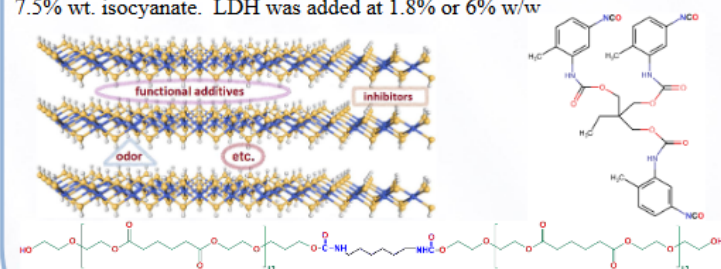


Fig. 2. Molecular architecture of LDH (left) and chemical structures of aromatic isocyanate (right) and a dominant component in the OH-prepolymer (bottom)



Fig 3. Capillary viscometer used in the study

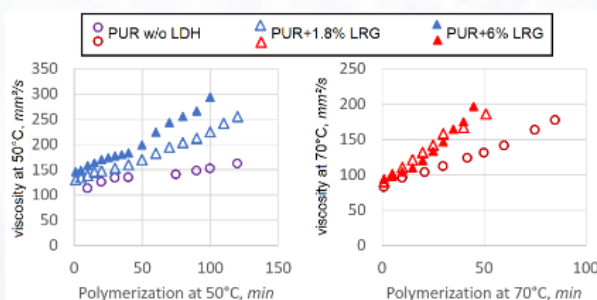


Fig. 4. Effect of LRG particles on PUR viscosity at 50°C and 70°C

Effects of LRG particles

Measurements showed that inclusion of LDH increases PUR viscosity in agreement with expectations. In case of LRG, whose particles were larger, the viscosity increase was somewhat proportional to the LDH concentration at 50°C, Fig 3. Viscosities were lower at 70°C, although by not as much as expected. At this temperature the concentration effect was not very clear, since both 1.8% and 6% LRG concentrations showed similar viscosity trends. No effect on polymerization kinetics could be observed, except of a slight and fairly uniform increase in the rate of thickening.

Procedure

Both OH-prepolymer and isocyanate were preheated individually and only then mixed by agitating for 0.5-1 min and pouring into a capillary Cannon-Fenske viscometer of 500 size (orifice of 2 mm ID), equilibrated at 50°C or 70°C. Kinematic viscosity was measured using an ASTM D445 procedure [3].

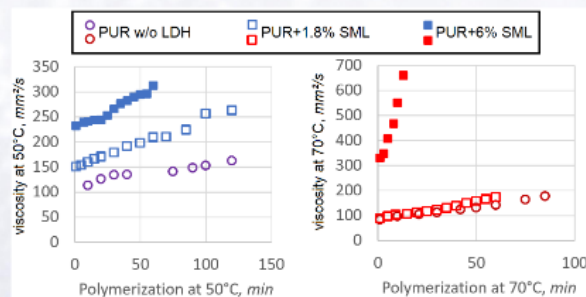


Fig 5. Effect of SML particles on PUR viscosity at 50°C and 70°C

Effects of SML particles

When SML particles were introduced, at 50°C the viscosity increased more significantly than in case of LRG particles. Viscosity almost tripled after adding 6% SML, Fig 4. At 70°C the addition of 1.8% SML was not very noticeable viscometrically, as opposed to the observations at 50°C. However, when 6% SML was added, the effect was really dramatic. The mixture was not only thickened over 4 times, but the rate of the viscosity increase with the ongoing polymerization became much faster. This implies that the addition of 6% SML changed the polymerization mechanism by introducing catalytic or some other effects.

Polymerization and evaporation

The PUR mixture was reacting within the viscometer, leading to the increase of average molecular weight. Therefore, viscosity of the mixture was growing with longer durations in all measured samples. Evaporation of ethyl acetate could also contribute to viscosity. But the capillary was quite narrow, so the vapor losses should be negligible

Conclusions

- Inclusion of dry LDH into PUR mixtures does not disrupt polymerization or inhibit its rate significantly.
- Even dry LDH can change the reaction mechanisms significantly, dramatically increasing the rate of polymerization.
- Particle size of LDH or their surface area could be responsible for the dramatic change in kinetics, but this remains uncertain.
- Caution must be exercised when adding LDH at high concentrations, especially if moisture is present.

References

- [1] N.B. Allou, P. Saikia, A. Borah et al., Hybrid nanocomposites of layered double hydroxides: an update of their biological applications and future prospects. *Colloid Polym Sci*, vol. 295, pp. 725–747 (2017) DOI 10.1007/s00396-017-4047-3
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