

## **Effect of cyclic butylene terephthalate (CBT) oligomer on the processability and mechanical properties of a thermoplastic polyester elastomer**

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**Abstract:** *In this study the effect of CBT oligomer on the processability and mechanical properties of a polyester-based thermoplastic elastomer (Hytrel) was investigated. CBT with (CBT160) and without (CBT100) catalyst were mixed to the elastomer, up to 20 wt%, in a laboratory twin screw extruder. Tests were performed on specimens cut off from plaques produced by injection molding from the pelletized blends. Rheological (melt flow index) tests indicate that with increasing CBT content the viscosity of the thermoplastic elastomer decreases (resulting in better processability), and the viscosity reduction is less pronounced for the catalyst-free (CBT100) than for the catalyst-containing CBT (CBT160). The tensile strength was unaffected, whereas the tear strength, E-modulus and elongation at break increased slightly or prominently as a function of CBT content acting as reinforcement. At the same CBT content CBT160 outperformed CBT100 with respect to the mechanical properties.*

**Keywords:** *cyclic butylene terephthalate oligomer (CBT), polyester based thermoplastic elastomer, flow properties, mechanical properties*

### **1. INTRODUCTION**

Rubbers, distinguishing themselves by large elasticity from thermosets and thermoplastics, and with distinct characteristics from metals and ceramics, have their own wide application fields. Moreover, they have replaced some other engineering materials due to their exceptional properties and low cost. In the related applications rubbers are rarely used alone, i.e. without fillers, additives or other modifiers. Active fillers or reinforcing agents are added to improve certain physical and mechanical properties (hardness, tensile strength, moduli at different elongations, impact strength etc.). Though filler incorporation increases the mechanical performance but reduces the flexibility of the molecule chains (restricting the number of conformational positions of chain segments near the filler surface) reflected by decreased elongation at break, and set properties [1]. Incorporation of fillers (type, amount, and surface treatment) is a key factor to tailor the properties of rubbers upon request. However, with increasing filler content the processability of rubbers is strongly reduced [2, 3]. As a consequence parts of complex shape, requiring long flow paths, cannot be produced. Even substantial rising of the (injection) pressure may result in underfilling of the mold. Therefore plasticizers, extenders are incorporated to decrease the viscosity of the related mixes. However, they must be completely compatible with the parent rubbers and other compounding ingredients [4]. In addition, if they are added in too high amount, the physical

properties of the products can be negatively affected. Accordingly, an additive which works as reinforcement and viscosity reducer at the same time should be a perfect solution.

The traditional rubber fillers are carbon black (CB) and silica. Both of them are “preformed” nanofillers having a high specific surface area. CB is mainly used as pigment and reinforcement in various rubber and plastic products. The wear properties of CB and/or silica filled rubber products are excellent. The CB reinforced products are black. Therefore for colored products silica is the right choice. By increasing the interaction between the rubber matrices and silica, using different silanes, rubber compounds with very good mechanical and wear properties can be produced (e.g. [5]).

According to our research philosophy suitable candidates to meet the abovementioned task combination, i.e. viscosity reduction during processing and reinforcing after solidification, are cyclic butylene terephthalate oligomers (CBT). CBT is a commercially available macrocyclic oligomer that can be polymerized in the presence of suitable catalysts into the related poly(butylene terephthalate) (PBT) [6]. The CBT oligomers soften at 140°C and melt completely at 160-170°C [7]. The polymerization can be controlled by type and amount of the catalysts. As the polymerized CBT has some peculiarities (e.g. higher crystallinity, higher molecular weight) compared to the traditional PBT produced by polycondensation, it is referred pCBT. CBT is marketed with and without catalysts. With catalyst, CBT can be polymerized into pCBT and it is offered for casted and composite products, for rotational molding and for tooling materials. CBT without catalyst is offered as melt flow enhancer for thermoplastics materials (PC, polyester thermoplastics (PET, PBT, PCT etc.), nylons, acetals (POM), polyolefins, polyphenylene ethers, PVC, ABS, SAN and PMMA.) already. Since the molten CBT have a very low viscosity (about 30 mPas at 190°C – where rubbers are usually processed/cured) it can reduce the viscosity of the rubber mix and markedly improve its processability.

When the polymerization of CBT into pCBT takes place only partly, or does not even occur, the remaining CBT oligomers recrystallize from the melt. The crystals formed by this way may work as reinforcement in the related rubber mix [8-9]. This allows us to replace the traditional rubber fillers (CB, silica) and produce “white” rubbers of reduced density. The latter is due to the fact that the same mechanical performance can be reached at lower CBT content compared to the above active fillers. This strategy has not yet been followed for thermoplastic elastomers. Aim of the present work was to check whether CBT can reduce the viscosity and act simultaneously as reinforcement in a thermoplastic polyester elastomer. The latter was selected to show some inherent compatibility toward CBT.

## **2. MATERIALS, MANUFACTURING AND TESTING**

### **Materials**

As matrix material a polyester-based thermoplastic elastomer (Hytrel<sup>®</sup> G3548L, DuPont USA) was used with a recommended processing temperature of 180°C. The additive was cyclic butylene terephthalate oligomer with (CBT<sup>®</sup>160 – 20 wt%) and without catalyst (CBT<sup>®</sup>100 – 0...20 wt%) provided by Cyclics Europe GmbH, Germany. Table 1 shows the ratio of the components.

	Additive	Additive content	Matrix content
	[-]	[wt%]	[wt%]
1	CBT <sup>®</sup> 100	0	100
2	CBT <sup>®</sup> 100	5	95
3	CBT <sup>®</sup> 100	10	90
4	CBT <sup>®</sup> 100	20	80
5	CBT <sup>®</sup> 160	10	90

**Table 1** Additive amount and type in blends

### Material preparation

The two components were mixed using a Labtech Scientific modular twin-screw extruder with a screw speed of 50 min<sup>-1</sup>, a Labtech water cooling tub and a LZ-120/VS type pelletizer. Table 2 shows the set extruder zone temperatures.

Temperatures										
Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Zone 8	Zone 9	Zone 10	Die
[°C]										
175	180	180	180	180	185	185	185	190	190	185

**Table 2** Extruder zone temperatures

From the pelletized compounds plaques of 80x80x2 mm<sup>3</sup> were produced by an Arburg Allrounder Advance 370S 700-290 injection moulding machine. Prior to the injection moulding the materials were dried for 6 hours at 80°C. Table 3 and Table 4 show the zone temperatures and the injection moulding parameters.

Temperatures						
Hopper	Zone 1	Zone 1	Zone 1	Zone 1	Nozzle	Mould
[°C]						
20	185	195	200	205	210	40

**Table 3** Injection moulding zone temperatures

	Volume	Switch over point	Holding pressure	Holding time	Cooling time	Injection pressure
	[cm <sup>3</sup> ]	[cm <sup>3</sup> ]	[bar]	[s]	[s]	[bar]
matrix	50	11	400	20	30	600
5 wt% CBT100	50	11	400	20	30	490
10 wt% CBT100	50	11	400	20	30	500
20 wt% CBT100	50	11	400	20	30	430
10 wt% CBT160	50	11	400	20	30	300

**Table 4** Injection moulding parameters

The required specimens for the static tensile and tear tests were cut from the injection moulded plaques. Specimens for static tensile test and tear tests were prepared according to the standard EN ISO 8256 Type 3 and EN ISO 34-1, respectively.

### Test methods

Flow properties were determined using a CEAST 7027.000 melt flow index tester at 190°C with 2.16 kg load according to the EN ISO 1133 standard.

Static tensile and tear test were performed on a Zwick Z005 testing machine with a crosshead speed of 100 mm/min at room temperature.

Phase structures of blend were inspected using a Jeol JSM-6380LA scanning electron microscope.

## 3. RESULTS

### Rheological properties

Figure 2 shows the results of the melt flow index (MFI) tests. The MFI value of the blends increased significantly with increasing CBT100 content (without catalyst). Interestingly, the polymerization catalyst-containing CBT (CBT 160) reduced the viscosity (and thus enhanced the MFI) even more than CBT100. The explanation of this finding requires further investigations.

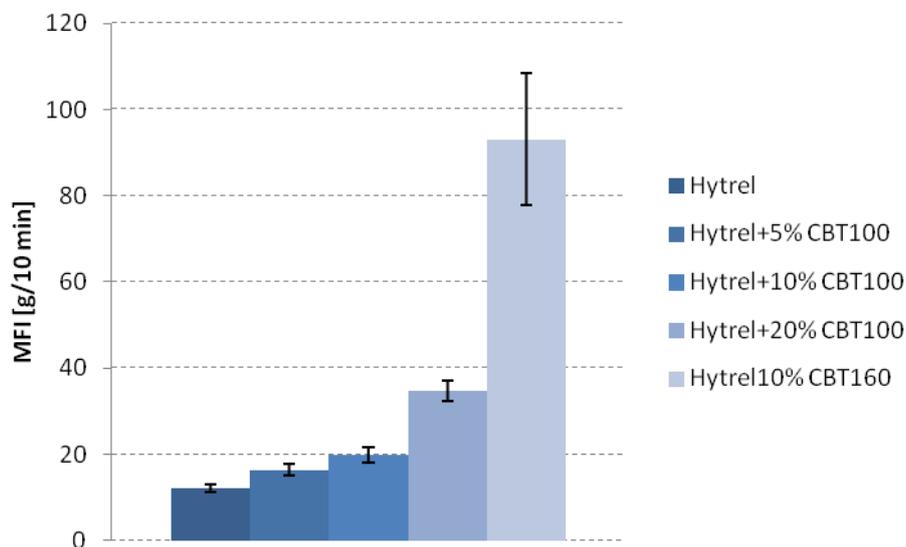
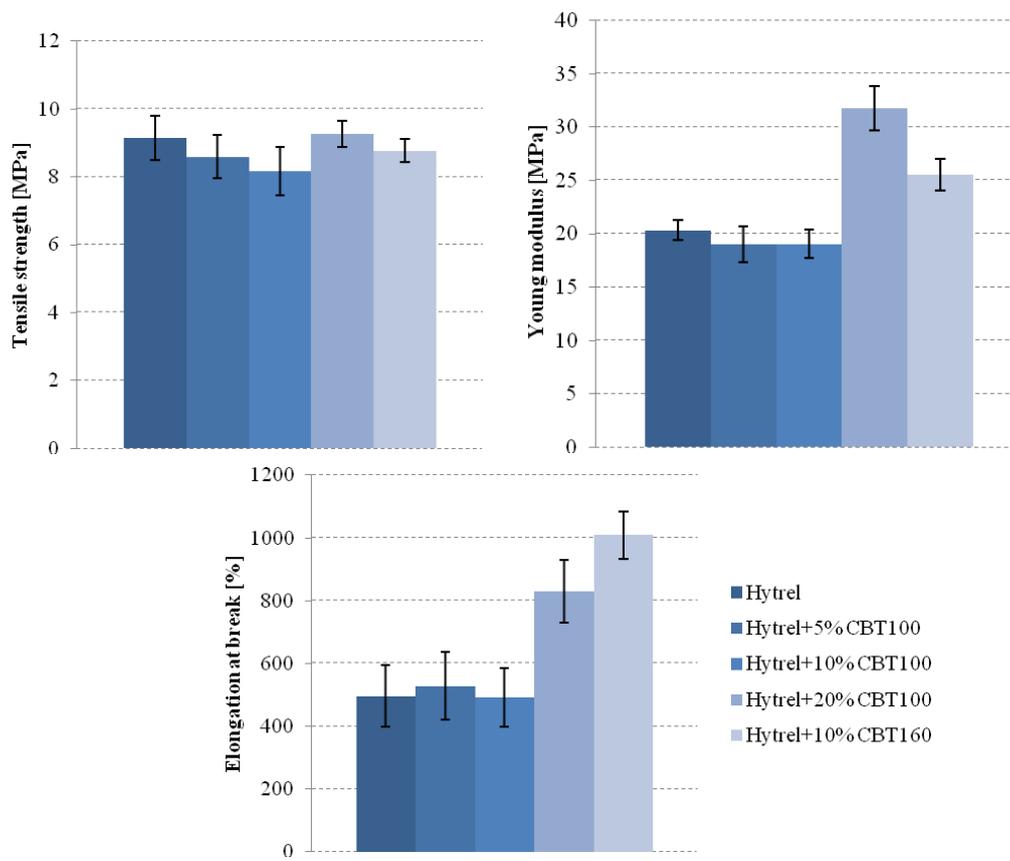


Fig. 2 Melt flow index of the different blends (at 190°C with 2.16 kg load)

### Static tensile tests

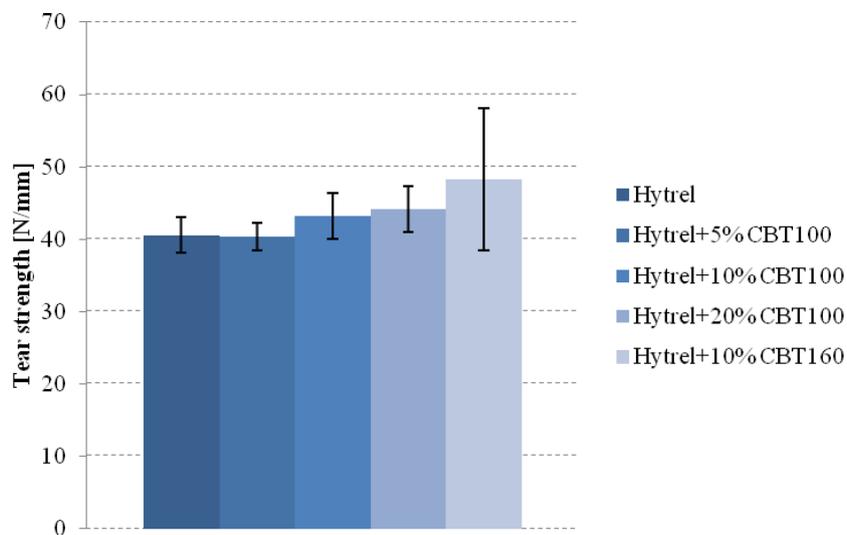
Figure 3 shows the mechanical properties of different blends. The tensile strength did not change significantly with increasing CBT content compared to the elastomer matrix. At 20 wt% CBT100 content a significant increase was observed for both tensile modulus and elongation at break values. The effect of the catalyst is again very pronounced: the tensile modulus and elongation at break values of the 10 wt% CBT160 containing blend are markedly higher than those of the blend containing 10 wt% CBT100.



**Fig. 3** Static tensile properties of the different blends

### Tear tests

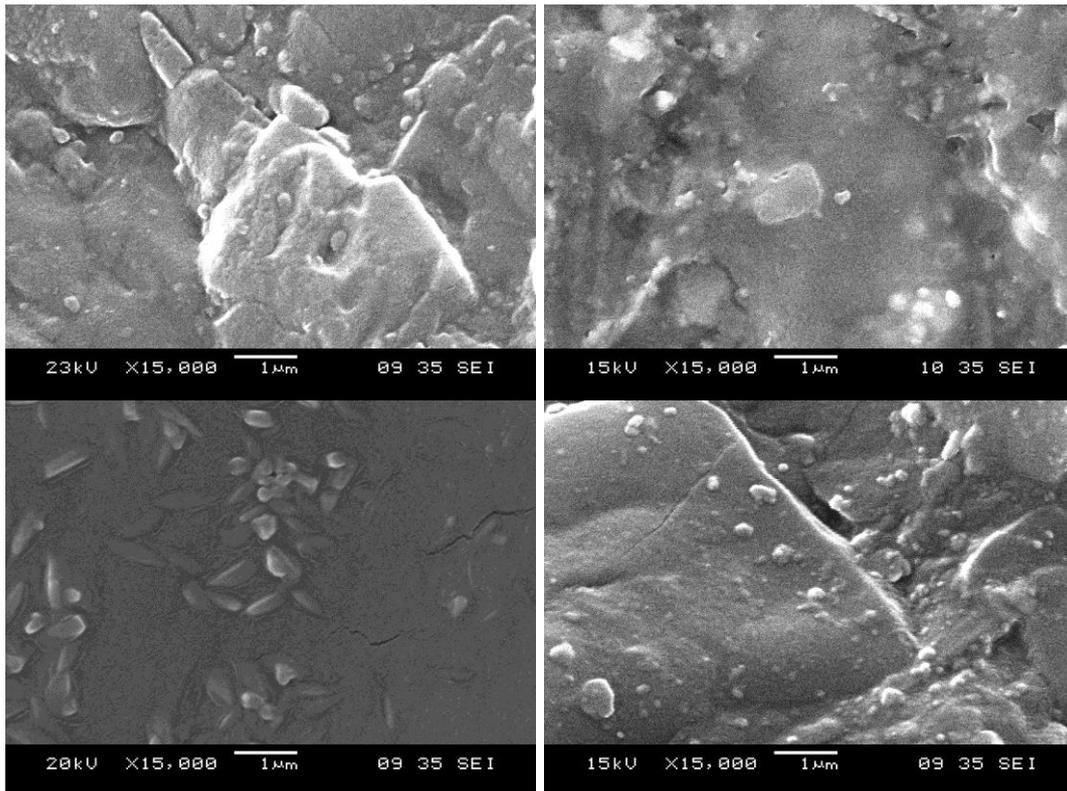
Figure 4 shows the results of the tear tests. The tear resistance slightly increased by adding CBT to the matrix, especially when it was CBT160. On the other hand, it was subject of a relatively large scatter. Further investigations are needed to clarify why the tear strength was only slightly enhanced even when 20 wt% CBT additive was present.



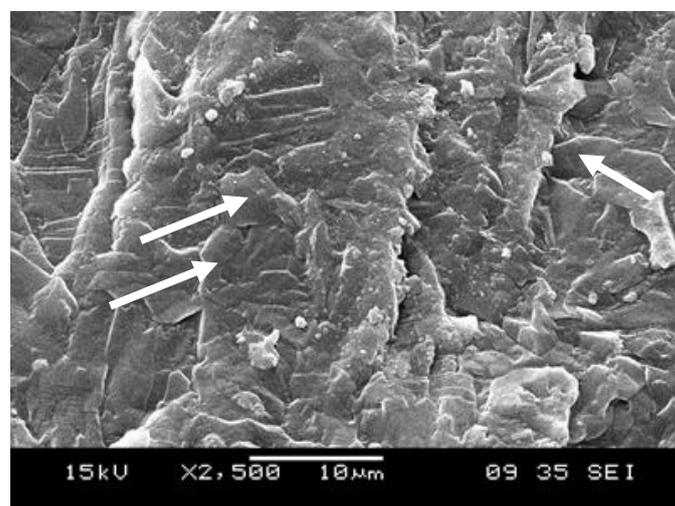
**Fig. 4** Tear strength of the different blends

### Scanning electron microscopy

Phase structure and distribution of CBT in thermoplastic elastomer matrix were observed by scanning electron microscope, analyzing cryo-fractured surfaces of specimens. Figure 5 represents that separate CBT crystals can be seen only by 20 wt% CBT100. This suggests that the solubility limit of CBT in the matrix is somewhere between 10 wt% and 20 wt%. In the blends with 10 wt% CBT 160 no well segregated CBT crystals were found. On the other hand some flat, disc-like domains can be resolved (Fig. 6). The related crystal entities work as reinforcements and this is the most probable explanation for the improvement in the mechanical properties.



**Fig. 5** Cryofractured surfaces of matrix (top left), 10 wt% CBT 100 blend (top right), 20 wt% CBT 100 (bottom left) and 10 wt% CBT 160 (bottom right)



**Fig. 6** Disc-like CBT domains in the TPE with 10 wt% CBT160 (arrows indicate)

## **5. CONCLUSION**

The aim of this paper was to investigate the effect of CBT oligomer on the processability and mechanical properties of a thermoplastic polyester elastomer. The CBT additive strongly enhanced the melt flowability of the modified thermoplastic elastomer. This reduces the energy-requirement of processing and allows the molding of complex parts requiring long flow paths. Besides this, CBT incorporation increased the basic mechanical properties, such as Young's modulus, tear strength and elongation at break. The latter result is highly unexpected because reinforcement should yield an opposed effect in the ductility. Interestingly, the effect of the polymerization catalyst containing CBT (CBT160) was much larger on both the rheological and mechanical parameters than the neat CBT. This suggests that CBT160 underwent ring opening yielding linear oligomers. The fact that the improvement in the mechanical properties was found  $\geq 10$  wt% CBT, whereas MFI increased monotonously with the CBT content hints for some solid phase solubility of CBT in this thermoplastic polyester elastomer. Based on the above beneficial effects CBT seems to be a promising new additive for the rubber industry.

## **ACKNOWLEDGEMENTS**

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