

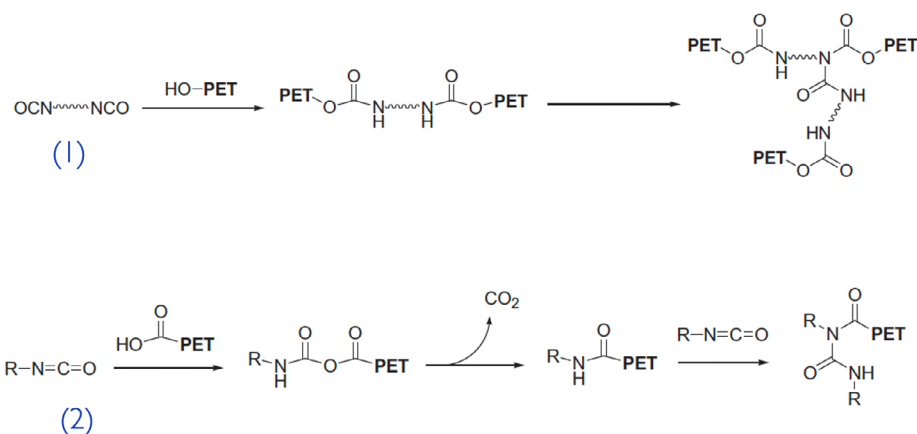
# In-situ monitoring of chain extension reaction of Poly(ethylene terephthalate) (PET) in Xplore MC15 HT using a diisocyanate

## Background

Poly(ethylene terephthalate) (PET) is one of the most widely used polymers in large-scale industrial productions all over the world, especially in manufacturing of soft-drink beverage bottles, rigid packaging trays, packaging films and industrial/textile fibers. Owing to increasing concerns on circularity, recycling of PET attracts great attention. However, recycling of PET is not a straight-forward processing operation since it undergoes hydrolytic and thermo-oxidative degradation during mechanical recycling resulting in some serious molecular weight reduction and change of the chemical structure, which limit PET's use in many added value applications by lowering the melt-viscosity, melt strength and mechanical properties [1].

One of the methods potentially used to upcycle PET is the usage of chain extenders. Chain extenders are usually small molecules that contain at least two functional groups

capable of reacting, in the case of PET, with the carboxylic and/or alcoholic end groups of the macromolecule with the formation of new covalent bonds. Depending on the nature, reactivity and number of functionalities present on the chain extender molecule, different chemistries of the bridging functional groups and different macromolecular architectures can be obtained, leading to different properties of the final material. Linear aliphatic or aromatic di-isocyanates are known to be reactive towards both type of functionalities of PET, such as -OH and -COOH. The reaction with -OH is much faster and leads to the formation of a stable carbamate, while the reaction with -COOH of PET yields unstable O-acylcarbamates that eventually decomposes to amides by releasing CO<sub>2</sub> (see Figure 1).



**Figure 1.** A schematic showing the reaction of a di-isocyanate with (1) -OH end groups of PET; (2) -COOH ends groups of PET [2]

In comparison to the advanced characterization techniques which require detailed analysis of large data sets for statistically relevant quantitative assessment of polymer structures, such as, thermal analysis, IR-spectroscopy, XRD, etc., rheological analyses enable macroscopic evaluation of polymer melts and possess relevant data regarding to chemical architecture of the molecules. Therefore, monitoring the change in the rheological properties of a polymer melt during reactive processing, such as chain extension, gives direct access to track the structural changes in the polymer melt [3].

Xplore MC15HT, the flagship of Xplore's instrument portfolio, is equipped with a high-resolution on-line torque measurement system (0-40 Nm range with a resolution of 0,01 Nm), where torque can easily be associated to the change of the melt-rheology of a polymer-melt during processing. In combination with the rheology software of Xplore (See: <https://www.xplore-together.com/products/software-rheological>), it is even possible to track the changes in the shear viscosity of a polymer melt once it is molten and while being compounded. In this application note, we demonstrated in-situ monitoring of chain extension reaction of an amorphous PET resin during reactive processing.

### Experimental

Glycol modified PET (known as PETG) was used as the base resin. 1,4-phenylene diisocyanate (PDI) (Sigma-Aldrich) was preferred as the

chain extender. Its melting and boiling point is reported as  $T_m=96-99^{\circ}\text{C}$ ,  $T_b=260^{\circ}\text{C}$ , respectively. Prior to processing, PET was dried at  $80^{\circ}\text{C}$  for 12 hrs in a vacuum oven to remove the moisture.

An Xplore MC15-HT, a co-rotating, intermeshing twin-screw micro-compounder, was used as the processing instrument. The barrel temperature and screw speed were set to  $230^{\circ}\text{C}$  and 50 rpm, respectively. Feeding of PET was completed in 30 seconds from the top water-cooled hopper of the compounder (see Figure 2). This was followed by allowing the PET to homogeneously melt for 1,5 min. After that period, chain extender (2% by weight) was added directly to the melt from the top of the MC15HT. The torque along the processing was monitored with respect to time. As a control experiment, similar process was repeated for a neat PET resin under same conditions.

To judge the change of the molecular weight of the PET resin before and after the chain extension, gel permeation chromatography measurements were conducted using an Agilent GPC. Hexafluoroisopropyl alcohol was used as the mobile phase for GPC analysis based on polystyrene standards. Samples were run at 0.1% (wt/vol) using an injection volume of 25  $\mu\text{l}$  and a flow rate of 1 m/min

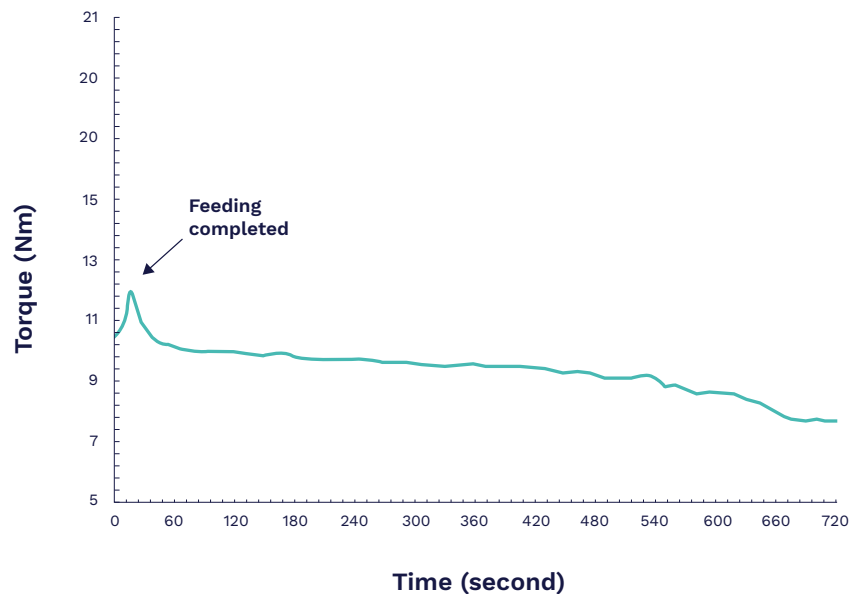


**Figure 2.** Both PET resin in pellet form and the chain extender in powder form added from the top water-cooled hopper of MC15 HT

## Results and discussion

Figure 3 shows torque versus time plot, the in-situ torque measurement, of PET in the absence of a chain extender. The peak torque seen around 30 s is due to the feeding of the PET granules into MC15HT. Since the granules were continuously fed to the compounder at 100 rpm, crushing and melting of these solid granules increased the torque value abruptly in the beginning of the process. Melting and shear-thinning of polymer occurred because

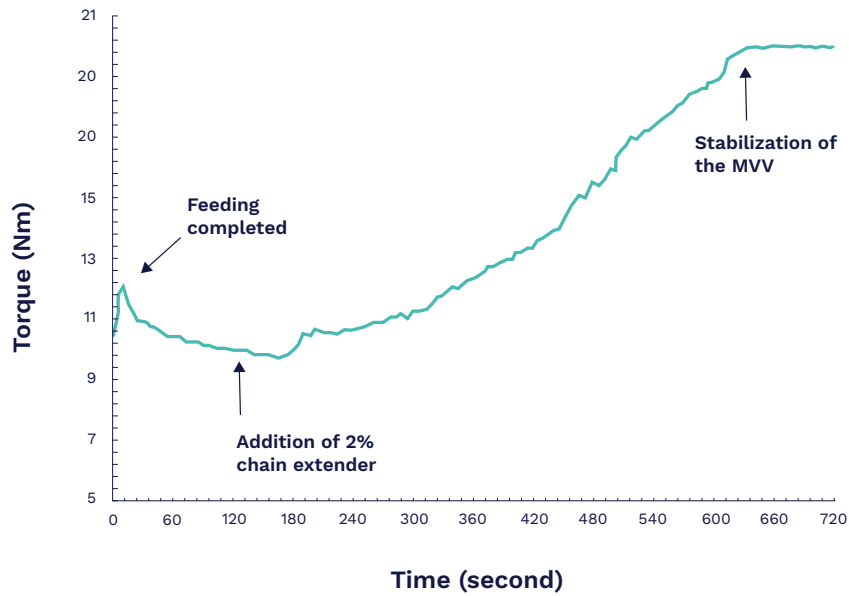
of the shear forces exerted onto PET granules by the co-rotating twin-screws together with the heat input through the barrel. As a result, the torque value started to decrease. Since the PET was dried prior to processing, we did not see a sharp decrease in torque value during the melt processing till 8th min. After that, torque dropped down drastically due to possible chain scission caused by thermo-oxidation and hydrolysis of PET.



**Figure 3.** Torque vs time for PET in the absence of a chain extender

In the presence of a chain extender, the characteristics of torque vs time curve was different (see Figure 4). After feeding and melting of granules, the isocyanate chain extender was introduced directly into the melt at 2nd min. After an induction period of 1 min, during which diisocyanate melted and mixed with PET, torque started to increase. By the help of the diisocyanate, PET molecules coupled to form linear and/or branched structures that resulted in an increase of both number average and weight average molecular weight of PET. Hence,

the melt viscosity improved, meaning that more torque was needed to maintain the same rpm to sustain the processing. The rise of the torque continued till it was doubled. After approximately 10 min, torque vs time plot reached to a plateau since all the chain extender, which was added in the beginning, consumed intra-chain reactions. Reaching to this maximum point depends on several factors, such as, the type and concentration of chain extender, the screw speed and barrel temperature, and the initial moisture content of the polyester.



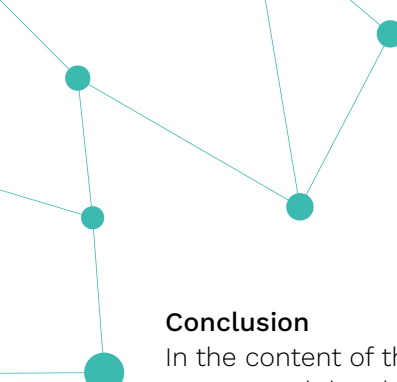
**Figure 4.** Torque vs time for PET in the absence of a chain extender

**Table 1:** GPC results of PET resin before and after chain extension

Sample name	M <sub>n</sub> (g/mol)	M <sub>w</sub> (g/mol)	PDI
Before Extension	12,030	31,200	2.59
After Extension	17,425	56,310	3.23

To judge the effectiveness of the chain extender after reactive processing, GPC measurements were conducted (Table 1). It was found that after chain extension, both number and weight average molecular weights of PET was

increased, approximately 55% and 70%, respectively. In addition, the polydispersity of the extended PET was also increased from 2,59 to 3,23, showing that branching of PET was also happened besides linear extension.



## Conclusion

In the content of this technical note, we demonstrated the chain extension of PET using phenylene diisocyanate (PDI). Having relatively higher boiling point and high affinity towards the chain ends of PET, especially to -OH ends, PDI is a high potent chain extender for PET. It was found that both Mn and Mw of PET resin was increased after reactive processing. It was shown that MC15 HT is a versatile tool to simultaneously perform reactive compounding and to monitor the in-situ change of the melt rheology during processing at small scale. Thanks to high resolution torque measurement of MC15 HT, each processing step, such as feeding, melting, induction time and chain extension/branching can be tracked. MC15 HT gives researchers the opportunity to both prepare a sample using a small amount of material for further testing such as mechanical or thermal tests at a shorter turnover time and to observe the variations in rheology triggered by the change in morphology and chemical architecture of the polymeric material.

## References

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