

## PET foaming: development of a new class of rheological additives for improved processability

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**Abstract.** Polymer foaming is a process broadly used for manufacturing light weight packaging solutions. Polystyrene (PS) is the most widespread material for this application, as it combines easy processability, low cost and high performance of the resulting items. However, foamed PS is difficult to recycle and highly polluting for the oceans and aquatic environment. Polyethylene terephthalate (PET) is, instead, commonly recycled and R-PET is broadly used for several industrial applications. Yet, PET quickly loses viscosity during the foaming process, due to thermo-hydrolytic and oxidative degradation thus causing poor foaming. In this paper, an innovative combination of chain extenders, anti-oxidants and nucleating agents to modify PET rheology is studied. The additives were experimented both in off-line and in-line apparatus. The experimental results show PET rheology can be customized by appropriately modulating the content of the different additives, thus making PET suitable for foaming process of high-quality items.

### Introduction

Expanded Polystyrene is widely used for containers and packing materials in fishing, agriculture, and household applications. Its characteristics of lightness, thermal/acoustic insulation and hygienic-food safety have favored its large scale development. EPS (expanded polystyrene, also called XPS), as well as PS is technically a potentially recyclable material through thermo-mechanical or chemical recycling. However, there are many factors that limit the effective recycling of this material: first of all, in most of the countries that carry out differentiated waste collection, including Italy, there is no supply chain dedicated to the collection of EPS, which is conferred to the plastics section and should hypothetically be sorted and separated from other waste to be sent to specific EPS recycling plants. The selection phase turns out to be extremely complicated because due to the mechanical characteristics of EPS products, they tend to crumble during the collection phase, making separation from other waste practically impossible. Moreover, unwanted dispersion of EPS products in the environments is very common thus causing formation of microplastics extremely polluting and harmful to the aquatic ecosystem and indirectly to human health. These reasons prompted the European Union to include disposable EPS products in the list of products banned by the SUP directive (dir. 904/2019). PET on the other hand is the most recyclable and recycled plastic in the world. The European average amount of recycled PET (r-PET) is more than 90% of virgin PET. The foam industry has therefore turned its attention towards the development of expanded PET in order to exploit the PET recycling chain already widely distributed in many countries, mainly driven by recycling of PET bottles. However, in the

transition from EPS to EPET, producers of foam products have encountered some difficulties related to the rheological differences of the two polymers.

PET, like all polyesters, is sensitive to thermo-hydrolytic and thermo-oxidative degradation phenomena triggered by the presence of impurities and excessive humidity levels. Such phenomena cause breakage of the polymer chains, loss of molecular weight and therefore reduction of the viscosity. During the direct gas injection process used for the production of foams, a high viscosity is required to allow the expansion of the molten polymer and the formation of the typical cell structure.

A low molecular weight (MW) does not favor the foaming operation in a direct gas injection extrusion process of foamed sheets. During this process the polymeric melt undergoes intense elongational deformations which are not supported by the typically low MW of PET, characterized by low viscosity values, low strength and elasticity of the polymer melt. As a result, uncontrolled cell expansion and unstable growth of bubbles can occur. Higher viscosity (shear and intrinsic) and improvement of melt strength provides a higher resistance to bubble coalescence and a better stability of the cellular structure during the foaming process.

Improved rheology is generally associated with increases in MW and molecular weight distribution (MWD) as a result of polymer chain extension and branching. Degradation of PET during processing can be overcome by adding toughening reactive agents [1,3] and chain extenders in the presence of various catalysts [2,4–7] to obtain materials with controlled rheology and tailored mechanical performance. Chain extenders usually contain at least two functional groups capable of reacting with the carboxylic and/or alcoholic end groups of PET. According to the type, reactivity and number of functionalities present on the chain extender molecule, different reaction mechanisms of the functional groups and different macromolecular architectures can be obtained. Oxazolines [8,9], react very quickly with the carboxylic end groups of PET chains and are able to favour linear chain extension of the polymer by formation of stable bis-amide bridging segments. Pyromellitic dianhydride (PMDA) [10] and organic phosphites [11,12] have also been successfully used as PET chain extenders. Moreover, combinations of PMDA bis-oxazolines have also been studied [13]. Epoxides react with carboxyl moieties of PET [14], leading to the formation of esters and a secondary hydroxyl group which can eventually take part in transesterification reactions with other PET chains, resulting in chain branching and chain scission. Some studies [14, 15] describe the use of polyfunctional chain extenders such as branched low molecular weight or linear oligomeric polyepoxy compounds [14,15] and oligomeric polyisocyanates [16] to obtain branched chain extended PET with rheological properties appropriate for the production of PET foams.

In the present work the effect of three commercially available chain extenders and their combination on melt viscosity of PET was investigated. Inline test during extrusion trials allowed to measure torque and die pressure at various screw speeds. Offline tests on a measuring mixer allowed to observe the torque trend over an extend amount of time (20 minutes), comparable to process time during industrial direct gas injection.

## Experimental

### *Materials*

The PET grade selected for this study (Cleartuf P82, Gruppo Mossi & Ghisolfi, Italy) is a food grade characterized by intrinsic viscosity equal to 0.8 dl/g, melting point at 249 °C, with a content of carboxyl groups CC equal to about 27-28 equiv/10<sup>6</sup>g. PET was dried, prior to all tests, at 130°C for 4 h and stored in oxygen barrier thermally sealed bags. Different additives and combinations to promote linear chain extension and branching were selected.

Several chain extenders based on polyepoxides can be profitably used to modify the rheological properties of PET. Diepoxides (characterized by 2 functionalities), triepoxides (f=3) and tetraepoxides (f=4). In relation to the molecular weight of the individual chain extenders, a more or less marked effectiveness of the regradation process will be obtained. Poly-epoxides, i.e.

molecules characterized by a very high number of epoxy functionalities are widely available on the market. In this study Joncryl ADR 4468, a polyepoxy commercialized by Basf (Germany), containing more than 20 epoxy functionalities was considered. This kind of chain extender favours branching reactions which occur by combining the hydroxyl end groups of the PET molecule with the polyepoxide epoxies. The end result is a PET with a comb structure. By suitably controlling the chain extension reaction, it is possible to limit the formation of gels and obtain the desired increase in molecular weight and, therefore, in intrinsic viscosity required by the PET expansion process.

Oxazolines are, like polyepoxides, capable of combining with the carboxyl end groups present on PET. Differently from polyepoxides, oxazolines present a molecular configuration with functional groups placed at the end of the molecule which can favor purely linear chain extension mechanisms. This aspect is certainly important, as the use of oxazolines reduces the risk of gel formation during the extrusion process. Oxazolines have two functional groups and are relatively small molecules (low molecular weight), therefore they are potentially effective at relatively low concentrations in the finished product (0.2 - 0.3 %). In this study 1,3-phenylene-bis-oxazoline (PBO), by the commercial name of Nexamite A99 (Nexam Chemical, Sweden) was selected.

Rheology improvements of PET by using tetracarboxylic dianhydrides as chain extenders has been described as an efficient strategy by several patents throughout the years [17-22, 26-29]. For example [17-18] report how PET extrusion with the addition of 0.3 wt% pyromellitic dianhydride (PMDA) increased melt strength of PET. No parison sag was observed during extrusion blowing and intrinsic viscosity was increased to 0.86 dl/g in PET bottle walls.

*Table 1 Reaction characteristics of selected chain extenders*

Additive	F [eq./mol]	MW [g/mol]	F <sub>Eq</sub> [g/eq.]	Reactive Group	Reaction	% Stoich.
<b>PBO</b>	2	140.14	70,1	Carboxylic	Linear CE	0.3
<b>BTDA</b>	4	322.23	80,6	Hydroxyl	Linear CE	0.72
<b>PMDA</b>	4	218.11	54,5	Hydroxyl	Linear CE	0.49
<b>Polyepoxy</b>	23.8	7250	304,6	Carboxylic	Branching	0.85

Known the number of carboxyl and hydroxyl end groups available in the specific PET commercial grade, the stoichiometric quantity of additive capable of reacting with PET may be calculated by applying the following formulas:

- (1)  $Wt \% = (MW \times CC) / f \times 10^4$
- (2)  $Wt \% = (MW \times HC) / f \times 10^4$

Where MW is the molecular weight of the additive, CC and HC are respectively the content of carboxyl and hydroxyl groups of PET in equiv/10<sup>6</sup>g and F are the functionalities available in the additive. It is, therefore, possible to deduce the stoichiometric amount of each chain extender needed to saturate the carboxyl functionalities on the chosen PET grade (Table 2). Table 2 also reports characteristics of Benzophenone tetracarboxylic dianhydride (BTDA), to show how not only the number of functionalities, but also molecular weight influences the effective amount of chain extender needed to react with PET moieties.

Addition of small quantities of PE to PET leads to improved thermoformability of foams as described by [24]. In the former patent 2-4 wt% polyolefin (LLDPE) in combination with 0.6 wt% sterically hindered phenolic antioxidant was added to the PET recipe, used for foam extrusion of a thin cellular sheet. The foamed sheet was thermoformed into trays characterized by reduced density, 15% less than the cellular sheets. PET foam modified by polyolefin provides therefore a better flexural and impact properties according to [23,24].

Anti-oxidants allow to compensate oxidative degradation, accelerated by the high temperatures during the extrusion process. Anti-oxidants are classified into primary antioxidants that terminate the chain and secondary antioxidants which act by decomposition of hydroperoxides. Mixtures of stabilizers with different mechanisms are today the state of the art. Therefore, addition of High Density Polyethylene (HDPE) (DOW 410), and a primary/secondary antioxidant mixture (ADK Adeka Stab A611) was evaluated in this study.

*Characterization methods*

Offline and inline testing procedures were adopted in this study. Offline tests were conducted using a Brabender mixer (Brabender GmbH & Co., Germany) with a 50 ml internal chamber operating at 250°C and 50 rpm, with a mixing time of 20 min. Stoichiometric amounts of the given chain extender were added into the pre-heated mixing chamber 2 minutes after the introduction of PET. Table 2 summarizes the formulations tested on the Brabender measuring mixer. The evolution of the torque (Nm) during the mixing observation time was recorded.

*Table 2 Recipes tested on the Brabender measuring mixer*

Sample ID	#1a	#2a	#3a	#4a	#5a	#6a	#7a
Components	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %
PET	100	97,4	97,325	96,72	97,045	97,725	97,12
HDPE	0	2	2	2	2	2	2
PMDA	0	0,4	0,4	0,4	0	0	0
PBO	0	0	0,075	0	0,075	0,075	0
Joncryl	0	0	0	0,68	0,68	0	0,68
Adeka ADK Stab A-611	0	0,2	0,2	0,2	0,2	0,2	0,2
<b>Totale</b>	100	100	100	100	100	100	100

Inline tests consisted in reactive extrusion of PET with stoichiometric amounts of selected chain extender additives (Table 1), using a twin screw extruder (Leistritz 27ZSE iMAXX, Leistritz GmbH, Germany). A constant temperature profile of 250°C was used along the barrel for all the extrusion tests. The feed rate was set constant at 5%, while the screw speed was varied from 100 to 300 rpm. At low feed rates the screw speed significantly influences the throughput time. The torque and melt pressure during the extrusion process was recorded. The resulting compounds were dried at 110°C for 4 hours and stocked in oxygen barrier thermally sealed bags. Subsequently the melt flow rate of each compound was measured at 260°C with a 2.16 kg load.

**Results and Discussion**

PET was processed as is as reference for processing of chain extended PET. MFR results show how at higher screw speed, meaning lower throughput time, processed PET features lower MFR, suggesting higher residence time caused major degradation of PET at lower speeds.

*Table 3 MFR of as-is processed PET*

Sample ID	FR [%]	Screw speed [rpm]	MFR (260°C, 2.16 kg)
#1 PET	5	50	22.7
	5	100	21.0
	5	300	16.0

Subsequently Joncryl, Oxazoline and PMDA were added to PET. Extrusion of PET with Joncryl at 0.85% led to a stable process, torque values decrease from 49% to 23% by increasing the screw speed. Higher screw speeds allowed faster throughput, lower residence time and lower filling rate of the barrel, hence leading to a lower torque. The addition of Joncryl makes it possible to halve the MFR of PET, in all working conditions, confirming the regradation effectiveness of the additive. Even PET with PBO is easily processable. PET additivated by PBO features higher MFR values compared to PET+Joncryl samples, thus suggesting Joncryl might be more effective in chain extending PET compared to PBO. However, higher torque values were registered during the extrusion of PET+PBO compared to PET+Joncryl. Higher torque values are generally measured for more viscous polymers, hence suggesting PBO may indeed have modified rheology of PET.

*Table 4 Results of inline tests*

Sample ID	Torque [%]	Die Pressure [bar]	FR [%]	Screws speed [rpm]	MFR (260 °C, 2.16 kg)	
#2	PET + PMDA	58	43	5	50	4.6
		X	X	5	100	X
		X	X	5	300	X
#3	PET + PMDA + PBO	55	38	5	50	6.2
		X	X	5	100	X
		X	X	5	300	X
#4	PET + Joncryl + PMDA	55	55	5	50	2.9
		X	X	5	100	X
		X	X	5	300	X
#5	PET + Joncryl + PBO	63	45	5	50	6.1
		40	50	5	100	4.3
		30	40	5	300	3.8
#6	PET + PBO	60	33	5	60	15.6
		43	31	5	100	13.8
		30	24	5	300	21.7
#7	PET + Joncryl	49	48	5	60	10.3
		31	34	5	100	10.6
		23	24	5	300	13.4

Combination of the polyepoxy and PBO was also investigated. No processing issue was observed, the extrudate featured good melt strength and optimal pelletization. MFR progressively decreased with increasing screw speed, reaching the lowest value for the compound produced at 300 rpm, equal to 3.8 g/10 min. Therefore, the influence of screw speed is confirmed. The combination of PBO and Joncryl appears extremely effective in lowering MFR of PET. Higher viscosity is also confirmed by torque and die pressure values. Extrusion of PET with stoichiometric PMDA (0.49 wt.%) gave place to uncontrolled swelling of the extrudate, as shown in Figure 1. The amount of PMDA was therefore slightly decreased. The same swelling phenomena appears at 0.4 wt.%, while at 0.3 wt.% processing was possible. PMDA proved to be extremely efficient in reducing MFR of PET. Amounts lower than the stoichiometric quantity were able to reduce MFR of PET as low as 4.6 g/10 min. Issues caused by the die swelling phenomenon could be easily solved by adopting a different pelletizing system (i.e., under water cutting system). The screw speed had a significant effect on PET rheology and, subsequently, processing, for all scenarios where PMDA was involved. Screw speeds higher than 50 rpm led to viscosity increase in the molten polymer which caused a twisting effect on strands exiting the die. The strands were extremely unstable and strand transport across the cooling bath to the pelletizing system was impossible.



*Figure 1 Die swelling phenomenon for PET+PMDA*

Blending PMDA with Joncryl and PBO gave place to the same die swelling phenomena, nonetheless the material was processable at 50 rpm with a 5% feed rate. Combination of PMDA and Joncryl determined a significant viscosity increase as shown by the measured MFR, equal to 2.6 g/10 min and die pressure equal to 55 bar. Combination of PMDA and PBO was also effective causing MFR reduction of PET to 6.2 g/10 min, comparable with MFR registered for the combination Joncryl+PBO under the same processing conditions.

Offline tests allowed to evaluate torque trends on a longer observation time. The extrusion residence time is 1-2 minutes depending on screw speed, whereas residence time in the measuring mixer is independent from other parameters. Torque values of PET and chain extended PET were measured after 5, 10, 14 and 20 minutes mixing inside the Brabender mixer (Table 5). Offline tests on the measuring mixer proved effectiveness of all the studied additives, coherently with inline tests.

*Table 5 Torque values registered during measuring mixer tests*

Sample ID	5 min	10 min	14 min	20 min
#1a PET	4.5 Nm	3.3 Nm	2.9 Nm	\
#2a PET+PMDA	6.1 Nm	9.9 Nm	15 Nm	14.9 Nm
#3a PET+PMDA+PBO	6.7 Nm	13.5 Nm	15.5 Nm	13.2 Nm
#4a PET+PMDA+Joncryl	7.1 Nm	13.6 Nm	15.5 Nm	13.2 Nm
#5a PET+Joncryl+PBO	9.2 Nm	8.3 Nm	7.1 Nm	6.3 Nm
#6a PET+PBO	5.5 Nm	4.3 Nm	3.7 Nm	3.2 Nm
#7a PET+Joncryl	8.8 Nm	6.8 Nm	5.5 Nm	4.6 Nm

PBO was the least effective in increasing torque, compared to as-is PET. PMDA and its combination with Joncryl and PBO gave place to the higher torque values. The combined additive solutions caused a faster torque increase, whereas PMDA alone was more persistent for a longer time.

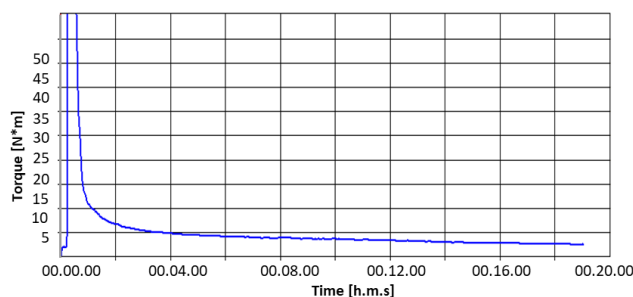


Figure 2 Torque trend of as-is PET

Figure 2 and Figure 3 show the torque trends for a 20 minute observation time. The figures clearly highlight the efficiency and persistency of PMDA in PET regradation. The combination of polyepoxy (Joncryl) and Oxazoline is rather persistent since a very small torque reduction was recorded throughout the observation time. Nevertheless absolute torque values are much lower compared to samples containing PMDA. This behaviour could be associated to the reaction mechanism of PMDA with PET. PMDA is indeed the only selected additive involving reaction with hydroxyl groups, whereas all other additives exploit carboxyl groups reactions.

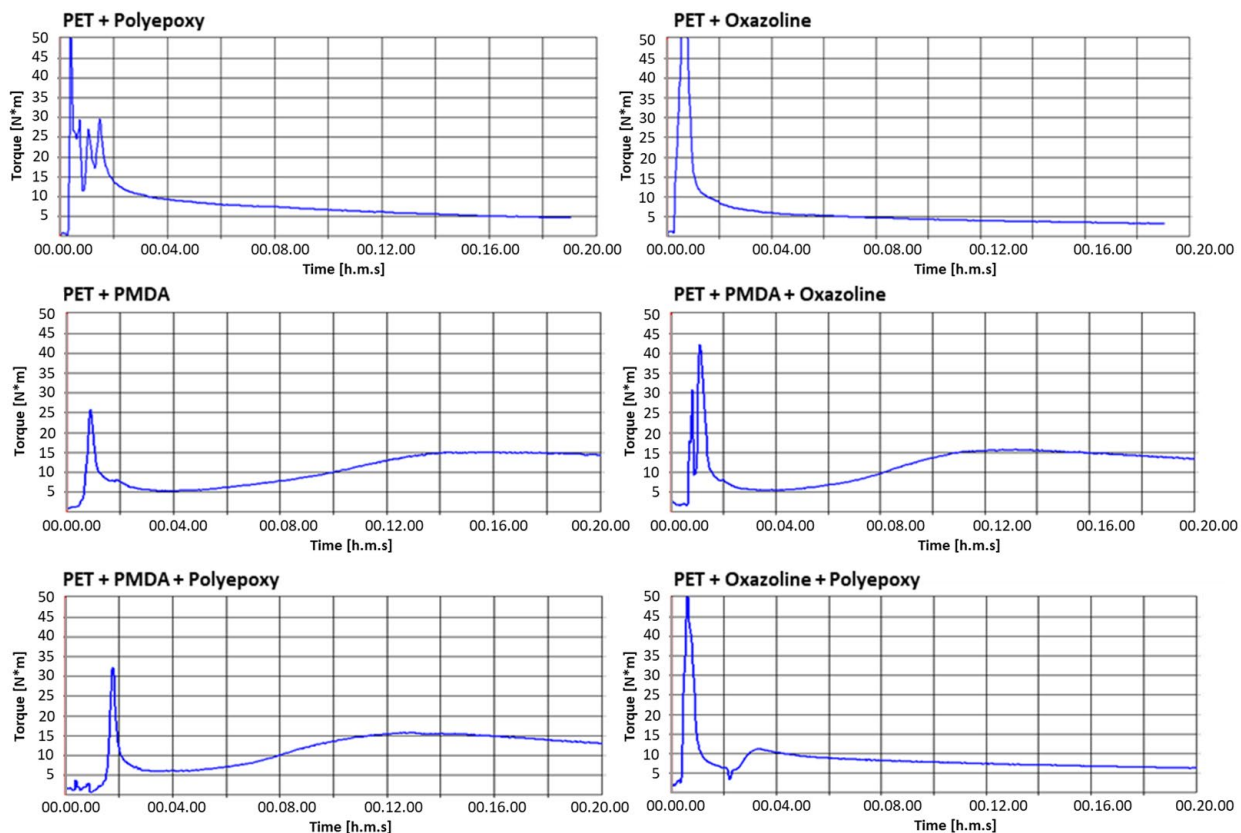


Figure 3 Torque trends of PET additivated with several chain extender additives

### Conclusions

Inline and offline tests were performed on chain extend PET to verify the efficiency of PBO, PMDA, Polyepoxy (Joncryl) and their combinations in regradation and rheology modification of PET. Torque and die pressure was registered during reactive extrusion and MFR was measured on resulting pellets to verify rheology variations on chain extended PET. Torque was also measured at set intervals for compounds mixed for a longer period inside a heated chamber. Both tests

showed the efficiency of the selected additives, with special reference to PMDA and its combination with other additives. Combination of PMDA with PBO and Joncryl gave place to faster reactions. The highest viscosity increase was registered for PET+PMDA in the inline tests and for PET+PMDA+Joncryl in the offline tests. Remarkable results were also observed for the Joncryl+Oxazoline combination. Inline tests showed good persistence of the combined additives and a nearly constant torque trend was observed during offline tests. In conclusion, the selected additives effectively increase viscosity of PET, thus allowing improved foaming of PET.

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