

# Facilitating the depolymerization of polyamide 6 (PA6) by ultrasound and microwave assistance using CaCl<sub>2</sub>-EtOH-H<sub>2</sub>O mixture for polymer dissolution

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## Highlights

- Heating of PA6 in CaCl<sub>2</sub>-EtOH-H<sub>2</sub>O mixture facilitates the depolymerization of PA6.
- Hydrogen bond breakage occurs faster by ultrasound than by microwave heating.
- The CaCl<sub>2</sub>-EtOH-H<sub>2</sub>O mixture solubilizes the PA6 bulk by hydrogen bond breakage.
- The molar EtOH:H<sub>2</sub>O ratio is critical for the solubility behavior.

## 1. Introduction

Given the problems of virgin plastic production from fossil resources and the growing amount of plastic waste, a rapid transition towards a circular economy is one significant societal goal. To meet the future recycling targets of the European Commission, several recycling approaches (e.g. mechanical, thermochemical or solvation processes) are actively investigated for thermoplastic materials. In the present study, we focus on polyamide 6 (PA6), due to its manufacture being one of the most energy and fossil resource demanding [1]. This commodity polymer is used e.g. in automotive sector, medical equipment or technical textiles. PA6 can be recycled mechanically, physically, chemically or thermally [2]. According to a recent review of chemical recycling, the amide bonds in PA6 establish principally thermodynamic and kinetic viability for chemical depolymerization, however, this only is insufficient to determine the commercial practicality [3].

The inter-chain hydrogen bonds in the semi-crystalline structure of PA6 is the dominating factor for the high chemical resistivity and inertia of this polymer. Here, we aim to realize a smooth initial disintegration of the tight PA6 structure by breaking down the hydrogen bonds. A mild pretreatment of the PA6 structure would be a highly beneficial for the subsequent catalytic depolymerization. An optimal preprocessing separates the polymer chains and creates a solution of the polymeric chains. Thereafter, we might focus on the amide bond-breaking reaction, aiming to remonomerize the polymer and to obtain the desired monomer, caprolactam. After a feasible pretreatment, the hydrolysis can be realized at moderate temperatures supported by homogeneous, enzymatic or heterogeneous catalysts.

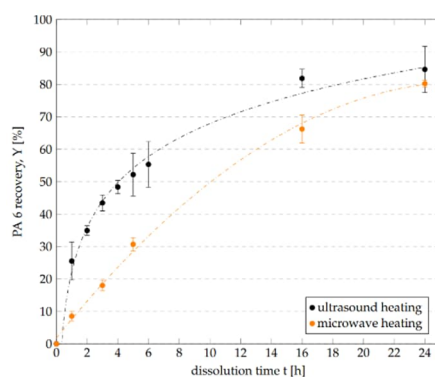
## 2. Methods

A low warp filament of PA6 (for 3D print,  $\phi$  1.75 mm) was cut into 10 mm pieces. A water bath was used for the decomposition studies of PA6 using an ultrasound-assisted (35 kHz) reaction intensification. For comparison of the ultrasound treatment with microwave heating, we used Discover 2.0 microwave synthesizer from CEM GmbH, Germany (2.45 GHz).

A homogeneous liquid solution CaCl<sub>2</sub>, EtOH and H<sub>2</sub>O was created in the ultrasound bath at 25°C. The solution comprised EtOH (99.9%),  $x_{\text{EtOH}} = 0.625$ , CaCl<sub>2</sub> (p.a),  $x_{\text{CaCl}_2} = 0.125$ , balanced with ultra pure water. For an experiment, 1 g of the PA6 was mixed with 8.5 g of CaCl<sub>2</sub>-EtOH-H<sub>2</sub>O solution. The sealed Pyrex glass vessel containing the PA6-liquid reaction mixture was placed in a preheated ultrasound bath for the desired time. Alternatively, after adding a coated stir bar the Pyrex vessel was placed into the temperature-controlled microwave reactor and stirred for the desired time. The experiments were carried out at 75°C. After an experiment, the undissolved, solid residue PA6 pieces were removed from the reactor, dried and weighed. After filtration, the reactor effluent formed a clear solution (comprising CaCl<sub>2</sub>, EtOH, H<sub>2</sub>O and solved polymer chains). To quantify the solved polymer chains, excess of H<sub>2</sub>O was added to the solution as an antisolvent. The obtained precipitate was analyzed (to confirm the exclusion of CaCl<sub>2</sub> precipitate) and weighted to check the mass balance of the PA6.

### 3. Results and discussion

The applied intensification method (microwave or ultrasound) had a clear effect on the solving rate of the PA6 pieces. Fig 1 shows PA6 recovery,  $Y$  [%] as a function of reaction time, obtained as the ratio of the weighted amount of *recovered* PA6 precipitate in relation to initial PA6 loading into the reactor. By the ultrasound intensified heating, the rate of PA6 dissolution was clearly higher than that using microwave (see Fig.1). About 50 % of the PA6 was solubilized in 4 h using ultrasound assistance. For dissolution times  $> 16$  h, the differences between the heating methods were less pronounced. Finally, with both ultrasound assistance and microwave heating we could achieve full solution of the PA6 after 72 h.



**Figure 1.** Influence of the heating method on the recovery of PA6 as a function of reaction time. Experiments with  $\text{CaCl}_2\text{:EtOH}$  (n:n 0.125:0.625 balanced with water) using PA6/solution ratio of 8.5 (wt:wt) and  $T=75^\circ\text{C}$ .

The observed phenomenon of breaking the tight hydrogen bond network of PA6 bulk pieces is crucial to realize a resource-efficient recycling. This mild pretreatment ( $T = 75^\circ\text{C}$ ) paves the way for catalytic depolymerization of PA6. By converting the solid PA6 pieces into a *solution* of the polymer chains, the sensitive amide bonds become more accessible to chemical reactions. So, the catalytic breakage of the amide bond in the polymer chains can be achieved to obtain caprolactam as a valuable, recyclable resource for further repolymerization. As next, heterogeneous catalysts are applied for the remonomerization reaction (amide bond breakage). Heterogeneously catalyzed remonomerization provides an enormous potential for more efficient and economically feasible polyamide recycling processes [2].

### 4. Conclusions

Ultrasound or microwave-supported treatments under mild temperature conditions are suitable to break down the hydrogen bonds between the PA6 polymer chains and in such a way facilitate the dissolution of solid PA6. Kinetically, the dissolution using the ultrasound-assisted heating is faster than the microwave-heated system. The ultrasound or microwave-supported dissolution of PA6 proceeds without an active amide bond scission, but the investigated thermo-chemical treatment is highly advantageous for the subsequent chemical depolymerization. The efficient breakage of the hydrogen bonds allows the catalyst access toward the amide moiety and, therefore facilitates the hydrolysis of the amide bonding under mild temperatures.

### References

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