

# PROCESS OPTIMIZATION FOR REACTIVE BLENDING AND COMPATIBILIZATION OF PA 6 AND PET IN EXTRUSION

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## Abstract

Blends of PA and PET do not have a minor significance in industrial production any more. Especially since the European beverage industry decided to use (multi- and single layer) PET bottles containing PA, the economic and ecological interest in recycling PA and PET is stringently increasing.

In former research projects, where IKV has been involved, the compatibilization of PA and PET in extrusion was simply established. New investigations, focussing on the process optimization, enable to correlate the process parameters with the material properties. Therefore an extruder cascade was developed for a one-step-in-situ compatibilization and in addition a new characteristic parameter was constituted which is independent of the type of extruder.

## Introduction and Motivation

After a rough mixing of two incompatible polymers like PA 6 and PET the phase character is generally presented as the morphology structure shows in Fig. 1 (above, left side). The forming of matrix and disperse phase of the components depends on different factors, e.g. mass or viscosity ratio of the components (1). In these investigations polyamide always forms the disperse phase.

After leaving the mixing zones of a twin screw extruder, the polymer melt is only loaded by the shear stress of simple conveying elements. As a result of the chemical incompatibilities in an uncompatibilised blend an enlargement occurred to the disperse phase caused by particle coalescence and a conditioned reunification (see Fig 1 below) (1). Finally the chemical and mechanical properties of the blend deteriorate enormously in respect to the properties of each single component.

## Solution

By using block copolymers, formed of both polymer components by reactive extrusion in a co-rotating intermeshing twin-screw extruder, a chemical compatibility is established in the boundary layer (2). The copolymers backbone consists of PA and PET sequences. Thus is possible for the macromolecules of both components to

"deposit" near to "it's" similar component of the copolymer chain, which is illustrated in Fig. 1 (above, right side). Thereby the morphological structure of the blend is stabilized and the tendency of the disperse particles to reunite is suppressed.

## Preliminary Experiments

For stabilizing the achieved particle size in the mixing zone, the following reaction steps, presented in (5), have to be done.

*Functionalization:* During the first step a PA 6 is converted using an acid anhydride (TMA), so that a low-functional polyamide is produced (Fig. 2, Step 1). The functionalized PA is pelletized and dried at a temperature of 80 °C to avoid a hydrolytic degradation of PET in the following separate extrusion steps.

The modified polyamide breaks down then in a *trans-esterification reaction* into the added PET to create low-molecular polyesteramides (Fig. 3, Step 2) initially. The blend is pelletized again and dried as described in the first Step .

In order to achieve the required improvement in the mechanical and chemical properties, the polyesteramide have to be *coupled up* to highmolecular block-copolyesteramides with bifunctional bisoxazoline or diurethane (Step 3).

All reactions take place in a separate extrusion process in a co-rotating intermeshing twin-screw extruder with a length of 41 D. For each step pelletizing and drying was apparently necessary. Obviously the thermal and mechanical load of the blend has a huge influence on the quality of the produced polymer (5). Considering these facts new investigations were made at IKV to optimize the process and the material properties: For each reaction step the screw design an the process parameters were evaluated in respect to their potentiality for an implementing into a one-step cascade process.

Preliminary tests with laboratory kneaders (Brabender Plastograph) and plate-to-plate rheometers have shown that during a residence time of less than 120 s the functionalisation is already terminated. Concerning to these results it was decided to reduce the length of the

functionalization-extruder to 29 D (instead of 41 D) with a residence time of three minutes. The reaction can take place during that time and the load of the melt is reduced.

These results led to the conclusion to execute the functionalization on a twin screw extruder with a length of 29D. Further on the process of trans-esterification and coupling is realizable at the same time in one twin-screw extruder with 41D by using different down stream feeding positions for each reaction.

### Effects on the morphological structure

For the optimization of the screw geometry special "sample-takers" are placed along the mixing zone. In that way the influence of the kneading elements can be observed online at any position along the screw by analysing the morphological structure of the blend.

The morphological structure of an *uncoupled* "simple" trans-esterificated blend is characterised in Fig. 3 (pictures 1 to 3 below). It is proved that in this test series more than three numbers of mixing blocks do not lead to a significant influence on the diameter of the polyamide particles. Leaving the mixing zone a slight enlargement of the particle size is perceptible, probably caused by coalescence effects, which were described above.

Adding the bifunctional coupler, the diameter of the disperse phase can typically be reduced (Fig. 3 pictures above) in comparison to the samples taken at the die, which were formed only by trans-esterification without coupling.

For the following experiments the process of trans-esterification as well as the coupling were done together in a twin-screw extruder with the length of 41D, whereby the number of kneading blocks was reduced to three, in order to minimize the shear stress. Moreover the design of the melting zone was changed to enable the connection of the functionalization-extruder for the cascade. The functionalization was done in a separate extruder so that the blend process was optimized to a two-step-process.

### Compounding Experiments with a Two-Step-Process

In past investigations (5) a correlation between process parameters and material properties could only be proved for tendencies. Well defined dependencies were not found out. One reason could be various interactions between the process and reaction parameters as well as the formation of the copolymer. Therefore the following test series of a two-step-process (separate functionalization, trans-esterification and coupling) are based on statistical process plans. Furthermore the influence of the new

characteristic parameter, the shear deformation, was examined as product of residence time and shear rate to constitute a parameter which is independent of the type of machine.

In Fig. 4 the average particle diameter of the PA phase depending on the shear deformation is illustrated. In this diagram the residence time is a constant parameter so that an increasing shear deformation only refers to a higher shear rate. The degree of functionalization is represented by the molecular weight. The influence of different molecular weights and different shear rates on the diameter corresponds to the expectations given by literature (1, 5). A smaller degree of functionalisation causes an increasing of the molecular weight of the functionalized PA and the viscosity of the PA approaches the PET. By this fact an improvement of the condition for smaller particle diameters is established.

Finally the influence of the coupling agent is characterized by a typical way. The linear dependency of the particle diameter on the coupler can be observed by a parallel displacement of the black graph down into the blue graph in Fig. 4.

### Compounding Experiments with an Extruder Cascade

To reduce the influences of pelletising and drying -and by that way reducing the load of the polymer- all reaction steps are now implemented into a one-step in-situ-process, which is presented in Fig. 5. The extruder which has been used previously for the trans-esterification and coupling is slightly changed. By adding a sidefeeder element in the mixing zone the functionalization-extruder "extruded" directly the functionalized PA 6 into the PET melt. All intermediate drying steps become unnecessary and the whole process becomes more economical. In the following chapter several results of the cascade experiments are presented to underline the improvement, profiting from the one-step-process.

In Fig. 6 the influence of coupler and mix ratio of PA/PET is represented. Obviously an improvement of the tensile modulus in dependency on the coupling agent can only be observed within an amount of 18 to 24 % PA. Above 24 % of PA a definite dependency can not be established. For a subsequent accurate modeling of the process strong dependencies are unavoidable, so that a mix ratio PA/PET of 20/80 is used.

During the experiments with the developed extruder cascade several important facts have been established: With this new extrusion concept strict requirements are placed on the handling of the start up phase to achieve a stabile process state. However the

process is running, the process time to produce the final blend is reduced enormously, as expected. Moreover no dryers have to be used and a change of material for a new charge is completed within *several minutes*. With respect to achieve an optimization of the blend process several mechanical properties of blends were produced with the two-step and one-step process, which are presented in Fig. 7. An increasing of all presented properties can be noticed for the one-step process.

The investigations have shown that it is possible to compatibilise an immiscible polymer blend. However for an industrial perspective it is necessary to minimize the effort and complexity of the compatibilisation process: Not every company has the opportunity to install a full compatibilization process but a conventional compounding extruder. If the compatibilized blend can be formed with a high amount of coupled copolyesteramid, it may possible to generate a masterbatch of copolymer. An improvement of the mechanical properties could be expected precisely by adding this masterbatch to uncompatibilised PA and PET in a conventional compounding process.

Concerning to these expectations several tests were done with post consumer PET and PA. In Fig. 8 the mechanical properties of different blends are represented. Evidently the fracture stress of post consumer material increases for the blend, which is produced by the one-step-process. Similar results are presented for blends while only a copolyesteramide masterbatch is added (right column). Unfortunately the graph of the fracture elongation does not lead to a similar behavior. Further investigations have to be done to characterize that behavior. But it can be established that the employment of a compatibilised Masterbatch gives an important perspective for companies to recycle post consumer PA/PET material.

## Conclusions

The present investigations show that meanwhile a good forecast of the attainable particle diameters is given. With a good accuracy, correlations of individual process parameters are possible to material properties. To find conclusions for the morphology of the material properties further investigations have to follow. The "shear deformation" as an process parameter which is independent on the type of the extruder is proved as useful. Investigations at other screw configurations will enable additional conclusions. The modeling of the functionalization and coupling has been nearly finished. It can be implemented in a modular way into the new version of the simulation program MOREX.

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## Key Words

compatibilization, recycling, morphology, extrusion

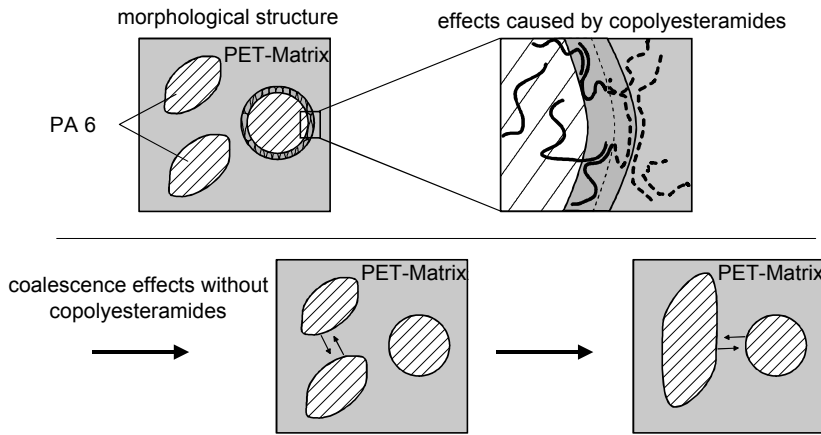


Fig. 1 Morphology of PET-PA-blends

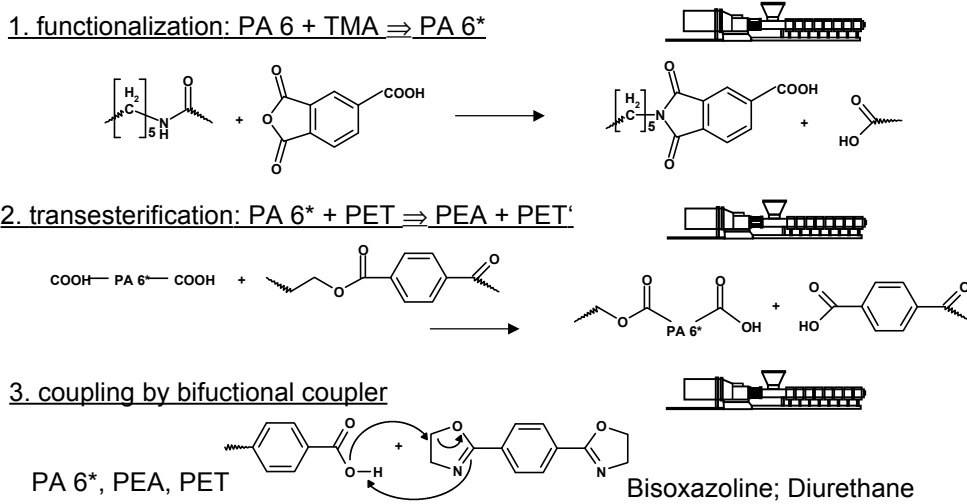


Fig. 2 3-Step-process for the formation of PA-PET block copolymers

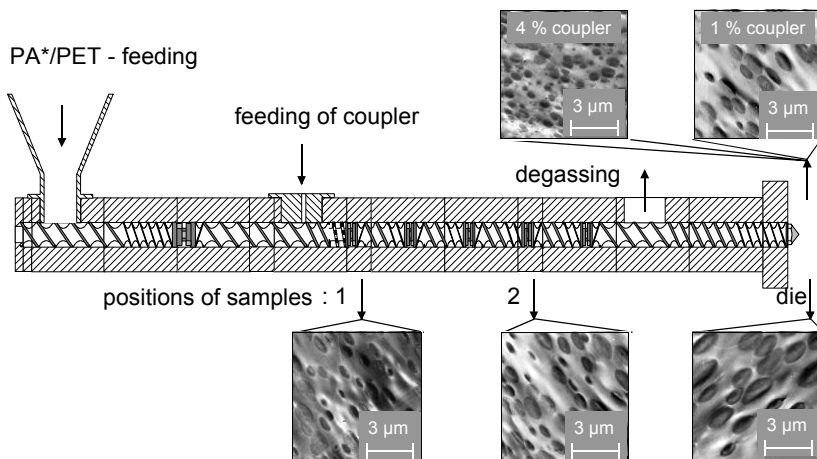


Fig. 3 Development of the blend morphology in a twin screw extruder

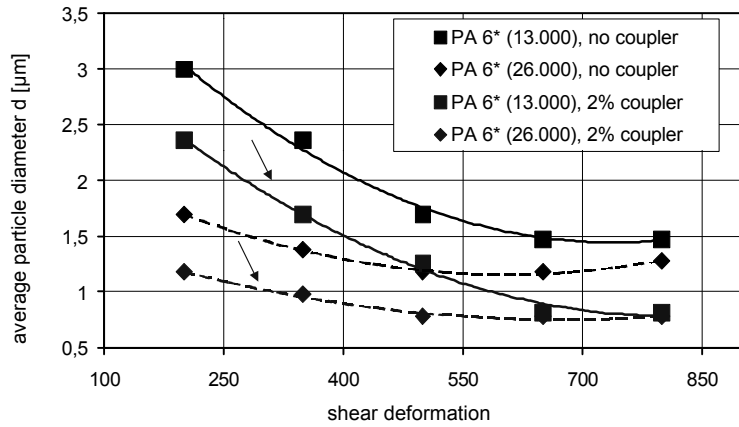


Fig. 4 Diameter of PA particles in the PET matrix in dependence on the shear deformation

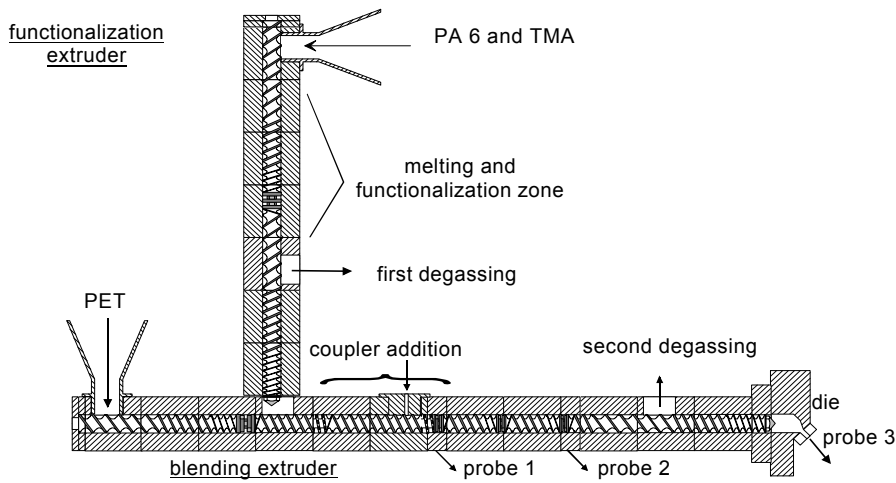


Fig. 5 Set-up for in-situ-compatibilization of PA6 and PET using a cascade extruder

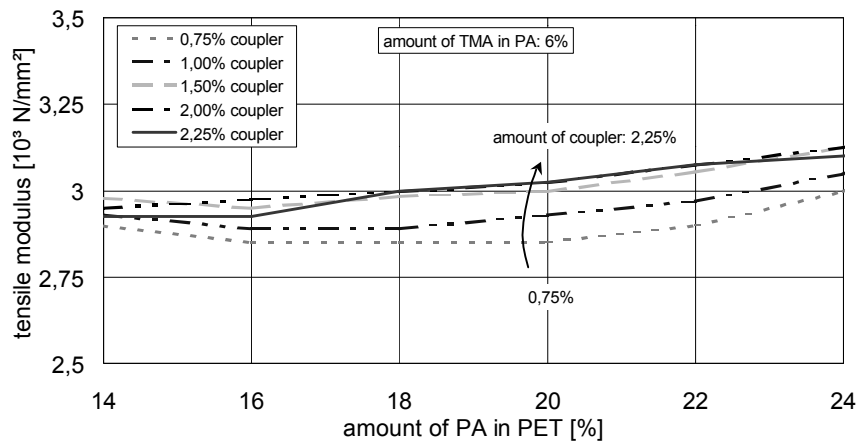


Fig. 6 Influence of coupler and mixing ratio of PA/PET on the mechanical properties

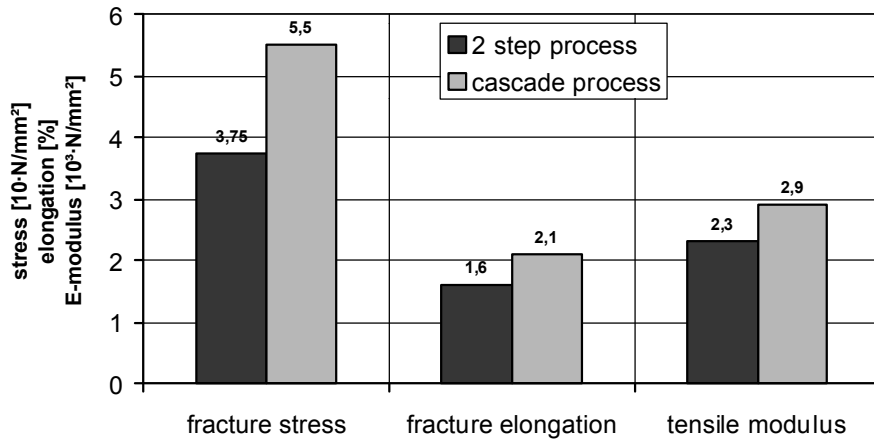


Fig. 7 Comparison of 2-Step-process and cascade extrusion process

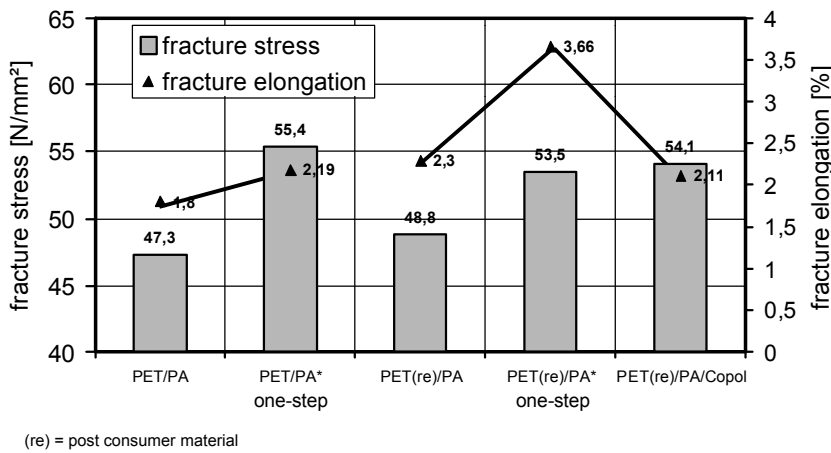


Fig. 8 Mechanical properties in dependence on different types of compatibilization