

Melt Polycondensation for the Synthesis of Polyester Amides using Kneader Reactor Technology

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Dedicated to Ennio Vanoli for his continuous & innovative support and inspiring art!

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Abstract: In this work, we discuss the process development and scale-up of the melt polycondensation of polyester amides from a laboratory scale to kg-scale in a kneader reactor. We identified and optimized the most important critical parameters and produced kg-quantities of polyester amides with Mn up to 25'000 g/mol and reproducible thermal and mechanical properties. The special kneader reactor allows safe and efficient scale-up of polymerisation reactions at high temperature and viscous melts due to good mixing and efficient mass transfer.

Keywords: Kneader Reactor · Polycondensation · Polyester Amides · Process Development

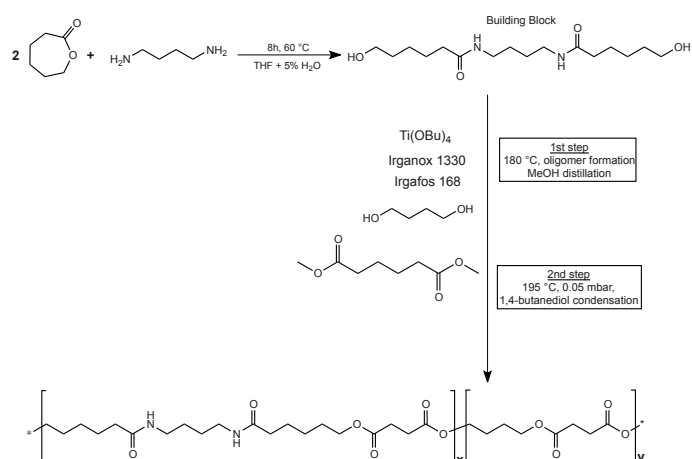
Introduction & Context

The packaging industry relies extensively on polymers due to their convenient properties such as transparency, flexibility, and robustness to mechanical strain. However, a large part of the polymers used in packaging are non-renewable (petroleum derivatives), non-biodegradable and difficult to recycle as they are often highly complex multi-laminate films. This and the large quantities of plastic that are produced every year contribute to today's known environmental problems with plastic waste and microplastics. Therefore, new approaches are required in view of circular plastic economy that includes recycling, composting and of course the search and development of new polymers.^[1]

Polyester amides (PEA) are a family of copolymers based on ester and amide linkages which allow physical and chemical properties in between polyesters (better biodegradability and solubility, lower melting temperatures) and polyamides (better mechanical resistance, efficient gas barrier abilities).^[2] The polymer properties can be tuned by varying the ratios of ester and amide linkages. These copolymers were first developed to achieve a biodegradable polymer with thermal and mechanical properties comparable to polyamides due the hydrogen bonding of the amide bonds.^[3,4] For these reasons, polyester amides are suitable candidates to replace part of the polymers used today in the packaging industry.^[5] In this work, a known bio-based biodegradable block polyester amide was selected to develop a melt polycondensation process. The application of this copolymer is to serve as a food packaging flexible film to replace polyolefins as the gas barrier properties are similar.^[6]

Synthesis of PEA – Lab Development

The polyester amide block copolymers can be prepared by melt polycondensation using an amide segment building block, *N,N'*-1,4-butanediylbis(6-hydroxyhexanamide), referred below as '6,4-bisamidediol', along with 1,4-butanediol and dimethyl adipate as the ester segment. The amide segmented building block was synthesized by the ring-opening of ϵ -caprolactone with 1,4-diaminobutane (Scheme 1).^[5,6] As purity of this building block is crucial for successful polycondensation we invested some time in optimizing the synthesis and purification thereof to remove any oligomeric impurities and remaining 1,4-diaminobutane to avoid coloration of the polymer. We observed that the reaction rate for the ring-opening of ϵ -caprolactone with 1,4-diaminobutane increased with water content in the solvent system. And a subsequent reaction between the ϵ -caprolactone and desired 6,4-bisamidediol leads to the formation of an oligomeric impurity, decreasing the overall selectivity. This impurity is rather difficult to eliminate and therefore significant quantities of the building block are lost during the purification step. A factorial design of experiment (DoE) was performed to improve the recrystallization yields. A clear result of this process is that a basic pre-treatment (1 mol/L KOH in methanol) is able to hydrolyse the impurity and yield a very pure building block. Other synthesis solvents were also tested along the DoE and tert-butyl-methylether (TBME) allowed a faster reaction and cleaner crude product (82% purity). It was also observed that this solvent enables the formation of granular shape crystals. This property allowed a much more efficient filtration and cleaning of unreacted diamine. Having the optimized process in hand the synthesis of the amide segmented building block was successfully scaled-up to kg-quantities.



Scheme 1. Synthesis of poly(ester-amides) via melt polycondensation of *N,N'*-1,4-butanediylbis(6-hydroxyhexanamide), 1,4-butanediol, and dimethyladipate.

Next polyester amides were prepared through melt polycondensation reactions using the amide segmented building block, 1,4-butanediol, and dimethyl adipate as reported by Lips^[5,7] and Stapert^[8] (Scheme 1). By allowing variations of the ratio between the hard and soft segments, a certain tuning of mechanical and

thermal properties of the copolymer is possible. In general, the higher share of hard-segment content, the more hydrogen bonding is created (between amide functional groups) leading to stiffer, less soluble and higher melting polymer. For our process development and scale-up studies we selected a PEA with 50% amide segment content which has oxygen-barrier properties similar to polypropylene.^[6]

On the lab scale, the melt polymerization was performed using a three-necked round bottom flask for a one-pot, two-step process. First a prepolymer was made at 180 °C with step-wise reductions in pressure (*ca.* 100 mbar) to distill off methanol. After methanol removal, the temperature was increased to 195 °C and high vacuum (0.04 mbar) was applied to remove 1,4-butanediol thus driving the reaction towards higher molecular weights for the PEA polymer. Titanium butoxide was used as the catalyst (*ca.* 0.3%) and the addition of antioxidants (Irganox 1330 and Irgafos 168) helped to prevent thermal degradation of the polymer at high temperatures. Different polymerisation conditions (stirrer geometry, stirring speed, reaction temperature, reaction time, vacuum pressure) were tested at lab scale (50 mL to 300 mL). The most important factors highlighted in these trials were the sensitivity of the melt reaction mixture to oxygen and the fact that the polycondensation rate is driven by the mass-transfer of 1,4-butanediol. At lab-scale, a colouration of the reaction mass was observed with an air leak (into the reactor) of 0.16 mbar (from 0.03 to 0.19 mbar). The reactions were operated at a temperature range of 180 to 195 °C during 6 to 9 hours yielding a light-yellow polymer (dark brown in presence of oxygen).

The PEAs prepared were routinely characterised by DSC, ¹H-NMR and FT-IR. The ¹H-NMR spectra confirmed the chemical structure of the polymers and allowed an estimation of the molecular weight by end group analysis. In addition, the molecular weights and molecular weight distributions of the PEAs were determined by size exclusion chromatography (SEC) measurements with hexafluoro-isopropanol as the eluent.

Process Development in the Kneader Reactor

The polycondensation process was scaled up to a 3L scale using a stainless-steel kneader reactor adapted for viscous melts (twin shaft mixer and back-mix mono-screw, CRP 2.5 Batch from List AG, Arisdorf) (Fig. 1).^[9] The double-axial mixing allowed an increase of the 1,4-butanediol mass transfer. However the vacuum quality was severely impacted due to the connection between the motor and the mixers being a stuffing box seal. The formed polymer has a dark brown colour, but the mechanical properties are very close to the lab-scale trials. The main difference was that, at a similar estimated molecular weight (*M_n*), the lab-scale sample (*M_n* = ~13'300 g/mol) was able to be stretched and the scaled-up process polymer sample (*M_n* = ~12'800 g/mol) was breaking at a comparable strain. The increase in molecular weight (*M_n* = ~12'800 to 19'000 g/mol) allowed for the yielding behaviour (stretching) to be present again. The reactions were carried at 195 °C for 10 hours yielding 1 kg of polymer per batch.

The reactor sealing variability was identified as the cause of the polymer colouration along with the building block quality. Both of these aspects were improved: the sealing material was reshaped in the reactor stuffing box and the following syntheses were done using the building block made with TBME, therefore cleared from diamine traces. These trials resulted in a clear light-brown polymer with higher molecular weight (*M_n* = 20'000 to 25'000 g/mol).

In summary, we have studied the melt polycondensation of polyester amides on a laboratory scale, identified and optimized the most important critical parameters and successfully scaled the process to kg-quantities in the kneader reactor obtaining polyester amides with *M_n* up to 25'000 g/mol and reproducible thermal and mechanical properties. This special kneader reactor allows safe and efficient scale-up of the polymerization reaction at high temperature and viscous melts. Although the vacuum is less efficient compared to lab scale, good mixing allows short reaction times and efficient mass transfer.

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Fig. 1. Scale-up of the melt polycondensation in the kneader reactor.