

PlastiCircle: *Improvement of the plastic packaging waste chain from a circular economy approach*

Grant Agreement No 730292



PlastiCircle Deliverable

D5.2: Technical description of the production processes in lab scale

Åge Larsen (SINTEF)



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730292.

Factsheet

Document name: D5.1: Technical description of the production processes in lab scale

Responsible partner: SINTEF

Work package: WP5

Deliverable number: D5.2

Version: 1

Version date: 15/11/2019

Date due: M30

Dissemination level

X	PU = Public
	PP = Restricted to other programme participants (including the EC)
	RE = Restricted to a group specified by the consortium (including the EC)
	CO = Confidential, only for members of the consortium (including the EC)

Authors: Åge Larsen (SINTEF), Richard McKinley (Axion), Sven Hendriks (Armacell), Amandine Magnet (Derbigum), Marco Monti (Proplast), Kjell Olafsen (SINTEF), Christian Karl (SINTEF)

Reviewers: All partners

Abstract

This deliverable describes the adoption of recycled plastics to the production processes of the project's manufacturing partners.

Partners

1. ITENE: INSTITUTO TECNOLÓGICO DEL EMBALAJE, TRANSPORTE Y LOGÍSTICA
2. STIFTELSEN SIN: STIFTELSEN SINTEF
3. ...
4. AXION: AXION RECYCLING
5. CRF: CENTRO RICERCHE FIAT
6. UTRECHT: GEMEENTE UTRECHT
7. LAS NAVES: FUNDACION DE LA COMUNITAT VALENCIANA PARA LA PROMOCION ESTRATEGICA EL DESARROLLO Y LA INNOVACION URBANA
8. ALBA: PRIMARIA MUNICIPIULUI ALBA IULIA
9. VELENJE: MESTNA OBCINA VELENJE
10. SAV: SOCIEDAD ANONIMA AGRICULTORES DE LA VEGA DE VALENCIA Spain
11. POLARIS: POLARIS M HOLDING
12. INTERVAL: INDUSTRIAS TERMOPLÁSTICAS VALENCIANAS
13. ARMACELL: ARMACELL Benelux S.C.S.
14. DERBIGUM: DERBIGUM N.V.
15. PROPLAST: CONSORZIO PER LA PROMOZIONE DELLA CULTURA PLASTICA PROPLAST
16. HAHN: HAHN PLASTICS Ltd.
17. ECOEMBES: ECOEMBALAJES ESPAÑA S.A.
18. KIMbcn: FUNDACIÓ KNOWLEDGE INNOVATION MARKET BARCELONA
19. PLAST-EU: PLASTICS EUROPE
20. ICLEI: ICLEI EUROPASEKRETARIAT GMBH
21. PICVISA: PICVISA MACHINE VISION SYSTEMS SL
22. SINTEF AS: SINTEF

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1. Publishable summary

PlastiCircle aims to develop and implement a holistic process to increase recycling rates of packaging waste in Europe. This will allow to reprocess plastic waste in the same value chain (i.e. Circular economy; closure of plastic loop). This process is based on four axes: collection (to increase quantity of packaging collected), transport (to reduce costs of recovered plastic), sorting (to increase quality of recovered plastic), and valorisation in value-added products (i.e. foam boards, automotive parts like engine covers/bumpers/dashboards, bituminous roofing membranes, garbage bags, asphalt sheets/roofing felts and urban furniture like fences/benches/protection walls).

A previous report details the requirements of the manufacturers who will be using the recycled materials, and identification of the challenges they have found through the assessment of materials available on the market today. The PlastiCircle project partners, products and polymers that are used in the products are given below in **Error! Reference source not found.**Table 1

Table 1 PlastiCircle partners and products investigated in study

Partner	Product	Polymer
Armacell	Foamed boards	Polyethylene Terephthalate (PET)
Centro Ricerche Fiat (CRF)	Automotive parts	Polypropylene (PP) PET
Derbigum	Bitumen roofing	PP
Hahn Plastics	Outdoor furniture and retention products	Low Density Polyethylene (LDPE) High Density Polyethylene (HDPE) PP
Interval	Refuse sacks bags	LDPE

Analysis by Armacell has shown that PET bottle flake is suitable for their product, however the PET from thermoforms is more challenging. In this step different sources of material have been tested and alternatives for material modification evaluated.

CRF in collaboration with Proplast are developing formulations for using recycled PP and PET in automotive parts. Two polymers have now been selected based on thermal resistance requirements for the selected applications.

Derbigum have analysed PP and PE samples from the market and approved three. Emphasis has also been PE fractions in PP and on transforming crystalline PP into amorphous PP, to allow incorporation of more recycled material into the product.

Interval needs high purity to ensure the quality of their end-product. To meet their demand, different washing techniques of post-consumer LDPE films will be tested.

Hahn already recycle large quantities of post-consumer waste in Germany and the UK and are ideally placed in this project to ensure maximum recycling rates. The key factor for Hahn is ensuring low PVC and PET levels. They will also evaluate the use of LDPE subjected to different washing procedures.

2. Introduction

The PlastiCircle project aims to develop additional end markets for recycled polymers derived from post-consumer household packaging waste.

Already there is successful recycling of post-consumer packaging, however in order to create more demand for recycled products, and therefore stimulate the industry further, research has been conducted in this project focused on five different products.

The PlastiCircle project partners, products and polymers that are used in the products are given below in Table 2.

Table 2 PlastiCircle partners and products investigated in study

Partner	Product	Polymer
Armacell	Foamed boards	Polyethylene Terephthalate (PET)
Centro Ricerche Fiat (CRF)	Automotive parts	Polypropylene (PP) PET
Derbigum	Bitumen roofing	PP
Hahn Plastics	Outdoor furniture and retention products	Low Density Polyethylene (LDPE) High Density Polyethylene (HDPE) PP
Interval	Refuse sacks bags	LDPE

Work has mostly focused on existing recyclate on the market, as the amounts of the specific material fractions from the PlastiCircle pilots are small. The main point has been to work with post-consumer materials.

The main activity in the project has been related to testing of available post-consumer polymer grades.

To meet the specific demands on the products in Table 2, routes of polymer analysis and chemical modification have been investigated. Results have been achieved related to optimizing properties for foaming and reduction of crystallinity in PP.

The process for Interval and Hahn in the PlastiCircle project differs from the other manufacturing partners. Interval and Hahn both look to use material derived from film. There is little recycling of household film across Europe, so sourcing material on the market has not been possible. In a next step, collected films from the project pilots will be subjected to different washing procedures and evaluated by Hahn and Interval.

Work on this topic will continue completing the presented results to provide better foundation for the manufacturing partners in their production.

3. Foamed PET boards

3.1 Recycling of mixed PET from Household collection to produce PET Foam Boards at ARMACELL - Summary

Within this work package (T5.2) Armacell studies the recycling of the PET fraction possibly coming from the PlastiCircle system. To develop and optimize possible formulations and to adopt process parameters, Armacell tests different fractions of rPET received from partners or obtained from the market. The material is tested on laboratory and pilot line scale to gain insight on the specific behavior in the foaming process. The results demonstrate the different behavior the individual rPET fractions and how formulation and process parameter adjustments can enable the processing to high quality foam products. At a later stage, the results will be benchmarked with samples from the PlastiCircle pilots.

3.1.1 Background

Mechanical recycling of PET bottles is a well-established process in the plastics industry. Bottles are collected and sorted through a variety of systems, process to flakes by shredding, separation steps and hot washing. The flakes can be used for a variety of applications such as bottle-to-bottle recycling, thermoforming sheets or strapping bands. Armacell was the first to use 100% rPET flakes to produce PET foams. Armacell aims to use the rPET collected and sorted within the PlastiCircle framework for the production of high-quality PET foam boards for composite applications. Currently Armacell uses rPET flakes sources from post-consumer bottles to manufacture extruded foam boards. The process includes granulation of the flakes, extrusion of boards, welding, and slicing of the final foam sheets to customer specified thickness. The rPET fraction which is expected from PlastiCircle will contain a mix of different rPET sources such as beverage bottles, non-food bottles, trays (mono- and multilayer) and others. Therefore, the sorting process developed within PlastiCircle will feature separation of PET into bottles and monolayer trays and multilayer trays. Still the higher variability of the composition of the generated streams will require adjustments of the product formulation and process settings.

3.1.2 Introduction

As the pilots were not started yet and the volume of sorted material from the PlastiCircle pilots will not be sufficient to run full scale trials at Armacell, it was decided to develop the recipes and process settings with comparable material from other sources. After the assessment of the composition of rPET from the PlastiCircle pilots, the samples will be used for lab scale testing at Armacell. Based on the results and the comparison with other tested grades, a “comparative” rPET mixture will be defined for the full-scale trial.

3.1.3 Materials

The following **Table 3** summarizes the rPET material tested by Armacell.

Table 3 List of rPET material analyzed by Armacell

#	Source	Description	Appearance
1	Aixion	Post-industrial PET tray scrap that has been extruded and IV boosted (Gneuss)	Pellets
2	Aixion	Post-consumer PET tray material that has been extruded and IV boosted	Pellets
3	Aixion	Hot washed post-consumer bottle flakes	Flakes
4	Aixion	Post-industrial tray scrap from trays made using post-consumer tray material	Flakes
5	Axion	rPET Tray Mono	Flakes
6	Axion	rPET Tray ABA	Flakes
7	Suez	rPET Tray	Flakes
8	Suez	Black rPET Tray	Flakes
9	Multipet	rPET 80% bottle, 20%tray German household collection	Flakes

3.1.4 Methods

Intrinsic Viscosity (IV)

IV is measured by viscometry for diluted solution in a certified laboratory. The samples are grinded before dissolving in dichloroacetic acid (DCA)

Carboxylic End Groups (CEG)

The amount of carboxylic end groups (CEG) is measured by photometric titration in Armacell's lab. Titration is performed on dissolved samples using ethanolic KOH and bromophenol blue as indicator

Reactivity

Reactivity of the rPET flakes is measured upon addition of chain extenders using Armacell's proprietary testing method. The reactivity is a measure for the increase of the melt viscosity after adding the reactive additives.

Extrusion Foaming

Foam extrusion is performed with Armacell's extrusion pilot line with a throughput of ~40-80 kg/hr.

3.1.5 Results

3.1.5.1 Lab scale development with different rPET grades

A series of qualification tests on different rPET grades was performed by Armacell. In a first step, basic properties as IV and CEG of the materials was tested (**Table 4**)

Table 4 Properties of tested rPET samples

#		Appearance	IV	CEG [mmol/kg]
1	PI PET tray	Pellets	0,74	44,9
2	PC PET tray	Pellets	0,62	39,5
3	Hot washed PC bottle flakes	Flakes	0,75	28,7
4	PI tray scrap using PC tray	Flakes	0,65	51,6
5	rPET Tray Mono	Flakes	0,694	29,8
6	rPET Tray ABA	Flakes	0,663	33,8
7	rPET Tray	Flakes	0,671	31,3
8	Black rPET Tray	Flakes	0,62	33,2
9	rPET 80 % bottle, 20 %tray	Flakes	0,72-0,74	26,2

The results indicate differences among the molecular properties of the different

samples. Samples #1 and #2 were IV boosted, however #2 has a comparably low IV of 0.62. In general, it can be seen that material coming from trays have a higher CEG compared to material coming from bottles (#3). This indicates a higher number of end groups, thus shorter molecular chains. Sample #4 has a very high CEG which indicates serious degradation due to the multiple recycling processes. The samples of trays (#5-8) all show an IV slightly lower than usual bottle grade rPET and slightly higher CEG. Sample #9 has properties comparable to bottle grade rPET, apparently the effect of 20% trays is not very pronounced.

3.1.5.2 Reactive Modification Testing

Following the basic assessment, the reactivity which is proportional to the increase of viscosity in the test was analyzed. The results in **Table 5** are presented in non-dimensional values where 1 is the reference value typically observed by Armacell (bottle grade rPET).

Table 5 Reactivity of the tested rPET samples

Sample No.	CE level [-]	Reactivity [-]	Rating
Reference value	1	1 ± 0.2	+
1	1	0.11	--
2	1	0.36	-
3	1	0.68	o
4	1	0.06	---
5	1	0.48	-
6	1	0.23	--
7	1	0.35	-
8	1	0.24	--
9	1	0.35	-

Sample 1 has a low reactivity. As the IV is quite high, the low reactivity could be explained by contaminations like PVC. Sample 2 has a lower IV, still there is some reactivity observed. However, doubling the amount of chain extender does not improve the result. Sample 3 are typical bottle flakes. They show a moderate reactivity which is usually observed in case of small contaminations like PVC labels or multilayer bottles with a PA barrier. Sample 4 shows a very low reactivity which could be caused by both, contaminations or high level of degradation which is

indicated by the high CEG level. Samples 5 which is a monolayer tray still shows some fair reactivity while samples 6-9 are all in the same range of low reactivity.

3.1.5.3 Effect of Chain Extender Level

For selected rPET grades, the level of chain extender was varied to study the effect. If the reactivity increases upon increasing the dosage of chain extenders, this indicates that the modification takes place and that the material can potentially foamed. If the increase in chain extender dosage does not change or even lowers the result, this indicates that the reaction is either inhibited or that a certain level of degradation occurs.

Table 6 Reactivity of the rPET samples with different levels of chain extender

Sample No.	CE level [-]	Reactivity [-]	Effect of CE level
Reference value	1	1 ± 0.2	
2	1	0.36	○
2	1.24	0.32	
2	1.37	0.32	
2	2	0.34	
3	1	0.68	-
3	2	0.26	
4	1	0.06	-
4	1.24	0.03	
5	1	0.48	+
5	1,34	0.55	

3.1.6 Chain Extender Type B

For selected rPET grades, a different type of chain extender was tested at two levels.

Table 7 Reactivity of selected samples with chain extender Type B

Sample No.	CE B level [-]	Reactivity [-]	Rating
Reference value	1	?	+
2	1.15	2.1	+++ (crosslinking)
2	1.5	2.1	+++ (crosslinking)
4	1.14	0.98	+
4	1.42	1.27	++

The testing shows that even the grades with very low reactivity in the initial testing show a significant reactivity with CE type B. However, for sample 2, the reaction leads to severe crosslinking of the matrix which could negatively affect the thermoplastic processing properties and foaming behavior.

3.1.6.1 Chain Extender Blend

For selected grades, different blends of two synergistic chain extenders were used.

Table 8 Reactivity of selected samples with a blend of chain extenders

#	CE 1	CE 2	Total	Reactivity	Rating
5	1.00	0.00	1.00	0.48	o
	1.34	0.00	1.34	0.55	o
	0.50	1.03	1.54	0.23	-
6	1.03	0.51	1.54	0.66	o
	1.03	1.03	2.06	1.28	++
	0.74	1.32	2.06	0.87	+
	1.49	0.00	1.49	0.36	-
7	1.00	0.00	1.00	0.35	-
	0.57	0.57	1.14	0.45	-
9	1.00	0.00	1.00	0.35	-
	1.00	0.51	1.51	0.85	+
	1.29	0.27	1.56	0.32	-

3.1.6.2 Development with C-TR-04 (#9) on pilot scale

After testing different sources of rPET (post-industrial, post-consumer, tray regrind, bottles, pelletized) a grade of post-consumer household collection material was identified for a foaming trial on Armacell's pilot line. The rPET contains ~20% of monolayer trays and 80% of clear bottle.

3.1.6.2.1 Raw Material Testing

The rPET material (Grade C-TR-04, Multipet GMBH, Germany) was received in form of flakes and tested according to Armacell's inhouse standards. The tests were performed on 2 out of 4 Big-Bags (4ton total). After granulation, the reactivity was tested again.

Table 9

Lot	Reactivity flakes	Reactivity pellets	CEG	IV	NIR scan
BB1	2.6	3.7	22.33	0.744	99.81 % PET 0.08% PES 0.1% PET with contaminants
BB3	3.1	4.0	26.1	0.723	99.89% PET 0.04% PES 0.02% PET with contaminants 0.04% PMMA
Reference	12-14		28-30	0.74	OK

The test results show that the reactivity of the material is lower than the reference bottle grade. Also, the CEG (carboxylic end groups) is lower, which can only explain partially the lower reactivity. The IV is in the range of the reference, so the measured reactivity should not be impacted by a too low viscosity. The nIR scan did not show any excess concentration of contaminants. The reactivity of the material after granulation is in the same range as the flakes. This confirms that there are probably no contaminants that lead to degradation of PET in the granulation process. The low reactivity could be either a result of the type of PET and additives used for tray grade PET.

3.1.6.2.2 Pilot line extrusion (75mm twin-screw; 40kg/h)

The trial was started with a reference rPET which is usually used for production of rPET foams (Grade "S5"). After stabilization of the reference process, C-TR-04 was

added in steps of 20, 40, 60 and 97,5% of the total recipe (see **Table 10**). The level of chain extender (1= standard concentration for reference grade) was adjusted to keep the die pressure in the range of 65-68 bar.

Table 10 Test recipes with resulting die pressure and density

Lot	Reference rPET (S5) [%]	C-TR-04 [%]	Nucleation Agent MB [%]	Chain extender level [-]	Die Pressure [bar]	Density [kg/m ³]
Reference	97.5	0	2.5	1	64	93
Test 1	77.5	20	2.5	1	59	91
Test 2	57.5	40	2.5	1.13	67	92.5
Test 3	37.5	60	2.5	1.23	68	93
Test 4	0	97.5	2.5	1.35	67	93

Figure 1 and **Figure 2** show samples of the five different recipes. The change can be seen in the color because the reference grade was green. The foam quality remains almost constant. Also, the density remained constant and no collapsing of cells was **observed**.

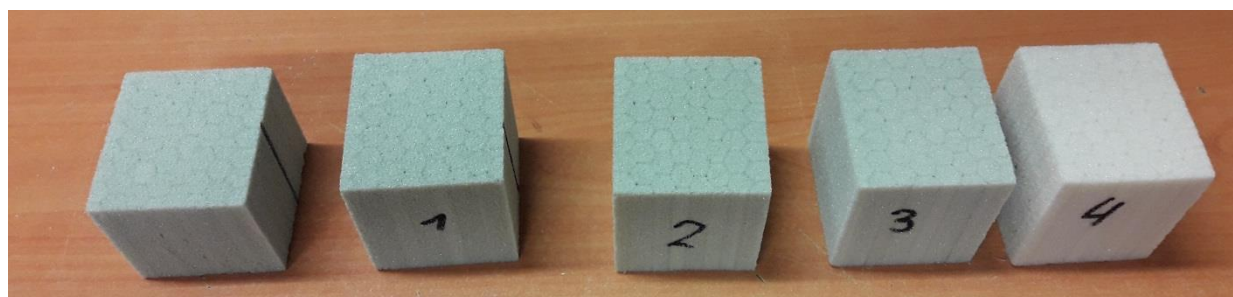


Figure 1 Samples of the tested recipes (Reference + Test 1-4)

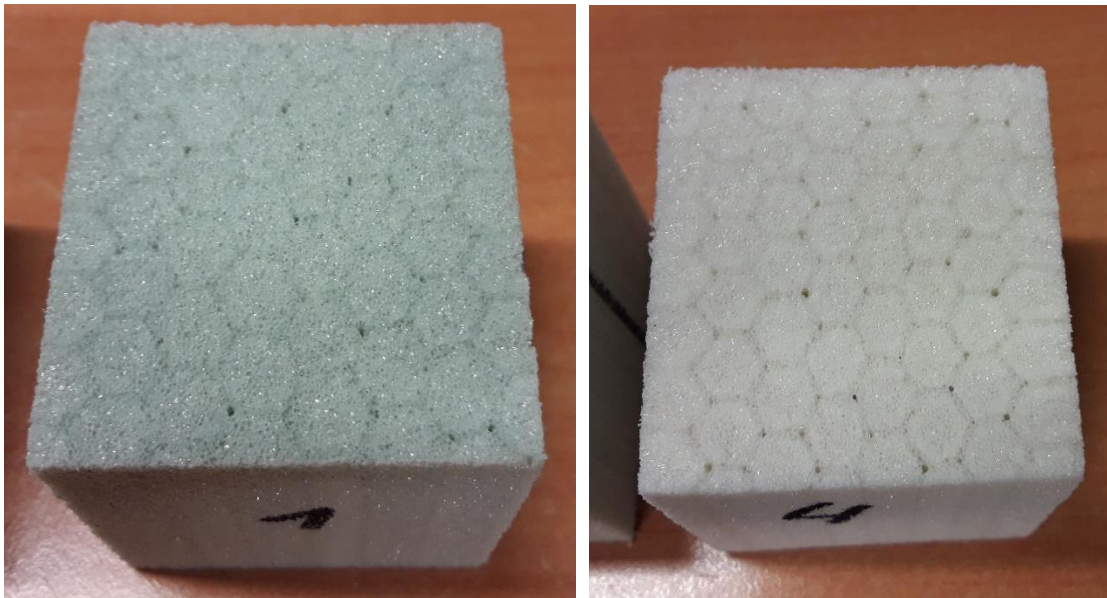


Figure 2 Visual appearance of the foam boards Test 1 and Test 4

3.1.6.2.3 Physical Properties and evaluation

The physical properties of the pilot line samples were tested according to relevant standards for Armacell PET foam boards. The results are summarized in **Table 11**.

Table 11 Physical Properties

	Compression strength X [MPa]	Compression strength Z [MPa]	Shear modulus Y [MPa]	Shear strength Y [MPa]	Shear elongation Y [%]	Tensile modulus X [MPa]	Tensile strength X [MPa]	Tensile Elongation X [%]
Reference	1.29	0.43	14.37	0.747	19.87	54.04	1.79	7.02
Test 1	1.26	0.43	13.06	0.743	21.13	48.04	1.68	7.00
Test 2	1.33	0.43	14.20	0.721	16.17	57.26	1.91	7.28
Test 3	1.30	0.42	13.80	0.675	14.17	56.06	1.71	5.34
Test 4	1.34	0.43	13.00	0.727	15.90	60.00	1.69	4.92

Most of the properties don't show a significant dependence with regard to the C-TR-04 grade in the recipe. However, for high loadings of C-TR-04, the shear and tensile elongation of the foam decreases, which can usually be attributed to a more brittle behavior. This could be caused by the higher loading of the chain extender, which is known to produce more brittle products.

3.1.7 Conclusion – mixed rPET

The study of properties and reactive behavior of different types of rPET originating from trays or bottles shows large differences in the molecular properties and reactive behavior. Armacell developed different reactive formulations that can be adapted to the properties of the rPET and that allow to control the viscosity and enable foaming. These formulations will be used as a toolbox in further trials within PlastiCircle.

The feasibility to use rPET containing post-consumer tray material for foam extrusion was demonstrated on Armacell's pilot line for foam board extrusion. Despite the small amounts of trays in the test grade, the impact in the reactivity of the material is high and the amount of chain extender had to be increased by 35% which also has a significant impact on recipe cost. For foam board production on a production line with a throughput > 500 kg/h, we expect that we could only use ~30% of C-TR-04 in the final recipe because of a narrower process and recipe window compared to the pilot line. More research and trials would be required allow higher loadings of tray PET in the recipe without reducing mechanical properties.

Further analysis of molecular properties is also needed to understand the effect of tray PET on the reactivity in the foam extrusion process. It is not understood yet if the lower reactivity is caused by the material itself, certain additives or unknown contaminants.

3.2 Modifying properties of rPET with chain Extenders

3.2.1 Summary – testing chain extenders

Three different PET types (batches A, B and C from tray flakes) and four different chain extenders (CE) (Clariant, Joncryl, Irgafos 126 and Pyromellitic dianhydride, PDMA) have been investigated to obtain a polymer with optimal properties for the foaming process. The samples were compounded in the mini batch extruder at 280°C for 3 or 10 minutes depending on the type of chain extender. When the CE reaction has already started, the plateau levels are reached very fast for two types of chain extenders (Clariant and PDMA). Only the sample containing 1,5 % of the chain extender (CE) Joncryl exhibits a little higher tensile stress at yield value. The tensile stress values of the other samples do not differ very much from each other. The rheological investigations have shown a possible polycondensation of PET in N₂ and a slight degradation of PET.

3.2.2 Background

Armacell produce foamed PET boards that can be used as insulation or core boards for composite parts. Currently Armacell use washed PET flakes from PET bottles; it was the first company to use 100% rPET flakes to produce PET foams. Armacell use both clear PET and coloured PET, as the product is not usually visible to the consumer.

The aim of PlastiCircle is to ensure Armacell can use the PET generated from the project in the engineered foams. More specifically, the challenge is to determine whether PET from thermoforms can be used as well as PET from bottles.

The foaming of polymers depends on viscosity. Contaminants can affect the reactivity of the foaming process and prevent an acceptable product from being made.

In the present work we have investigated the option of using different types of chemical chain extenders (CE) to obtain a polymer with optimal properties for the foaming process.

3.2.3 Introduction/Literature

Polyethylene terephthalate (PET) is a common polymer in the plastic industry and PET-based products are extensively recycled. The physical recycling of PET by melt reprocessing is the most indicated since it is relatively simple, requires low investments, utilizes established equipment, is flexible in terms of feedstock volume and has little adverse environmental impact.

Many studies have been carried out with the use of CE to recover properties of low molecular weight PET. Experiments with different CE used in the chain extension of PET have been reported in literature [1-5]. Especially the CE Joncryl [1-4] was used in many research works. But also, pyromellitic dianhydride (PMDA) [5] and Irgafos 126 [5] have shown that the molecular weight is increased, and the crystallinity is decreased. Furthermore, the processing behaviour was changed using Irgafos 126 which is a secondary stabilizer. It was shown that it acts also as a chain extender

like PMDA and Joncryl. During the melt reprocessing of PET, the polymer undergoes chemical, mechanical, thermal, and oxidative degradation that reduces its molar mass and its viscosity, melt strength and mechanical properties. Hence, it limits the usefulness for many applications. The increase in the PET molar mass can be attributed to the reaction of epoxy groups with carboxyl (and to a lesser extent, hydroxyl) ends of PET fragments, resulting in the combination of two or more fragments and the extension of the PET chain as schematically shown in **Figure 3** [1].

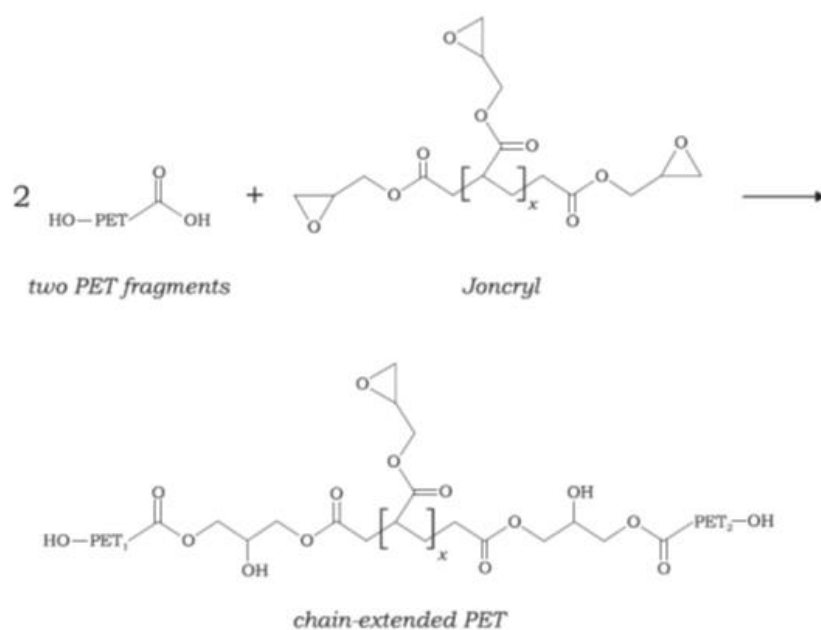


Figure 3 Scheme of the chain extending reaction of PET by a multifunctional epoxidic oligomeric additive (Joncryl) [1].

Figure 4 illustrates possible reactions between hydroxyl groups of PET with Irgafos 126. The two phosphorus atoms in molecule of Irgafos 126 represent reactive sites that can react with hydroxyl groups of PET to form a polymer-extender chain bonding, releasing a sterically hindered phenol. This reaction can also occur in the other extremity of Irgafos 126 molecule, generating the polymer extension. Subsequent reactions between hydroxyl groups of PET with phosphorus atoms lead to the formation of a chemical structure which three polymeric chains are bonded to one phosphorus atom, releasing one molecule of a tetrahydroxyd glycol [5].

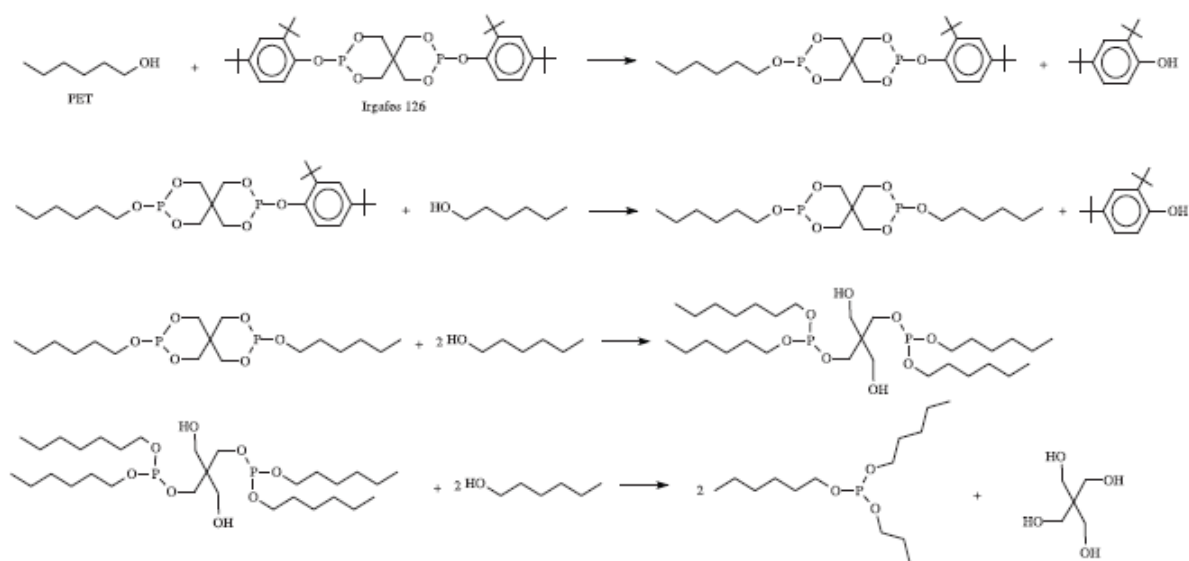


Figure 4 Mechanism of reaction between Irgafos 126 and PET [5].

3.2.4 Materials

PET: Batch A, B, C (from tray flakes)

Batch A ("high quality/bright green"; measured reactivity = increase of viscosity in the internal test is 12,8 Nm)

Batch B ("low quality/greyish green"; measured reactivity = increase of viscosity in our internal test is 6 Nm)

Batch C ("white")

Chain extenders:

-NEA0050311-ZC (Clariant)

-Joncryl ADR-4368 (BASF)

-Irgafos 126 (BASF)

-Pyromellitic dianhydride (PDMA, Sigma-Aldrich)

3.2.5 Compounding

The PET samples A, B and C were dried at 140 °C for 17 h and the chain extenders (1-4) were dried at 120 °C for 3 h before use. Samples (PET Batches A, B and C as well as mixtures of A/B 75%/25% and different amounts of CE were used depending on the type of chain extender) were compounded in the mini batch extruder Midi2000 from DSM, with the chamber walls kept at 280 °C for 3 min (CE NEA0050311-ZC, Irgafos 126, Pyromellitic dianhydride) and 10 min (Joncryl ADR-4368). The extruder is equipped with screws with enhanced feeding zone. The extruder barrel was permanently flushed with N₂ during compounding. In the trials the extruder is filled by operating the piston of the hopper manually which means the time required may vary from batch to batch. The rotation speed is set to 70 rpm and the experiment runs till interrupted. The pressure built up along the screw is balanced by the force on the extruder barrel at the bottom under stable flow

conditions this force will depend on the melt viscosity and is stored as function of time.

F(t) curves of selected samples:

Figure 5 displays the evolution of the measured force during a compounding trial on the mixture of batches A and B with no chain extender. The increase of the force corresponds to the material entering the screw during manual feeding. The force remains constant reaching a plateau level.

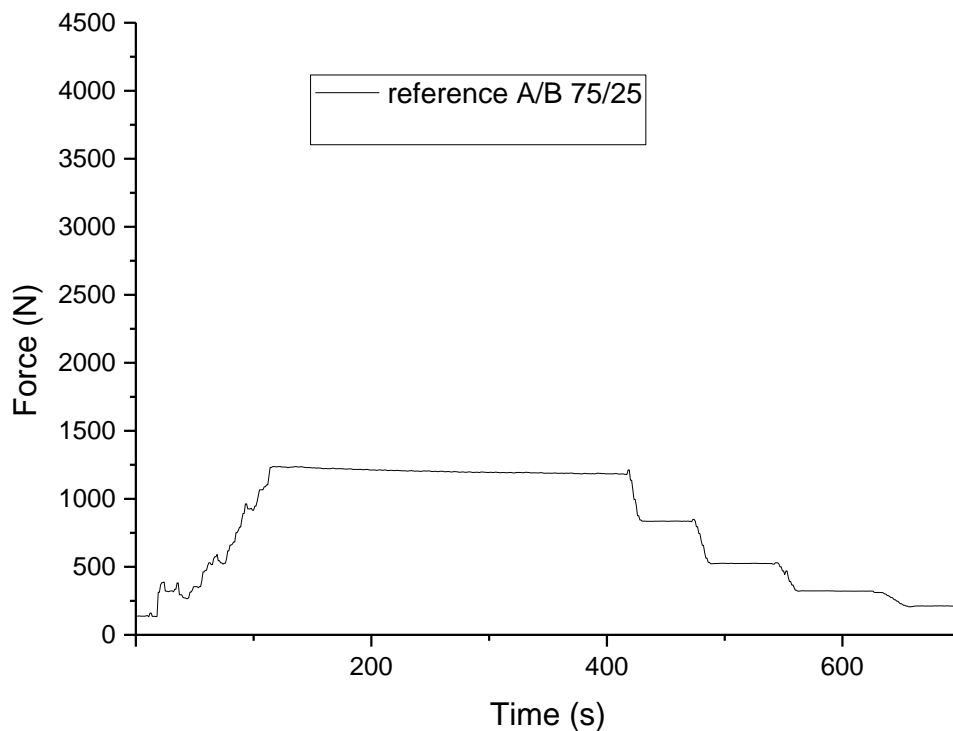


Figure 5 Force vs time for the PET reference sample (mixtures of batches A/B 75%/25%).

Due to the manual filling it is difficult to reproduce the filling sequence exactly. When the CE reaction has already started, the plateau levels are reached very fast concerning the CE of Clariant and PDMA. The sample with the CE Irgafos reveals a sharp peak in the beginning. The CE Joncryl reacts quickly (60 sec residence time at 280 °C will provide 99% completion, [6]). However, during this very short period, the chain extender reaction has already started and there is no steady state in this case. We see this in **Figure 6** where we compare the initial phase of the extrusion compounding of the reference sample versus the sample containing 1,5 % CE Joncryl (BASF). As the CE starts reacting while the melt is being homogenized, the level of the force will vary with the feeding and the CE concentration.

The step-shaped course results from the fact that quantities were taken for certain specimens.

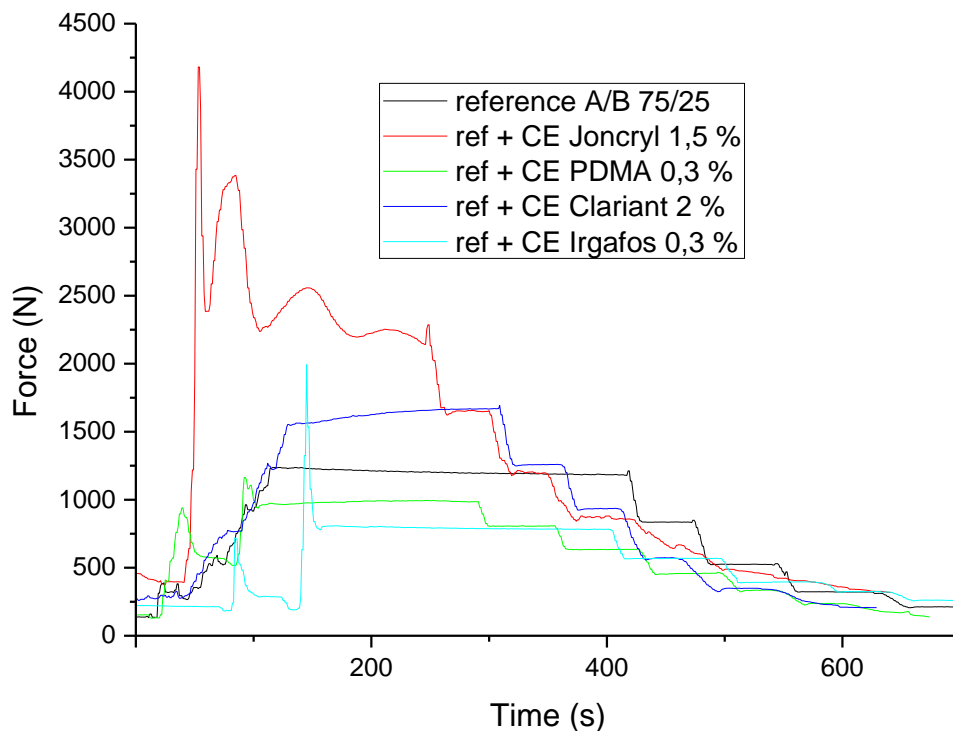


Figure 6 Force development during the initial phase of compounding for PET samples (mixtures of batches A/B 75%/25%).

3.2.6 Results

3.2.6.1 Mechanical testing

Results of the PET samples with mixtures of batches A/B 75%/25%:

The tensile strain at yield values of the mixed batch A and B samples have almost identical values (see **Figure 7**). As far as the mechanical properties of the mixed A/B samples are concerned, only the sample containing 1,5 % of the CE Joncryl exhibits a little higher tensile stress at yield value (see **Figure 8**). The tensile stress values of the other samples do not differ very much from each other.

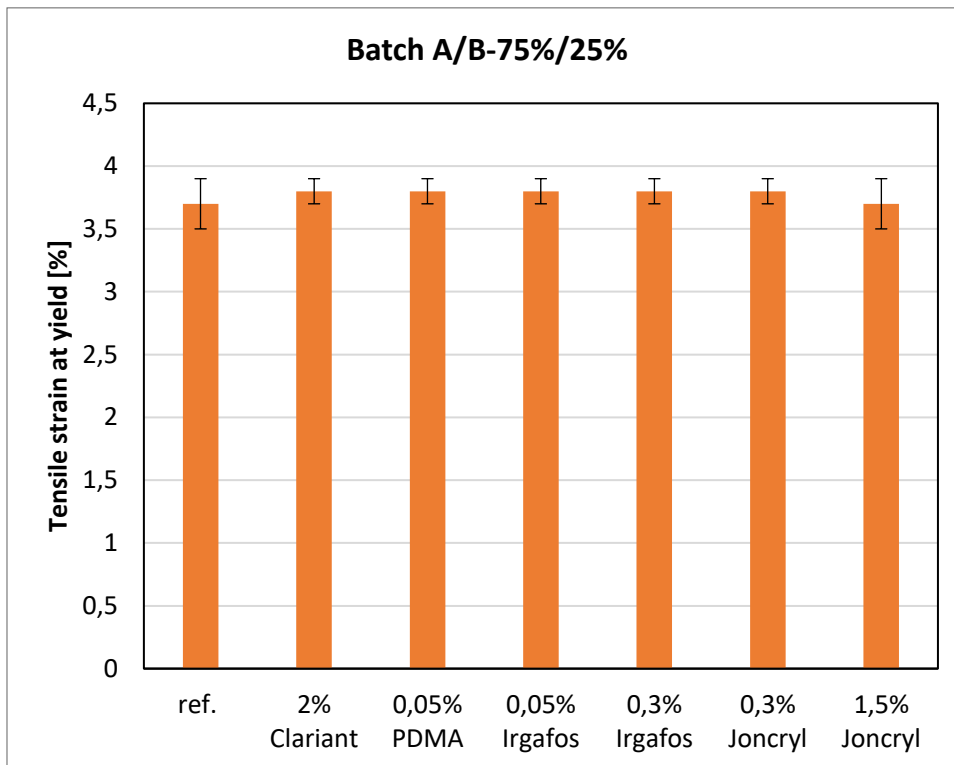


Figure 7 Tensile strain at yield values of the mixed batch A and B samples (75% A and 25% B) which contain different chain extenders.

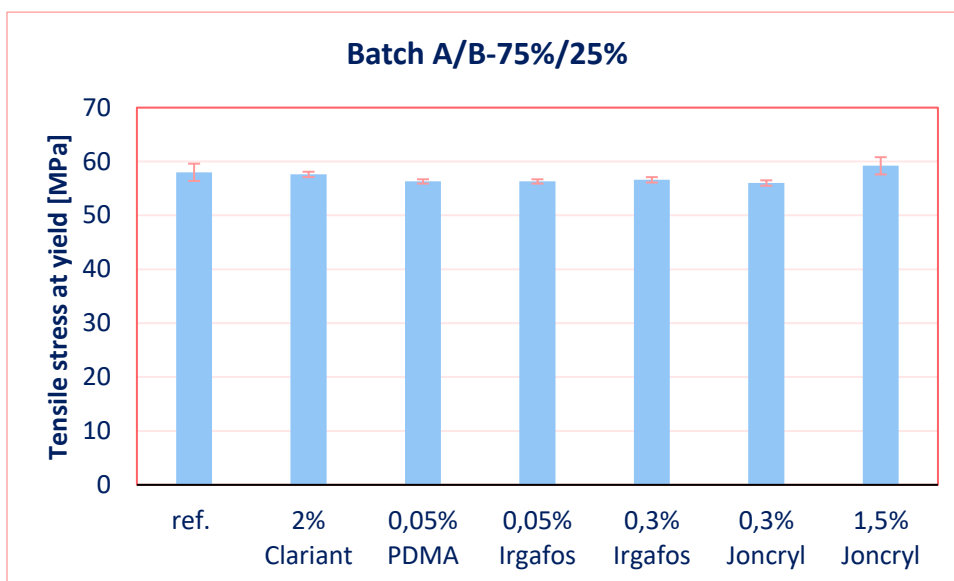


Figure 8 Tensile stress at yield values of the mixed batch A and B samples (75% A and 25% B) which contain different chain extenders.

Results of the PET samples with batch C:

Tensile strain at yield values of the batch C samples and selected CE have also almost identical values (see **Figure 9**). As far as the tensile stress at yield values are concerned, the addition of 2 % CE from Clariant leads to a little higher value exhibiting the highest stress value of the processed samples. Also, the sample containing 2 % of the Joncryl CE leads to a slight increase in the tensile stress at yield value (see **Figure 10**).

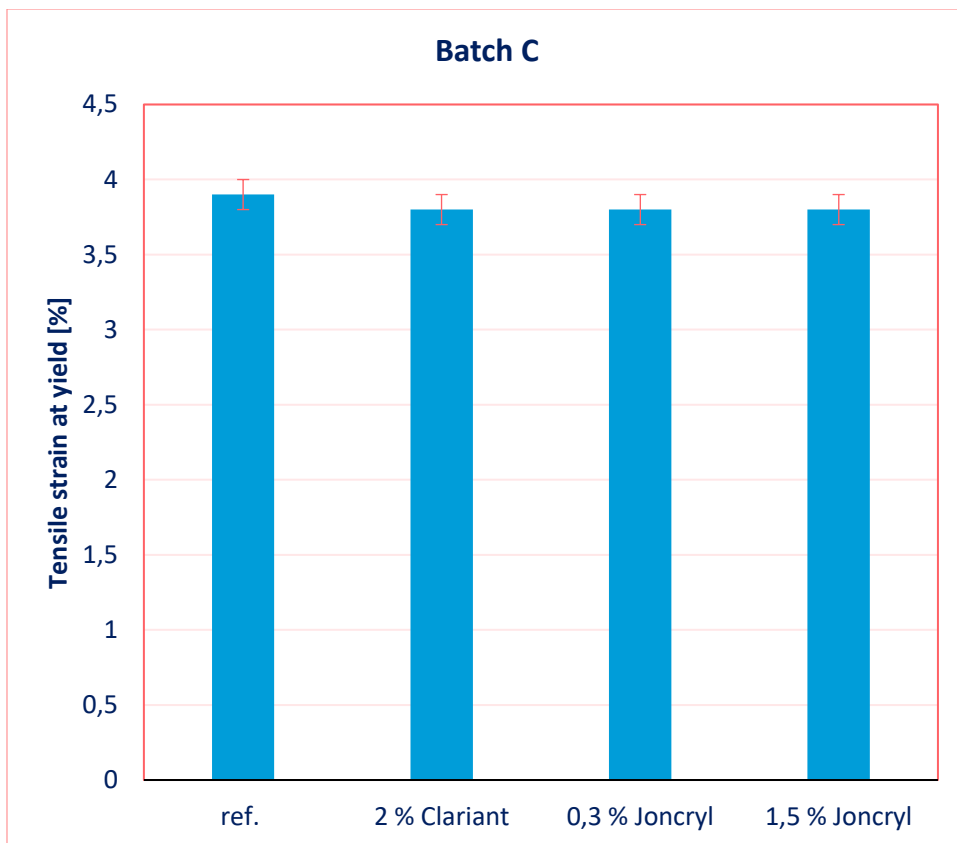


Figure 9 Tensile strain at yield values of the batch C samples which contain different chain extenders.

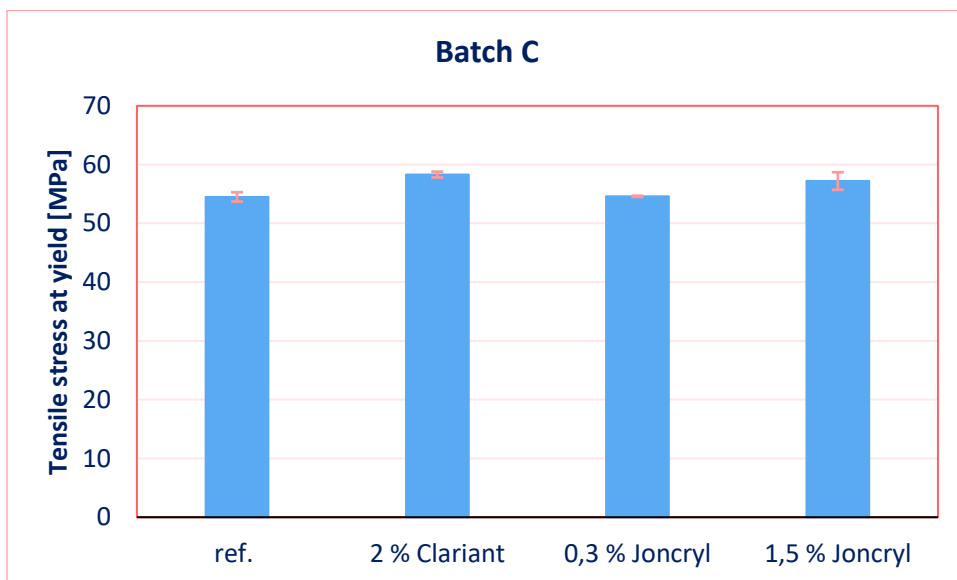


Figure 10 Tensile stress at yield values of the batch C samples which contain different chain extenders.

3.2.6.2 Rheology

The results of the frequency sweep measurements (in nitrogen) of the mixed batch A and B reference sample and the sample containing 2 % CE from Clariant are revealed in **Figure 11** and **Figure 12**. They were performed by the decreasing mode (3141 rad/s to 0.1 rad/s). The graphs indicate that the effect of polycondensation of PET in N₂ takes place as it is described in literature [7]. The loss modulus of the sample containing the chain extender shows little higher values. The reproducibility experiment has shown some deviations. This is possible due to slight degradation of the PET.

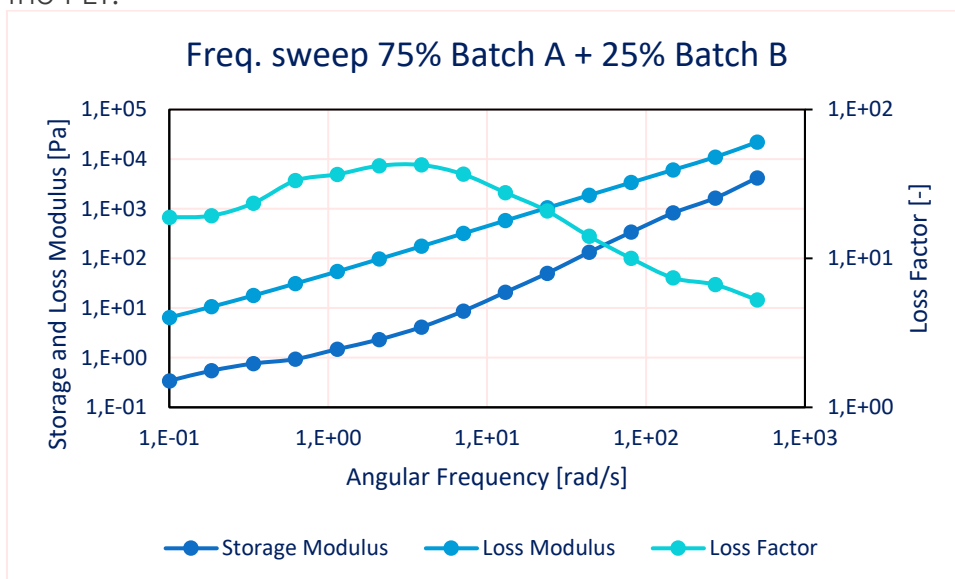


Figure 11 Storage, loss modulus and loss factor of the mixed batch A and B reference sample (frequency sweep measurements in nitrogen).

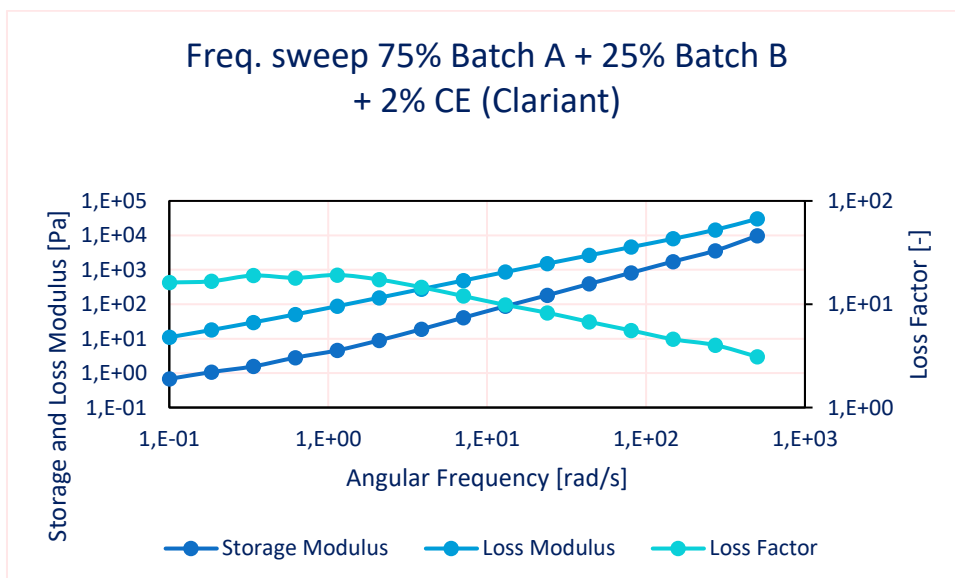


Figure 12 Storage, loss modulus and loss factor of the mixed batch A and B sample containing 2 % of the CE from Clariant (frequency sweep measurements in nitrogen).

3.2.7 Further investigations

Due to the high temperatures, a degradation of the PET takes place. This affects the physical and chemical properties of the samples. Further investigations (e. g. DSC-TGA-MS) will be carried out to determine the crystallinity and the composition of the PET samples. FTIR and NMR experiments are important to evaluate possible chemical changes occurred in PET after the reaction with Irgafos, PMDA and Joncryn. Furthermore, the rheological investigations are also important to evaluate the effective action of chain extenders on PET as well as the increase in polydispersity during the measurements depending on the types of chain extenders.

References

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4. Automotive parts

Centro Ricerche Fiat (CRF) is a research institute for Fiat, the automotive company. CRF investigate how to develop parts from new materials. In the automotive industry there is a significant usage of Polypropylene (PP) and Polyamide (PA). To evaluate alternative feedstocks, CRF will be investigating using PET in place of PA.

4.1. CRF/Proplast Lab scale formulation for automotive applications

The study has dealt with the development of new formulations based on recycled plastics coming from the urban collection system, suitable for being used in several application in the automotive sector. For this reason, as a first step, CRF – with the support of Proplast – selected several target applications in which the use of recycled plastic is industrially and technically feasible. This means that the aesthetic and mechanical requirements are not so harsh to make them unlikely to be used. These applications have been described elsewhere, in any case each of them has a specific technical target, reported in the FCA documents, and a restricted list of commercial grades. The following table summarize the selected commercial grades for all the application of the project.

Table 12

Material	FCA code	Producer	Selected grade
PP-TD10	PP 48.380	SABIC	PPC7175
PP-GF15 TD15	PP 130.50		
PP-TD20	PP 50.20 R	POLITEC	
PP-TD30	PP 58.80 R	POLITEC	
PA66 GF30	PA 240.80	RADICI	RADILON A RV300W
PBT GF30		DuPont	CRASTIN HR 5330 HF

Based on the different thermal resistance requirements for the selected applications, two different polymers have been selected as raw material from recycled feedstock: r-PET for replacing PA66 and PBT, and r-PP for replacing virgin PP. In particular:

- Multicolor PET (in Italy PET bottle separation is based on the color: transparent, blue and multicolour) from DENTIS
- PP BRETENE from Breplast / Montello

In the next sections, all the work that has been carried out will be presented. The first section reports the approach and the results obtained with the formulations based on PP. The second one reports the formulations based on PET. All the formulations have been prepared by melt compounding process in a co-rotating twin extruder Leistritz 27, with a modulated screw profile, **Figure 13**.



Figure 13

4.2. PP FORMULATION

The development of r-PP formulations suitable to be used in the automotive sector has involved several steps.

4.2.1. FIRST STEP

As a first step of the work, the approach has been to study:

- The influence of impurity dimensions on compound performance, by using two PP grades filtered with different mesh dimensions (1 mm and 200 micron)
- The influence of the amount of PE fraction in PP performance (PP/PE 80/20; PP/PE 90/10)
- Effect of the reinforcing additives to the performance of the final material

4.2.1.1. Materials and methods

The selected additives are:

- Talc: H4 IMIFABI
- Glass fibers: Lanxess CS7952

The first series of compound has been based on the 1-mm filtered PP, and the list of the recipes is:

- Extruded neat PP
- PP + 10% Talc
- PP + 20% Talc
- PP + 30% Talc
- PP + 20% GF (main hopper)
- PP + 20% GF (side feeder)

Note that glass fibers have been added to the polymer following two process layouts, that is adding them in the main hopper and in the side feeder (formulation 5 and 6). The chosen screw profile for the PP formulations is the one reported in **Figure 14** (die on the left side of the screw).

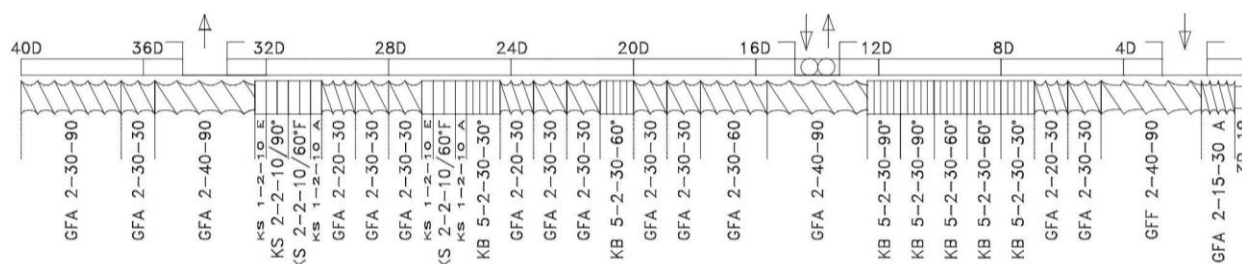


Figure 14

The produced materials were injection molded for the production of the specimens for the characterization. The injection molding was carried out with an injection molding press Arburg AllRounder 370S 500/170 (Clamping force: 500 kN – Max. swept volume 58 cm³ – Max. Injection Pressure 2500 bar).

As for the characterization of the materials, several tests have been performed, namely:

Tensile tests. Tensile tests were performed according to ISO527 standard, using a Zwick Roell dynamometer Z010, with a 10 kN load cell (1 mm/min Elastic modulus speed – 50 mm/min test speed).

Charpy impact test (notched). Charpy impact tests was performed according to ISO 179/A standard, using an ATS FAAR IMPACT-15 equipment with a 1 J pendulum impact energy. The A-type notch has been obtained according to ISO2818 using a 6816 Notchvis Instron-CEAST equipment.

Morphological analysis (optical microscopy). The morphological study on the prepared samples was performed with a KIM 3020DE optical microscope (33-210X) from ARCS.

DSC. Differential scanning calorimetry (DSC) analysis was performed using a Q2000 TA Instrument under inert atmosphere with the scan rate set at 10°C/min and the temperature range of 25-225°C (three cycles: 1st heating – cooling – 2nd heating). All the data has been calculated from the curves by using the Universal Analysis software from TA Instrument.

TGA. Thermal gravimetric analysis (TGA) analysis was performed with a Q550 equipment from TA Instruments, under air and nitrogen atmosphere. The temperature range was set at 50-800°C and the specimens were placed in a platinum holder.

4.2.1.2. Results and discussion

Tensile tests. The results of the tensile tests are reported in **Table 13** and **Figure 15**. AS it is possible to observe, the elastic modulus of the neat PP is lower than the one typical for a PP virgin homopolymer, and it is most likely due to the presence of PE fraction, which is known to have a lower stiffness as compared with PP. No effect has been detected caused by the extrusion process. The effect produced by the talc is in accordance with what is expected from the general technical literature, which basically consists in an increase of the stiffness and of the brittleness, proportional with the content of talc. The addition of glass fibers from the main hopper is detrimental for the fiber length, and for the final mechanical properties of the compound. Indeed, as it can be seen, the performance of the PP+20%GF is significantly higher when the glass fibers are added from the side feeder.

Table 13

Material	Elastic Modulus (MPa)		Yield Stress (MPa)		Strain at yield Stress (%)		Stress at break (MPa)		Strain at break (%)	
	Media	DevSt	Media	DevSt	Media	DevSt	Media	DevSt	Media	DevSt
Neat PP (1 mm filter)	1113	(0)	25.6	(0.1)	10.5	(0.0)	20.1	(0.4)	19.5	(0.6)
Extruded neat PP	1117	(8)	25.8	(0.2)	10.3	(0.3)	14.9	(8.7)	24.5	(10.2)
PP + 10% Talc	1424	(13)	25.3	(0.1)	8.2	(0.2)	20.9	(1.9)	14.9	(2.3)
PP + 20% Talc	1935	(30)	25.0	(0.1)	6.0	(0.1)	22.0	(1.2)	10.7	(1.5)
PP + 30% Talc	2248	(30)	25.1	(0.2)	4.8	(0.2)	23.4	(0.5)	7.2	(1.2)
PP + 20% GF (main hopper)	1564	(26)	21.7	(0.1)	7.9	(0.1)	17.2	(1.2)	23.8	(6.3)
PP + 20% GF (side feeder)	2401	(72)	24.0	(0.3)	7.7	(0.2)	18.5	(2.1)	16.0	(1.5)

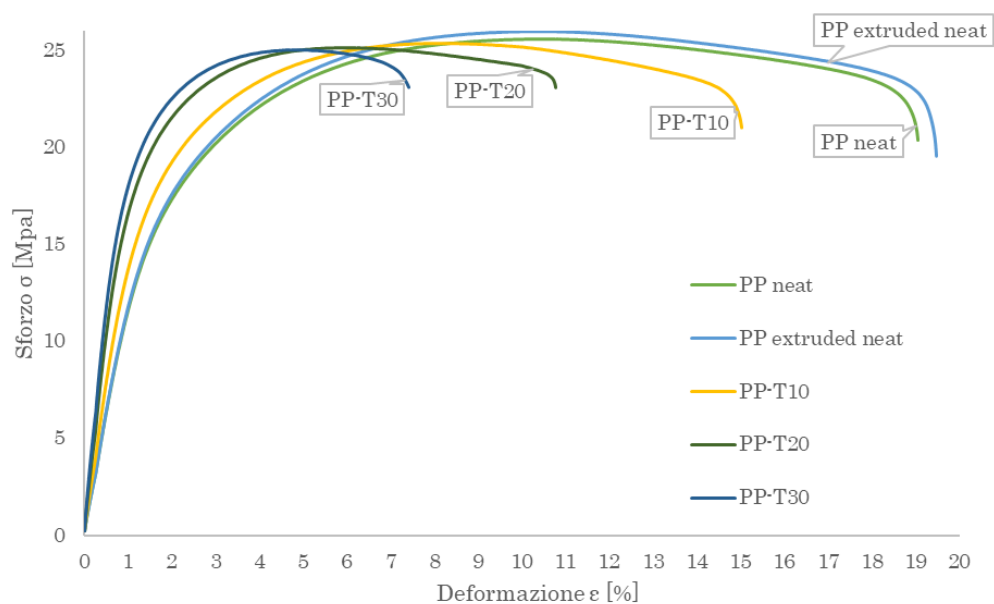


Figure 15

Impact properties.

Table 14 reports the results of the Charpy impact tests. As is can be seen, the neat PP has a value lower than the one of typical virgin PP, and all the fillers lead to a reduction of the resilience of the materials. This means that it this phase, the obtained results do not fulfil the required target and a more in-depth study is needed in the following phases.

Table 14

Material	Notch type	Charpy Impact Strength, notched (23 °C) (KJ/m2)		Type of Fracture
		Avg	StDev	
Neat PP (1 mm filter)	A	7.4	(0.9)	C
Extruded neat PP	A	7.1	(0.7)	C
PP + 10% Talc	A	5.1	(0.6)	C
PP + 20% Talc	A	3.9	(0.4)	C
PP + 30% Talc	A	3.3	(0.3)	C
PP + 20% GF (main hopper)	A	4.4	(0.3)	C
PP + 20% GF (side feeder)	A	4.5	(0.4)	C

Morphological analysis (optical microscopy). **Figure 16** reports the results of the morphological characterization performed by optical microscopy. As it can be seen, several huge impurities can be observed, and this is clearly the reason for the drop of impact properties.

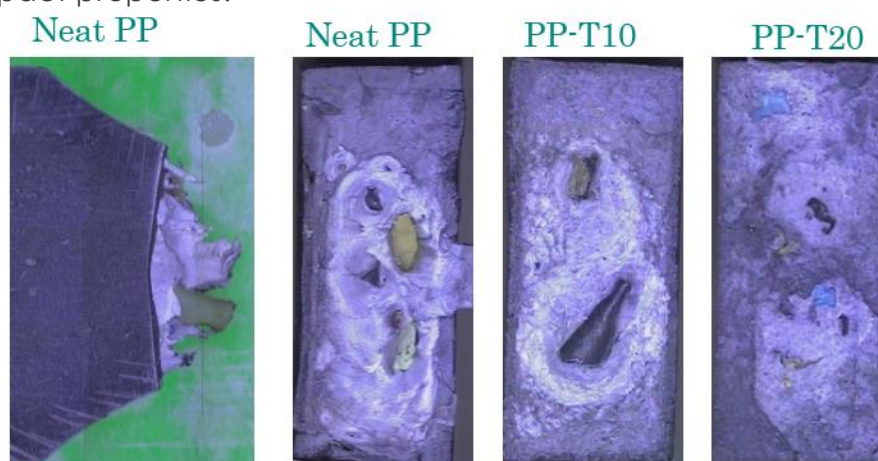


Figure 16

DSC. **Table 15** and **Figure 17** (which shows as an example the first heating of the neat PP) report the results of DSC analysis. As it can be seen from **Figure 17** two endothermic peaks – which are related to the melting transition of the polymers – are clearly visible, indicating the presence of two different polymers: PP ($T_{\text{melting}} = 165^{\circ}\text{C}$) and HDPE ($T_{\text{melting}} \approx 130^{\circ}\text{C}$). The reciprocal amount of these two polymers cannot be evaluated by DSC: for this reason, in **Table 15**, the crystallinity of the materials cannot be calculated. As for the results reported in **Table 15**, it can be noted that no significant variation is led by the presence of the fillers.

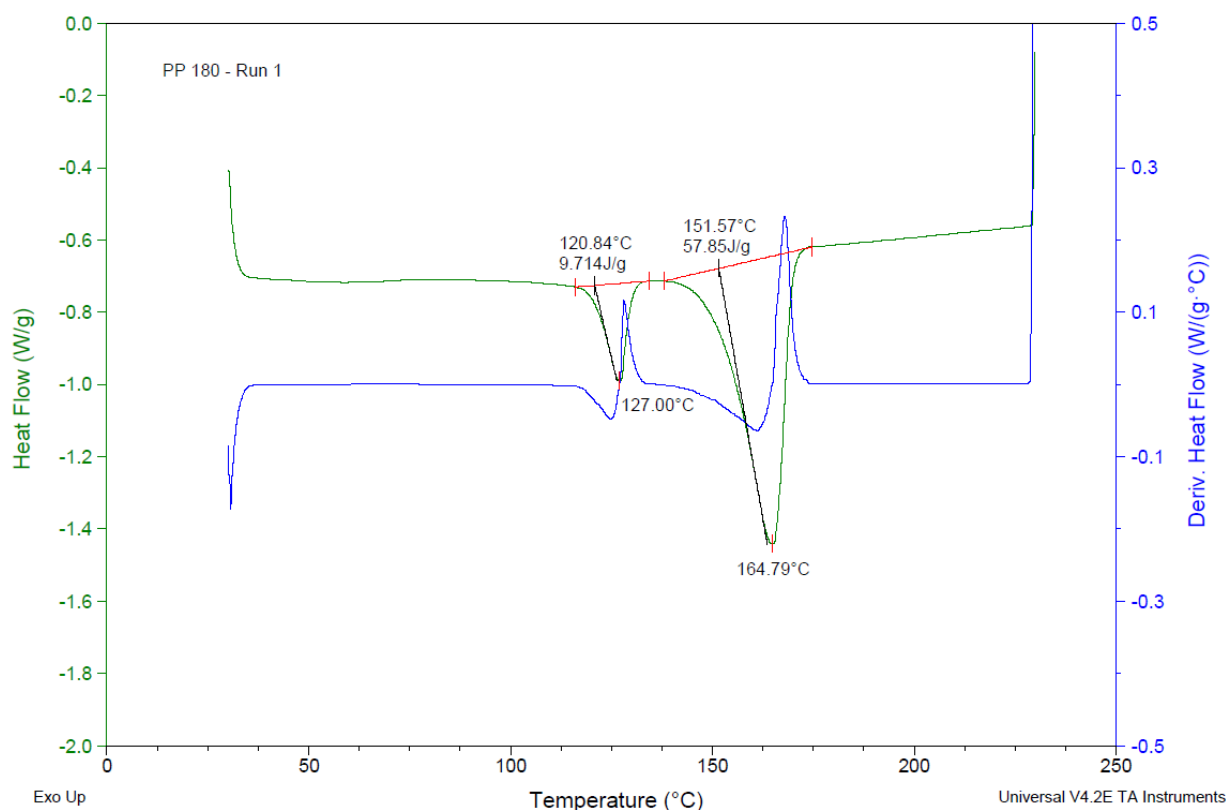


Figure 17

Table 15

Material	1st heating					Cooling		2nd heating				
	Tm1 (°C)	ΔHm1 (J/g)	Tm2 (°C)	ΔHm2 (J/g)	Xc (%)	Tc1 (°C)	Tc2 (°C)	Tm1 (°C)	ΔHm1 (J/g)	Tm2 (°C)	ΔHm2 (J/g)	Xc (%)
Neat PP (1 mm filter)	127.0	8.2	164.8	51.1	-	115.7	124.2	126.2	8.5	162.0	55.4	-
Extruded neat PP	127.0	9.7	164.8	57.9	-	114.4	124.7	126.1	9.9	161.7	60.3	-
PP + 10% Talc	126.9	7.82	165.4	50.7	-	117	124.9	127.1	8	162.4	52.2	-
PP + 20% Talc	126.9	7.1	165.5	44.9	-	118.22	125.5	127.2	6.9	162.4	46	-
PP + 30% Talc	127.4	5.9	165.7	39.2	-	118.86	125.2	127.8	5.7	163.4	40.1	-
PP + 20% GF (main hopper)	127.1	7.4	165.4	45.5	-	114.2	124.4	126.2	7.7	162.1	47.5	-
PP + 20% GF (side feeder)	127.2	6.2	165.9	46.1	-	114.2	124.1	126.4	6.6	162.1	49	-

TGA. **Figure 18** shows the TGA curves of the neat PP, in air and nitrogen atmosphere, and **Table 16** and **Table 17** summarized the obtained results in terms of: T5% (temperature at which the mass loss reaches 5%), DTGpeak (temperature of the peak/peaks of the derivative of the mass loss), residual mass (percentage of residual mass at the maximum temperature). With respect to the results in air, as it is possible to observe, in several cases (especially with the presence of the fillers), there is a split of the main degradation peak in two, with a smaller one at lower temperature. Moreover, it seems that the main peak shift to higher temperatures. As for the results in nitrogen, no significant difference can be detected. In both air and nitrogen tests, the evaluated residual mass is equal to the filler content, further confirming the accuracy of the dosing units during the processing.

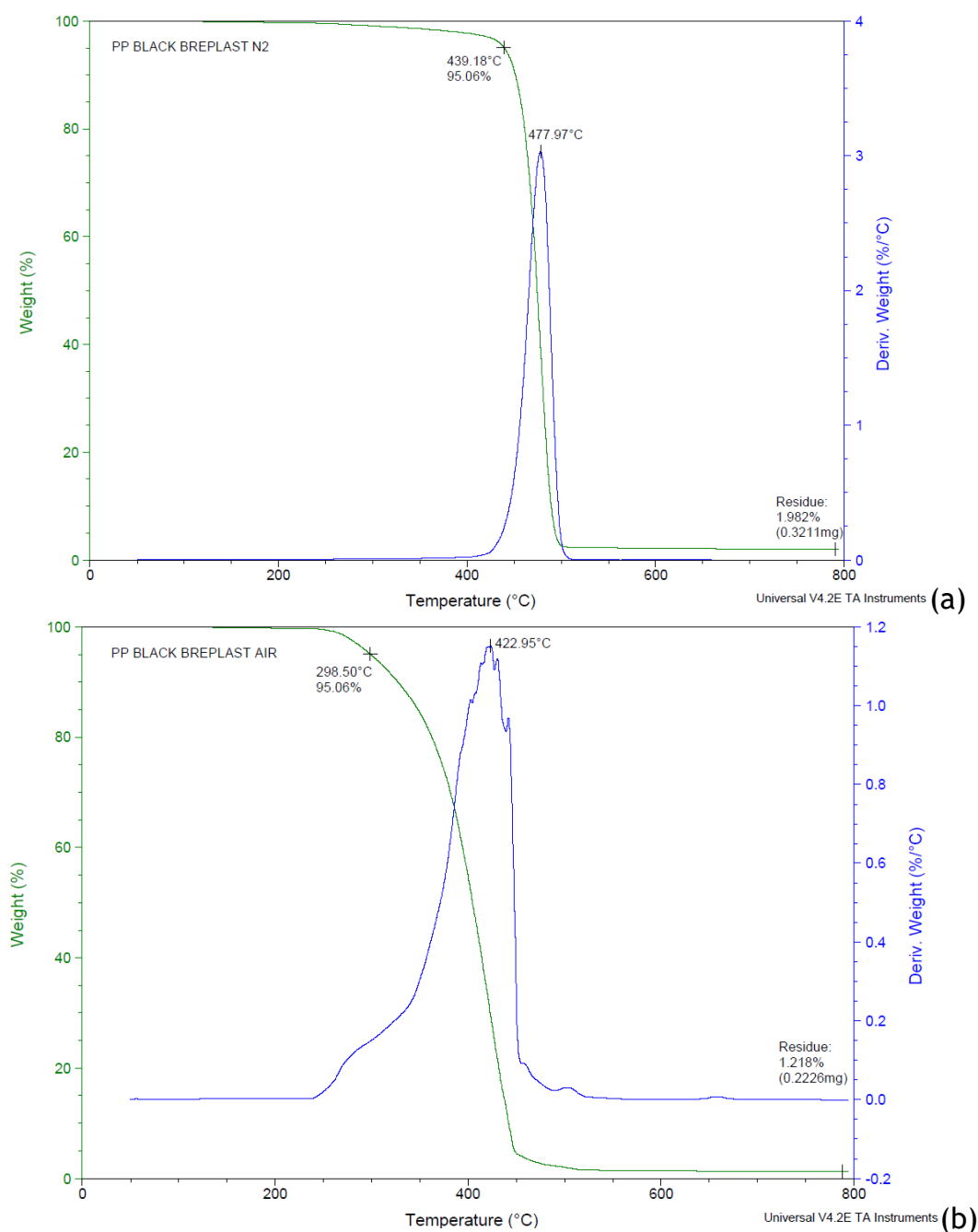


Figure 18 TGA thermograms of neat PP in (a) nitrogen and (b) air.

Table 16

AIR				
Material	T5% (°C)	DTG peak (°C)		Residual mass (%)
Neat PP (1 mm filter)	299	423		1.2
Extruded neat PP	311	418		1.0
PP + 10% Talc	326	445	426	10.8
PP + 20% Talc	332	447	425	20.1
PP + 30% Talc	331	434	396	30.6
PP + 20% GF (main hopper)	324	449	422	20.2
PP + 20% GF (side feeder)	313	440	408	20.7

Table 17

NITROGEN			
Material	T5% (°C)	DTG peak (°C)	Residual mass (%)
Neat PP (1 mm filter)	439	478	2.1
Extruded neat PP	440	476	1.7
PP + 10% Talc	436	474	11.7
PP + 20% Talc	439	475	20.9
PP + 30% Talc	438	472	28.9
PP + 20% GF (main hopper)	440	473	20.2
PP + 20% GF (side feeder)	426	468	21.1

4.2.2. SECOND STEP

4.2.2.1. Materials and methods

The use of 1-mm filtered PP has shown the severe presence of impurities with the effect of pure impact resistance and high variance of the mechanical properties. For this reason, a PP which has been filtered at 200 microns has been used for the following steps (hereinafter we refer to it as PP200 when needed to differentiate from the 1mm filtered). In order to detect the difference between the two PP grades, a DSC test was performed, and the results are reported in **Figure 19**. As it can be seen, the melting peak related to HDPE is significantly lower, indicating a lower presence of HDPE fraction.

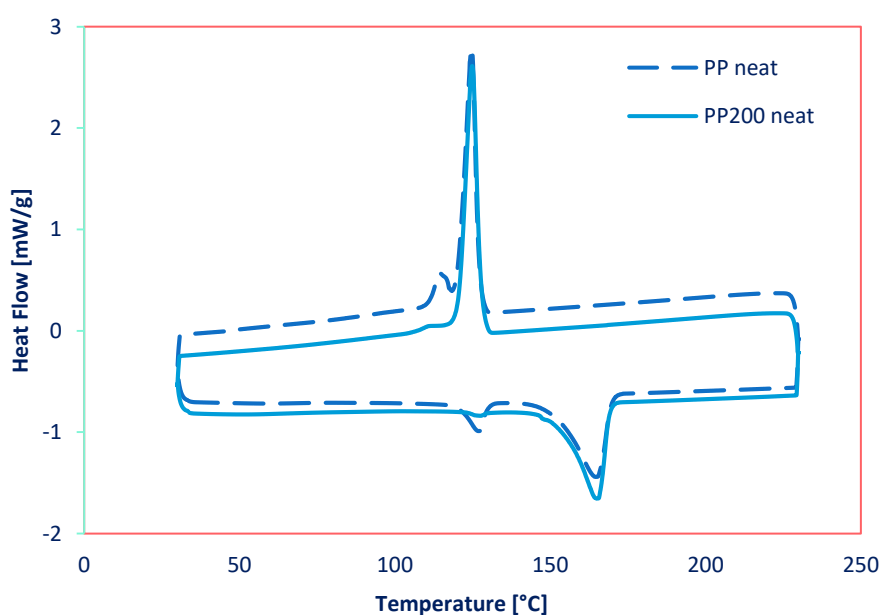


Figure 19

The new recipes that have been produced and studied in this second phase are listed below (all based on PP200):

- Extruded Neat PP (200 mm filtered)
- PP + 10% Talc
- PP + 20% Talc
- PP + 30% Talc
- PP + 10% GF
- PP + 20% GF
- PP + 30% GF
- PP - (GF15 + Talc15)
- PP - (GF10 + Talc20)
- PP - (GF20 + Talc20)

As it can be observed, they are directly focused on the specific selected targets. The processing layout and parameters are the same as in the first step, as well as the injection molding of the specimens. The characterization was based on the same tests as in the first step, apart from the impact properties, which was evaluated by Izod impact test instead of Charpy. This choice was made to stack with the FCA standards, which are based on this test.

IZOD impact test (notched). Izod impact tests was performed according to ISO 180/1A standard (notched), using an ATS FAAR IMPACT-15 equipment with a 1 J pendulum impact energy. The A-type notch has been obtained according to ISO2818 using a 6816 Notchvis Instron-CEAST equipment.

4.2.2.2. Results and discussion

Tensile tests. The results of the tensile tests are reported in **Table 18** and **Figure 20**. As it is possible to observe, the elastic modulus of the neat PP is lower than the one typical for a PP virgin homopolymer, and it is most likely due to the presence of PE fraction, which is known to have a lower stiffness as compared with PP. Nonetheless, it is a little higher than the one found with the PP used in step1, further confirming that the presence of PE is lower than in the previous material. The effect produced by the talc is in accordance with what is expected from the general technical literature and what obtained in Step 1. The addition of glass fibres generally increases the mechanical performance.

Table 18

Material	Elastic Modulus (MPa)		Yield Stress (MPa)		Strain at yield Stress (%)		Stress at break (MPa)		Strain at break (%)	
	Media	DevSt	Media	DevSt	Media	DevSt	Media	DevSt	Media	DevSt
PP200	1163	(13)	26.0	(0.1)	7.7	(0.1)	14.9	(6.2)	23.0	10
PP + 10% Talc	1569	(17)	26.0	(0.2)	6.5	(0.1)	18.3	(3.7)	14.8	(2.9)
PP + 20% Talc	1956	(13)	25.5	(0.1)	5.4	(0.0)	20.9	(1.5)	10.1	(2.0)
PP + 30% Talc	2379	(15)	24.7	(0.1)	4.4	(0.1)	20.9	(0.8)	8.9	(1.6)
PP + 10% GF	2591	(9)	35.6	(0.1)	2.8	(0.1)	33.3	(0.8)	3.9	(0.2)
PP + 20% GF	3811	(32)	42.1	(0.1)	2.0	(0.0)	41.3	(0.0)	2.3	(0.1)
PP + 30% GF	5044	(134)	41.9	(0.2)	1.4	(0.0)	41.4	(0.3)	1.6	(0.0)
PP - (GF15 + Talc15)	4046	(49)	42.0	(0.2)	2.3	(0.1)	41.5	(0.6)	2.5	(0.1)
PP - (GF10 + Talc20)	3840	(57)	38.8	(0.3)	2.5	(0.0)	38.0	(0.4)	2.9	(0.1)
PP - (GF20 + Talc20)	5107	(123)	42.3	(0.4)	1.7	(0.1)	41.9	(0.5)	1.8	(0.0)

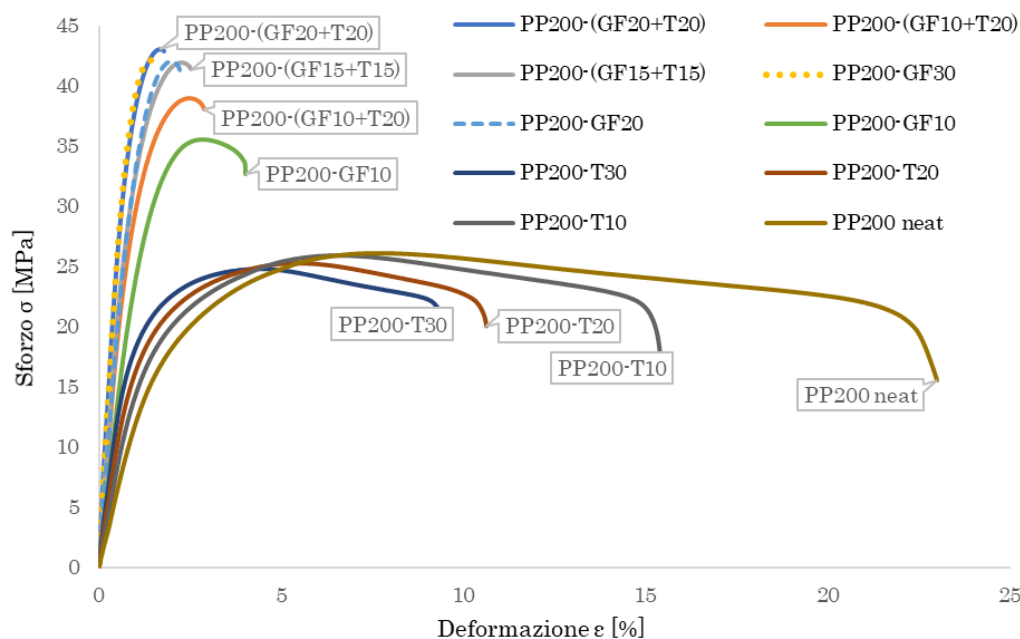


Figure 20

Impact properties. **Table 19** reports the results of the Izod impact tests. As is can be seen, the neat PP has a value lower than the one of typical virgin PP, and all the fillers lead to a reduction of the resilience of the materials. Only the presence of glass fibers allows the compound to slightly improve the performance. This means that in this phase, the obtained results do not fulfil the required target and a more in-depth study is needed in the following phases.

Table 19

Material	Notch type	IZOD Impact Strength, notched (23 °C) (KJ/m2)		Type of Fracture
		Avg	StDev	
PP200	A	5.5	(0.3)	C
PP + 10% Talc	A	5.3	(0.8)	C
PP + 20% Talc	A	4.3	(0.3)	C
PP + 30% Talc	A	4.7	(1.6)	C
PP + 10% GF	A	5.0	(0.3)	C
PP + 20% GF	A	5.7	(0.2)	C
PP + 30% GF	A	5.6	(0.3)	C
PP - (GF15 + Talco15)	A	5.9	(0.3)	C
PP - (GF10 + Talco20)	A	7.2	(1.9)	C
PP - (GF20 + Talco20)	A	5.1	(0.1)	C

Morphological analysis (optical microscopy). **Figure 21** reports the results of the

morphological characterization performed by optical microscopy (as an example only neat PP, PP-T10 and PP-T30 are reported). As it can be seen, only minor impurities can be observed with respect to the PP used in step 1, and this is another compelling evidence of the better quality of this material.

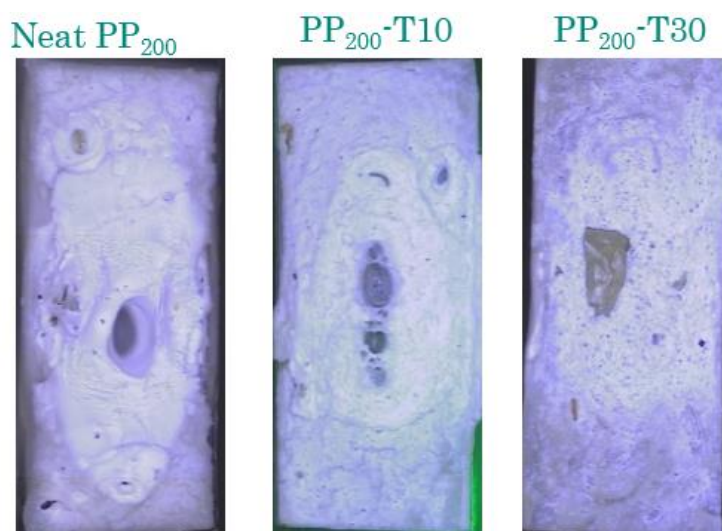


Figure 21

DSC. **Table 20** and report the results of DSC analysis. As it can be seen the endothermic peak related to the melting transition of the PE is less visible than in the step 1, indicating the minor presence of this fraction in the PP, determining a higher purity of this material. The reciprocal amount of these two polymers cannot be evaluated by DSC: for this reason, in **Table 20**, the crystallinity of the materials cannot be calculated. As for the results reported in **Table 20**, it can be noted that no significant variation is led by the presence of the fillers.

Table 20

Material	1st heating					2nd heating				
	Tm1 (°C)	ΔHm1 (J/g)	Tm2 (°C)	ΔHm2 (J/g)	Xc (%)	Tm1 (°C)	ΔHm1 (J/g)	Tm2 (°C)	ΔHm2 (J/g)	Xc (%)
PP + 10% Talc	127.7	0.6	166.2	54.8	-	125.5	0.9	163	56	-
PP + 20% Talc	126.0	1.1	165.0	49.7	-	125.9	1.0	163	53	-
PP + 30% Talc	127.5	0.3	165.5	41.4	-	126.0	0.4	163	43	-
PP + GF10	128.1	0.6	166.9	50.0	-	125.5	1.0	163	54	-
PP + GF20	127.4	0.7	165.8	48.1	-	125.0	0.9	163	50	-
PP + GF30	127.4	0.6	165.3	43.4	-	124.9	1.0	163	46	-
PP - (GF15 + Talco15)	127.6	0.4	165.9	42.0	-	125.7	0.6	163	43	-
PP - (GF10 + Talco20)	127.5	0.4	166.0	41.0	-	125.7	0.6	164	43	-
PP - (GF20 + Talco20)	126.9	0.3	164.9	30.7	-	127.7	0.2	163	33	-

TGA. **Table 21** and **Table 22** summarized the obtained results in terms of: T5% (temperature at which the mass loss reaches 5%), DTGpeak (temperature of the peak/peaks of the derivative of the mass loss), residual mass (percentage of residual mass at the maximum temperature). With respect to the results in air, as it is possible to observe, in this step the previous split of the main degradation peak in two, with a smaller one at lower temperature, is visible just in two cases, whereas

in most samples is not visible at all. The main peak shifts to higher temperature. As for the results in nitrogen, no significant difference can be detected. In both air and nitrogen tests, the evaluated residual mass is equal to the filler content, further confirming the accuracy of the dosing units during the processing.

Table 21

AIR			
Material	T5% (°C)	DTG peak (°C)	Residual mass (%)
PP + 10% Talc	308	418	11.8
PP + 20% Talc	323	429	21.3
PP + 30% Talc	335	434	29.4
PP + GF10	291	411	12.4
PP + GF20	303	417	21.8
PP + GF30	303	414	32.2
PP - (GF15 + Talco15)	326	428	33.0
PP - (GF10 + Talco20)	331	427	31.2
PP - (GF20 + Talco20)	335	428	40.7

Table 22

NITROGEN			
Material	T5% (°C)	DTG peak (°C)	Residual mass (%)
PP + 10% Talc	425	464	10.8
PP + 20% Talc	427	465	20.7
PP + 30% Talc	429	465	29.8
PP + GF10	427	463	12.0
PP + GF20	427	464	21.4
PP + GF30	430	465	30.1
PP - (GF15 + Talco15)	428	464	30.1
PP - (GF10 + Talco20)	430	465	31.1
PP - (GF20 + Talco20)	433	465	43.0

4.2.3. THIRD STEP

Based on the results of Step 2, the specific goal of the third step has been the optimization of the impact properties. Indeed, if we compare the results obtained at the end of step 2 with the benchmark (first line of each table), in terms of tensile and impact properties (**Table 23** through **Table 26**), we can deduce that in several cases (PP-T20, PP-T30, PP-(GF15+T15)) the target has been reached (the lower impact properties of PP-T30 with respect to the benchmark is considered acceptable by CRF). Nonetheless, the PP-T10 benchmark has a much higher impact resilience than the developed materials. For this reason, the third step has been focused on this formulation.

Table 23

PP-T10	E [MPa]	σ max [MPa]	ε [%]	IZOD [kJ/m ²]
PP-T10 benchmark	1192	18,3	21,6	42,6
Neat PP200	1163	26,0	23,0	5,5
PP200-T10	1569	26,0	14,8	5,3

Table 24

PP-T20	E [MPa]	σ max [MPa]	ε [%]	IZOD [kJ/m ²]
PP-T20 benchmark	2256	26,3	6,9	4,0
PP200-T30	2379	24,7	8,9	4,7
PP-T30	2248	25,1	7,2	3,3

Table 25

PP-(GF15+T15)	E [MPa]	σ max [MPa]	ε [%]	IZOD [kJ/m ²]
PP-(GF15+T15) benchmark	3320	40,2	3,2	5,1
PP200-GF20	3811	42,1	2,3	5,7
PP200-(GF10+T20)	3840	38,8	2,9	7,2

Table 26

PP-T30	E [MPa]	σ max [MPa]	ε [%]	IZOD [kJ/m ²]
PP-T30 benchmark	1820	17,4	12,6	13,5
PP200-T20	1956	25,5	10,1	4,3
PP-T20	1935	25,0	10,7	3,9

4.2.3.1. Materials and methods

Several polymers were selected from the market and used as additives, namely: INTUNE D5545 (Dow Chemicals) is a PP-based Olefin Block Copolymers (OBC) mix segments of PE and PP which is used to compatibilize PP and PE commonly present in the recycled PP.

ENGAGE8401 is one the Engage products from Dow. ENGAGE™ are polyolefin elastomers (POEs) designed to offer customers improved impact performance, melt strength, and processability over a broad spectrum of markets and applications. The selected grade has a good compromise between MFI and elastomeric behavior (see **Figure 22**).

KRATON G1657V (from Kraton Polymers) G1657 V is a clear, linear triblock copolymer based on styrene and ethylene/butylene with a polystyrene content of 13% (impact resistance).

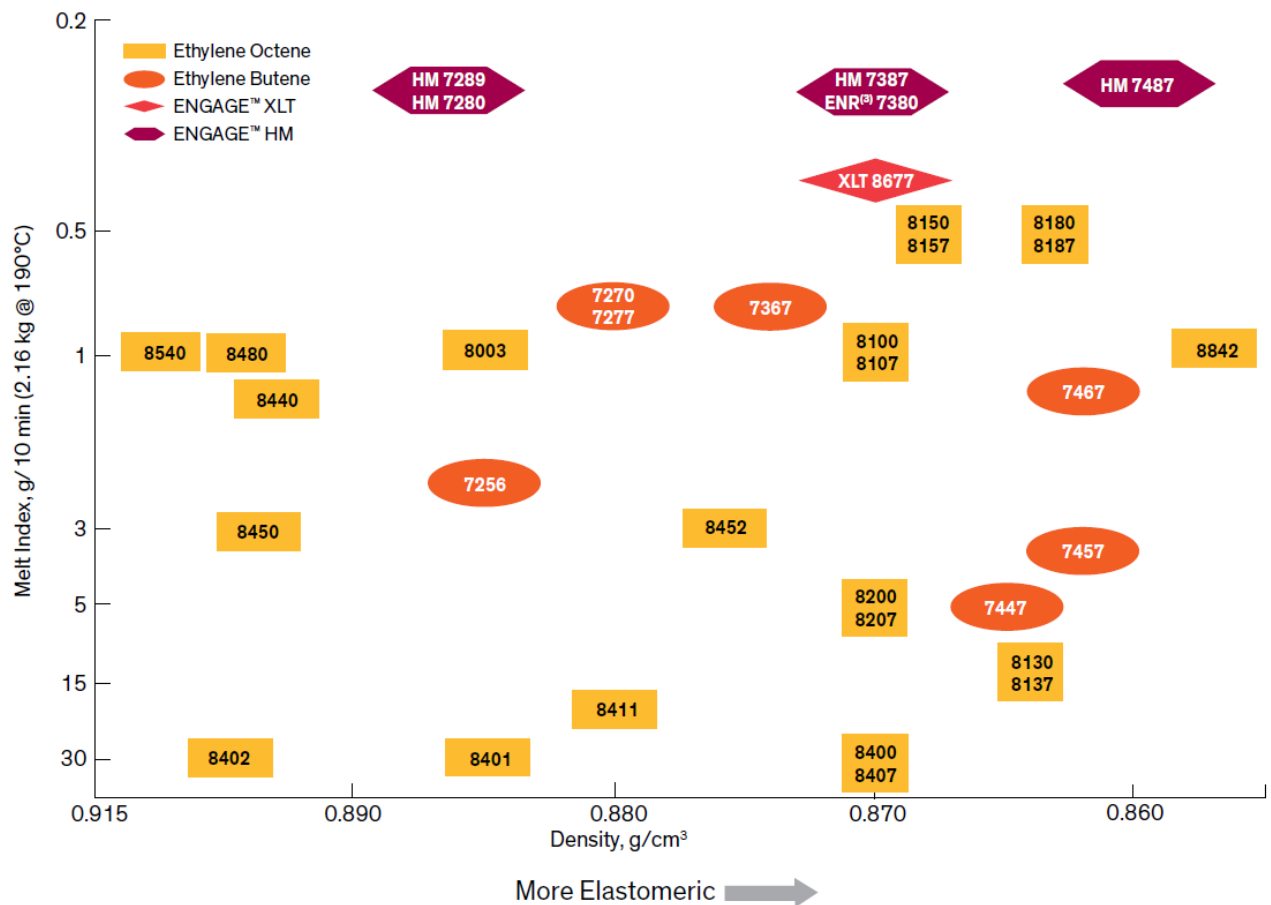


Figure 22

The produced formulations are as follows:

- PP + 5% Intune D5545
- PP + 5% Engage 8401
- PP + 5% Intune D5545 + 5% Engage 8401
- PP + 5% Kraton G1657V
- PP + 5% Intune D5545 + 5% Kraton G1657V
- PP + 10% Talc + 5% Intune D5545
- PP + 10% Talc + 5% Engage 8401
- PP + 10% Talc + 5% Intune D5545 + 5% Engage 8401
- PP + 10% Talc + 5% Kraton G1657V
- PP + 10% Talc + 5% Intune D5545 + 5% Kraton G1657V

The formulations without talc has been produced in order to isolate the effect of the new additives and to check the presence of eventual interaction with the talc. The performed characterization was the same as in the previous step.

4.2.3.2. Results and discussion

Tensile tests. The results of the tensile tests are reported in Table 27.

Table 27

Material	Elastic Modulus (MPa)		Yield Stress (MPa)		Strain at yield Stress (%)		Stress at break (MPa)		Strain at break (%)	
	Media	DevSt	Media	DevSt	Media	DevSt	Media	DevSt	Media	DevSt
PP + 5% IntuneD5545	1019	(11)	24.1	(0.1)	9.8	(0.2)	7.7	(3.1)	111.6	(28.6)
PP+5% Engage8401	993	(37)	22.9	(0.2)	10.0	(1.1)	6.2	(5.4)	285.8	(151.9)
PP + 5% Engage8401 + 5% IntuneD5545	944	(27)	22.2	(0.2)	10.8	(0.1)	5.6	(4.9)	304.1	(116.9)
PP + 5% Kraton G1657V	929	(57)	21.9	(0.3)	11.1	(0.1)	7.9	(4.6)	197.8	(156.8)
PP + 5% Kraton G1657V + 5% IntuneD5545	896	(18)	21.6	(0.2)	11.3	(0.1)	10.9	(3.7)	272.1	(118.5)
PP+T10 + 5% IntuneD5545	1430	(18)	23.4	(0.1)	7.9	(0.1)	14.5	(2.6)	18.3	(3.8)
PP+T10 + 5% Engage8401	1342	(15)	22.4	(0.1)	8.6	(0.1)	4.3	(3.4)	49.6	(31.5)
PP+T10 + 5% Engage8401 + 5% IntuneD5545	1298	(20)	21.8	(0.2)	8.9	(0.1)	4.9	(4.4)	39.5	(15.5)
PP+T10 + 5% Kraton G1657V	1148	(11)	21.3	(0.1)	9.9	(0.2)	8.1	(4.0)	25.3	(3.1)
PP+T10 + 5% Kraton G1657V + 5% IntuneD5545	1168	(13)	21.1	(0.1)	9.9	(0.1)	6.5	(2.9)	30.9	(3.5)

Impact properties. Table 28 reports the results of the Izod impact tests, notched (type A) and unnotched. As is can be seen, in both cases Kraton G1657V seems to have the strongest positive effect on the impact properties. In particular, the effect is more pronounced in the unnotched test: in this test, both the additives (Kraton G1657V and Engage8401) show a strong effect in improving the impact properties. Moreover, according to the results of this test, also the use of the compatibilizer IntuneD5545 is useful to increase the impact behavior. This means that the used additives increase the crack initiation energy, with limited contribution to the resistance to crack propagation.

Table 28

Material	Notch type	IZOD Impact Strength, notched (23 °C) (KJ/m2)		Type of Fracture	Notch type	IZOD Impact Strength, unnotched (23 °C) (KJ/m2)		Type of Fracture
		Avg	StDev			Avg	StDev	
PP200	A	6.5	(0.5)	C	-	63.6	(7.1)	C
PP + 5% IntuneD5545	A	5.0	(0.3)	C	-	77.5	(16.0)	C
PP+5% Engage8401	A	5.8	(0.5)	C	-	83.8	(13.3)	C
PP + 5% Engage8401 + 5% IntuneD5545	A	5.4	(0.6)	C	-	97.0	(21.7)	C
PP + 5% Kraton G1657V	A	7.8	(0.8)	C	-	120.9	(4.7)	C
PP + 5% Kraton G1657V + 5% IntuneD5545	A	7.3	(0.6)	C	-	101.3	(15.4)	C
PP+T10 + 5% IntuneD5545	A	4.5	(0.7)	C	-	43.5	(9.6)	C
PP+T10 + 5% Engage8401	A	5.0	(0.8)	C	-	47.9	(9.2)	C
PP+T10 + 5% Engage8401 + 5% IntuneD5545	A	4.8	(0.6)	C	-	53.7	(10.9)	C
PP+T10 + 5% Kraton G1657V	A	6.7	(0.7)	C	-	67.3	(13.0)	C
PP+T10 + 5% Kraton G1657V + 5% IntuneD5545	A	6.0	(0.7)	C	-	80.7	(17.2)	C

4.3. PET FORMULATION

The scope of the work was the development of a high thermal resistant PET formulation having good mechanical properties with the target to substitute a PA or PBT compound currently used for the application.

In the first trial, already reported in D5.1, a wide screening of nucleating agents and the selection the proper amount of glass filler was done. As a result of this first trial, the challenges we still need to overcome to reach the desired target are:

1. Strong tendency to degradation when molten in the presence of moisture content and using a too aggressive screw profile
2. The slow crystallization rate during injection molding, in the presence of a not performing nucleating agent, prevent the possibility to obtain an injected part with high thermal resistance
3. An efficient impact modification agent is needed to obtain high impact resistance

Therefore, the second step of experimental phase was focused on:

- A. Study of the best screw profile and processing condition to avoid degradation
- B. Selection the best performant nucleating agent among the ones tested in the preliminary step
- C. Use of an impact modification system to improve impact resistance

4.3.1. SCREW PROFILE AND PROCESS OPTIMIZATION

4.3.1.1. Materials and Methods

A new screw profile was built reducing the kneading blocks and the compression elements in the feeding zone, adding conveying element. A mixing zone was kept in order to fully disperse the nucleating agents and other additives. In the side feeding zone, where glass fibers are added a mild mixing element was kept to avoid fiber breakage.

Drying condition were optimized. A Piovan dehumidification system was used having a dew point -40°C. Drying condition were: 140°C for 5h.

Materials and additives involved:

- Bruggolen P130 (processing aid) - Brüggemann
- Bruggolen P252 (nucleating agent) - Brüggemann
- Glass fibers CS 7967 - Lanxess
- Elvaloy AC12024S (polymer used as additive) - DuPont

The developed materials have been compared to the benchmark materials: Radilon A RV300 (PA66) and Crastin HR5330HF (PBT).

In the injection molding process, mold temperature was kept at 150°C and cycle time was modulated with the aim to compare thermal properties at about the same cooling time (especially for the composition containing glass fibers). Such high mold temperature was selected, inside the window of crystallization ability typical for PET (120-180°C) with the aim to increase crystallization rate. Such temperature was not completely optimized, a more extensive study on cycle time and mold temperature will be done in the next step on the more promising samples.

In Table 29 cycle time and cooling time of the different specimen bars we used for the mechanical analysis.

Table 29

Material	ISO 527		HDT	
	tot	raff	tot	raff
Extruded PET	155	135	151	130
PET + 1%P130	150	135	152	130
PET + 1%P130 + 0.5%P252	103	80	97	80
PET + 1%P130 + 0.5%P252 + 25% FV	146	130	148	130
PET + 19% FV	165	145	146	130
PET + 33% FV	158	140	156	140
PET + 1%P130 + 0.5%P252 + 22% FV + 5%Elvaloy	156	140	147	130
PET + 1%P130 + 0.5%P252 + 19% FV + 10%Elvaloy	147	130	147	130

The combined use of P130 and P252 additives permitted to extract a rigid and crystallized specimen decreasing cooling time to 80 sec also in absence of glass fibers. For all the other formula a stable cooling time was applied with the aim to compare formula in the same condition.

The characterization of the produced samples was based on the same tests described

in the PP section. The thermal mechanical resistance was performed by heat deflection temperature test, as described below.

Heat Deflection Temperature (HDT). The HDT test has been performed by ISO75 with a load of 1.8MPa, according to the procedure shown in **Figure 23**.

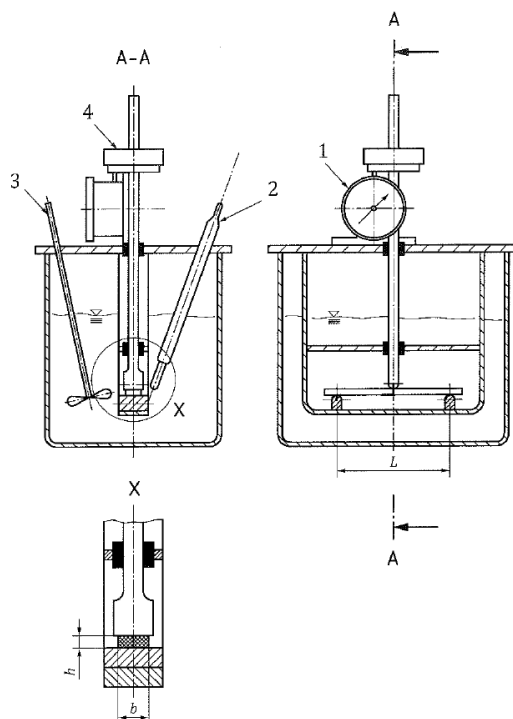


Figure 23

4.3.1.2. Results and discussion

Heat Deflection Temperature (HDT). The results of the heat deflection temperature test of the injected formulation are reported in **Table 30**.

Table 30

Material	HDT (°C)	
	Mean	StDev
PET	89.0	(2.7)
PET + 1%P130	87.7	(1.5)
PET + 1%P130 + 0.5%P252	87.1	(2.8)
PET + 1%P130 + 0.5%P252 + 25% GF	196.1	(2.9)
PET + 20% GF	193.7	(0.5)
PET + 30% GF	212.4	(4.4)
PET + 1%P130 + 0.5%P252 + 25% GF + 5%Elvaloy	191.2	(0.0)
PET + 1%P130 + 0.5%P252 + 20% GF + 10%Elvaloy	188.7	(4.5)

The presence of the nucleating agent without any reinforcing additives is not enough to increase the heat deflection temperature above 100°C. Glass fibers are needed to reach temperature in the range of 190-210°C.

As expected, the use of Elvaloy as impact modifier shows a decrease in thermal resistance with the increase of rubber content. A more extensive study on different impact modifiers have been done in the third step.

Tensile test. In Table 31 the results are reported and can be summarized as follow:

- The use of glass fiber (GF) shows an increase in stiffness as function of GF amount
- The amount of glass fibers needed to reach an elastic modulus comparable to the reference is about 15 % when none impact modifier is added and have to be increased to 20-22% when Elvaloy is added.
- The use of impact modification decrease stress at yield

Table 31

Material	Elastic Modulus (MPa)		Yield Stress (MPa)		Strain at yield Stress (%)		Stress at break (MPa)		Strain at break (%)	
	Media	DevSt	Media	DevSt	Media	DevSt	Media	DevSt	Media	DevSt
Regrinded PET	3324	(44)	56	(6)	1.9	(0.3)	55	(7)	1.9	(0.3)
PET + 1%P130	3202	(38)	73	(3)	3.5	(0.4)	67	(6)	5.9	(2.2)
PET + 1%P130 + 0.5%P252	3170	(65)	70	(1)	3.6	(0.0)	15	(12)	12.5	(4.1)
PET + 1%P130 + 0.5%P252 + 25% FV	9892	(289)	126	(2)	1.6	(0.1)	125	(3)	1.6	(0.1)
PET + 20% GF	7766	(99)	111	(2)	1.7	(0.1)	109	(3)	1.7	(0.1)
PET + 30% GF	10940	(230)	137	(4)	1.6	(0.1)	135	(3)	1.6	(0.1)
PET + 1%P130 + 0.5%P252 + 25% FV + 5%Elvaloy	6824	(59)	99	(1)	2.2	(0.0)	97	(1)	2.3	(0.1)
PET + 1%P130 + 0.5%P252 + 20% FV + 10%Elvaloy	6054	(29)	86	(0)	2.1	(0.0)	85	(1)	2.2	(0.1)
PET + 1%P130 + 20%FV	6761	(165)	83	(5)	1.3	(0.1)	82	(5)	1.3	(0.1)
PET + 1%P130 + 0.5%P252 + 30%GF	10186	(127)	132	(2)	1.7	(0.1)	131	(2)	1.7	(0.1)
Radilon A RV300 (conditioned)	6053	(158)	121	(1)	5.1	(0.3)	120	(2)	5.4	(0.3)
Crastin HR5330HF	7682	(170)	109	(1)	3.2	(0.1)	108	(1)	3.6	(0.1)

Impact properties.

Table 32 reports the results of the Izod unnotched impact tests. As is can be seen, the use of the impact modification slight improves the resilience. This may be due to the chemical nature of the impact polymer used or to an inhomogeneous dispersion of the rubber particles inside the PET matrix (lack of adhesion that prevents energy transfer from PET to rubber when high speed energy hits the sample). Further tests with new impact modification additives are needed to reach the performance of the two benchmark materials.

Table 32

Material	IZOD Impact Strength, unnotched (23 °C) (KJ/m ²)		Type of Fracture
	Avg	StDev	
PET + 1%P130 + 0.5%P252 + 25% GF	22.5	1.2	C
PET + 1%P130 + 0.5%P252 + 25% GF + 5%Elvaloy	25.0	2.6	C
PET + 20% GF	17.6	1.4	C
PET + 1%P130 + 0.5%P252 + 20% GF + 10%Elvaloy	25.6	1.6	C
Radilon A RV300 (conditioned)	89.5	3.4	C
Crastin HR5330HF	52.1	1.9	C

4.3.2. THIRD STEP (PET) – Impact modification study

In the last part of the work a deep study on resilience improvement was done evaluating several polymers able to give impact resistance to the system. (The first two steps involving PET were reported in deliverable D5.1).

Material selected are the following:

- Elvaloy AC12024S S (is a copolymer of ethylene and methyl acrylate- 24% acrylate)
- Lotryl 29MA03 (a random copolymer of Ethylene and Methyl Acrylate-27-31% acrylate)
- LOTADER AX8900 (a random terpolymer of ethylene, acrylic ester and glycidyl methacrylate-24% acrylate)
- Surlyn 8940 (an advanced ethylene/methacrylic acid (E/MAA) copolymer, in which the MAA acid groups have been partially neutralized with sodium ions)
- Bruggolen P252 and Bruggolen P130 (nucleating/lubricant coupled system)
- VIBA PET 01965 (nucleating agent)
- VIBA PET/c Slip 03016 (lubricant)
- Aclyn (lubricant)
- ADK Stab Na 05 (nucleating agent)

It was possible to have information about:

- The effect of acrylate amount on polymer rubber adhesion
- The effect of the presence of a co-monomer on polymer rubber adhesion
- The effect of acid moieties on PET–rubber compatibility
- The effect of molecular weight on rubber dispersion
- The effect of new nucleating agents on crystallinity rate
- The effect of new lubricants on injection molding processing condition (control and speed up of cycle time).

5. Bitumen roofing membrane

Derbigum produce polymer modified bitumen roofing membranes. The polymer used to modify the bitumen is Polypropylene (PP). The polymer prevents the bitumen from becoming too soft in high temperatures or too brittle in low temperatures.

Based on results from the first part of the project, a decision was made to investigate how the post-consumer recycled iPP can be transformed into aPP. Derbigum have researched this in the past, but with the growing cost of aPP and the lack of any recycled material available, it is now more viable to investigate

5.1. Derbigum analysis of candidate polymers

5.1.1. Introduction

In this report are presented the methods of analysis used and the results obtain with 23 recycled polymers during the first 5 semesters.

5.1.2. Methods of analysis

5.1.2.1. For Polymers

Table 33

<i>Analysis name</i>	<i>Method</i>
DSC (Differential Scanning Calorimetry)	<u>Sampling</u> < 10 mgr <u>Trial conditions</u> a) For APP polymers Two "runs" (= 2 meltings) First run: heating speed = 20°C/min (range from 50 to 190°C) Second run: heating speed = 10°C/min (range from -90 to 220°C) b) For IPP polymers Two runs (= 1 cooling/1 melting) First run: cooling speed = 10°C/min (range from 210 to 0°C) Second run: heating speed = 30°C/min (range from 0 to 240°C) <u>Calculation</u> Measure of enthalpy by integration of fusion peaks Identification of the peak's temperature to define the type of polymer

<p style="text-align: center;">Viscosity</p>	<p>1. By Brookfield model Trial conditions Temperature of the oven: 180°C Type of spindle: 27-28-29 (depending on level of viscosity) Analyzed quantity: Spindle 27: 9,5 – 10 gr Spindle 28 or 29: 12 gr Measurements: Viscosity at a zero speed by linear extrapolation of curve of measurements at different speeds.</p> <p>2. By Melt Flow Index (MFI) Trial conditions Temperature of the oven: 230°C Weight: 2,16 kg Capillary diameter: 2 mm Analysed quantity : +/- 6 gr Introduction Time : 1 min max Temperature stabilisation time before trial : 6 minutes including introduction time of the polymer in the oven Measurements Melt Index = weight in grams of melted polymer which passed through the capillary after 10 minutes</p> <p>3. By rheology Trial conditions Check before starting the trial : - Compressed air outflow (60 to 80psi) - Cool water circulation at 60°C All the test conditions are fixed and are related to - Trial temperature 180°C - Geometry : pp25 - Lift position 1.3 mm Measurement Viscosity at nought shearing rate and at 180°C Calculation Automatic calculation based on program Rheoplus included in the equipment</p>
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<p>IR (Infrared spectrophotometer analysis)</p>	<p><u>Trial conditions</u> Prepare a film as thin as possible of the sample to analyze and put it on the window of the equipment. Record the infrared absorption spectrum between 4000 and 600 cm⁻¹</p> <p><u>Measurements</u> Isotacticity percentage Relation between ethylene and propylene sequences for the copolymers</p> <p><u>Calculations</u> Calculations are automatically generated by a program integrated in the system</p>
<p>Ash rate</p>	<p><u>Sampling</u> 2 samples between 1 and 2 grams</p> <p><u>Trial conditions</u> Weigh two empty melting-pot: A1 and A2 in grams. Insert the two samples in the melting-pots and weigh: B1 and B2 in grams. Insert the melting-pots in the oven and program the rise in temperature:</p> <ul style="list-style-type: none"> - 250°C for 10 minutes - 400°C for 10 minutes - 800°C for 1 hour <p>After calcination and cooling in a dryer, weigh melting-pots and residues: C1 and C2 in grams.</p> <p><u>Calculation</u> $\frac{C1-A1}{B1-A1} \times 100 = D1 \text{ (\%)}$ $\frac{C2-A2}{B2-A2} \times 100 = D2 \text{ (\%)}$ The mean between D1 and D2 is the ash rate in %.</p>

5.1.2.2. For lab blends

Table 34

Penetrability	<p><u>Sampling</u> Pour the blend in a 5x5x5cm mold</p> <p><u>Trial conditions</u> Weight of needle and support: 100 grams 24 hours after pouring, immerse the block without the mold in a 60°C water bath for 1 hour. The device releases the needle in the sample for 5 seconds and measures the penetration in deci millimeter (dmm).</p> <p><u>Calculation</u> The device displays the results in dmm. The mean between 3 results in a sample is the final value.</p>
Viscosity	<p>By rheology: See the procedure above</p>
Rigidity	<p>Same procedure as viscosity by rheology. The result is also an automatic calculation by program Rheoplus included in the equipment</p>
Cold bending	<p><u>Sampling</u> Test specimen of blend 2.5x12 cm and 4 mm thickness.</p> <p><u>Trial conditions</u> Place the sample in the support of a CO₂ cooled chamber. The cooled chamber is provided with a mandrel which goes down on the samples and folds it.</p> <p><u>Calculation</u> The sample is tested until the temperature is too low and it breaks. The temperature chosen is the one before break.</p> <p>Rem.: The cold bending could also be done after 7 days at 80°C and 28 days at 80°C. It's cold "aged cold flexibility". This represent a simulation of the ageing of the blend.</p>

5.1.3. Polymers analysis

5.1.3.1. Polymers from Axion

Table 35

Polymer	Conclusion
A	This is an iPP polymer contaminated by some PE polymer. MFI is quite close to the range and ash rate is on the range. This polymer could replace our current iPP. We still need to be careful with the high enthalpy. Lab blend is feasible.
B	This is a PE polymer. Lab blend is not feasible.
C	The main presence is PE. Lab blend is not feasible.
D	This is an iPP polymer. MFI is very low which traduce a viscous polymer. Ash rate is a little bit higher than the range. This polymer could replace our current iPP. Lab blend is feasible
E	This is an iPP polymer contaminated by some PE polymer. MFI is quite close to the range and ash rate is on the range. This polymer could replace our current iPP. We still need to be careful with the high enthalpy. Lab blend is feasible
F	The main presence is PE. Lab blend is not feasible.

5.1.3.2. Polymers from Key Exports

Table 36

Polymer	Conclusion
A	This is an iPP polymer contaminated by some PE polymer. MFI is low and ash rate is really too high. Lab blend is not feasible.
B	The main presence is PE. Lab blend is not feasible.

5.1.3.3. Polymers from Indaver

Table 37

Polymer	Conclusion
PP grey	The enthalpy is given by PE, the blend will not be stable. Lab blend is not feasible.
PP green	The enthalpy is given by PE, the blend will not be stable. Lab blend is not feasible.
PP black	Ash rate is too high, enthalpy and MFI too low. Lab blend is not feasible.

5.1.3.4. Polymer from Bulgaria

Table 38

Polymer	Conclusion
A	This polymer is not going to melt in the blenders. Lab blend is not feasible.

5.1.3.5. Polymer from Serbia

Table 39

Polymer	Conclusion
A	The main presence is PE. Viscosity is really too low. Lab blend is not feasible.

5.1.3.6. Polymers from Montello

Table 40

Polymer	Conclusion
GS2	If enthalpy is principally given by PP, there is a large part given also by PE. MFI is low. For a lab blend, we prefer another polymer from Montello, see here below.
GS3	Enthalpy given by PE. Lab blend is not feasible.
GS5	Even if the MFI is low, lab blends will be tested

5.1.3.7. Polymers from Total

Table 41

Polymer	Conclusion
RPPC 02 GR	Enthalpy given by PE, MFI is low, ash rate is high. Lab blend is not feasible.
RPPC 06 GR	Ash rate too high. Lab blend is not feasible.
RPPC 35 GR	Ash rate too high. Lab blend is not feasible
RPPC 08 GR	Ash rate too high. Lab blend is not feasible
RPPH 35 GR	Ash rate too high. Lab blend is not feasible
RPPH 12 GR	Ash rate too high. Lab blend is not feasible

5.1.3.8. Polymer from Romcarbon

Table 42

Polymer	Conclusion
Rocaplen	This is an iPP polymer. MFI is low and ash rate is just above the range. Lab blend is feasible.

5.1.3.9. Polymer from Polyolefin

Table 43

Polymer	Conclusion
iPP Densificato	This is an iPP polymer. MFI is low and ash rate is just above the range. Lab blend is feasible.

5.1.4. Lab blends

Before each blend with the tested recycled polymer, a reference is done. Every analysis is repeated twice. In the tables, you will find a mean of results. Most of the time, the polymer will be tested on base sheet formulation. The reason is that to introduce recycled polymers, we want to be careful and begin in base sheet formulations before considering the feasibility on top sheets formulations.

5.1.5. Polymers from Axion

Table 44

Polymer D replace iPP (1 :1)	Polymer A replace iPP (1 :1) +1% aPP¹	Polymer E replace iPP (1 :1) +1% aPP
<p>Viscosity is out of range (coherent with the MFI result). Rigidity is more than twice as high as the reference. Penetrability is also out of range.</p> <p>This polymer is not usable on line scale.</p>	<p>Results are just satisfying.</p> <p>Viscosity and rigidity are higher than reference.</p> <p>Penetrability is high.</p> <p>To obtain those results, we had to add some extra polymer. This is not a viable proposition.</p> <p>This polymer is not usable on line scale.</p>	<p>If flexibility is quite good, the rest of the results is disappointing.</p> <p>Penetrability is high, rigidity is low and viscosity is lower than the reference.</p> <p>To obtain those results, we had to add some extra polymer. This is not a viable proposition.</p> <p>This polymer is not usable on line scale.</p>

¹ Reminder : Enthalpy is high, this is the reason why we added some aPP, to avoid a too crystalline blend

5.1.6. Polymers from Montello

Table 45

GS5 replace 8% of aPP and iPP	GS5 replace 4% of aPP and iPP	GS5 replace 1.5% of aPP and iPP	GS5 replace 1% of iPP
Analysis can't be done because the blend is too pasty, too viscous. This formulation is not usable on line scale	Analysis can't be done because the blend is too pasty, too viscous. This formulation is not usable on line scale	Viscosity is really high, cold bending is not on the range and penetrability neither. This formulation is not usable on line scale	Results are quite good. Cold bending is higher than the reference but still on the range. This formulation is usable on line scale; some trials were done. The only concern about this polymer is that Montello only provide big bags, what we can't handle

5.1.7. Polymer from Romcarbon

Table 46

<i>Rocaplen replace iPP (1:1)</i>	<i>Rocaplen replace ½ part of iPP</i>
<i>Viscosity is out of range. Rigidity is higher than the reference. This formulation is not usable on line scale.</i>	<i>This formulation is usable on line scale (MFI is weak for iPP). This formulation is usable on line scale.</i>

5.1.8. Polymer from Polyolefin

Table 47

<i>iPP Densificato replace iPP (1:1) in top layer</i>	<i>iPP Densificato replace ¼ part of iPP in base sheet</i>
<i>Viscosity is just above range. Rigidity is higher than the reference. This formulation is too risky to be usable on line scale.</i>	<i>This formulation is usable on line scale.</i>

5.1.9. Conclusion – Derbigum testing

24 recycled polymers tested; 3 approved (Montello GS5, Rocaplen, iPP Densificato). iPP Densificato is preferred over Rocaplen because at more or less same quality (ash rate is higher for Rocaplen than for iPP Densificato), the price of iPP Densificato is more advantageous.

Several trials were done on large scale (production line) with the Montello GS5 and with the iPP Densificato. The concern of the first polymer is that it is provided by big-bags which we can't handle. There is no possibility of bags delivery. About the second, there is a bag weigh instability which need to be solved.

5.2. Reducing crystallinity of PP

5.2.1. Summary

The target has been to reduce the crystallinity of PP. Based on previous results, we have compounded virgin PP with NBS and peroxide. The maximum reduction of crystallinity is by 50 %.

Crystallinity will vary with molecular weight and chain regularity like tacticity. An effect of compounding is the reduction of chain length as seen from the melt flow index. DSC thermograms show a trend with reduced melting temperatures which reflects a reduction in chain order. However, no clear correlation between the degree of crystallinity and degree of isotacticity can be seen.

5.2.2. Background

Derbigum produce polymer modified bitumen roofing membranes. The polymer used to modify the bitumen is Polypropylene (PP). The polymer prevents the bitumen from becoming too soft in high temperatures or too brittle in low temperatures.

Derbigum use a mixture of amorphous (or atactic) PP (aPP) and crystalline (or isotactic) PP (iPP). The amount of polymer used in the bitumen blend is approximately 20%. In the blend aPP is the predominant component.

Amorphous polymer means the structure is less ordered, and polymer is more flexible and blends more easily with the bitumen. Crystalline PP is more rigid and brittle and has a higher melting point.

Derbigum ideally require amorphous PP in order to use a large quantity of recycled polymer.

Aside from the crystallinity, the level of PE must be very low as this can act as a nucleating agent and cause the polymer to become more crystalline. A melt flow index of 15 g/10 minutes is also needed.

Several applications have been found for low-tacticity polypropylene, notably as hot-melt adhesives and bitumen modifiers [1]. New catalysts have reduced the amount of low-tacticity PP during iPP production. Low crystalline PP can be obtained from iPP. Recycled PP can be used rather than virgin PP, but the content of PE is expected to influence the results.

5.2.3. Introduction

Previous results from Derbigum have demonstrated the possibility to reduce the crystallinity of PP by around 90 % and similar results are also found in the literature. Previous work has been based on extruding virgin PP with peroxide and NBS using various extruder set-ups and processing parameters. Similar trials on rPP were not so successful which was linked to the presence of metals from contamination in rPP.

In the present work we have focused on repeating the extrusion trials on virgin PP analyzing the crystallinity, tacticity and melt flow index of the compounds.

To prepare work on rPP, we also performed element analysis by ICP-MS on both virgin PP and rPP.

5.2.4. Materials

- NBS – bromine compound
- Peroxide
- iPP - Rompetrol RTF-3
- rPP: post-consumer grade (ICP-MS)

Two levels of peroxide were added to PP combined with two levels of NBS.

5.2.5. Compounding

The materials were processed on a DSM Midi 2000 15 cm³ batch extruder. They were mixed at 200 °C till stable melt and then 3 minutes at 230 °C. Batches of 10-15 g were produced, **Table 48**.

Table 48 *Basis of produced compounds*

Compound	NBS	Peroxide [w%]
#1	High	High
#2	Low	Low
#3	Low	High

Samples produced are given in Table 49.

Table 49 *Samples produced from different compounds*

Sample no	Compound #	Time [min]	rpm
1	1	3	70
2	2	3	70
3	3	3	70
5	1	4	70
6	2	4	70
7	3	4	70
8	1	5	70
9	2	5	70
10	3	5	70
11	1	2	70
12	1	4	100

For compound #1 we tested a series with different rpm and processing times.

Table 50 *Processing times and rpm for samples of compound #1*

rpm	Process time
4 min	70
4 min	100
4 min	150
6 min	70
6 min	100
6 min	150
8 min	70
8 min	100
8 min	150

5.2.6. Characterization

DSC

Samples were run at Perkin Elmer DSC 8500. Heating rate was 10 K/min from 30 °C to 200 °C with isothermal steps at the start and stop to ensure instrument stability. Sample weights were about 5 mg.

FTIR

Measurements were performed with a Cary 670 FTIR spectrometer from Agilent Technologies using Attenuated Total Reflection mode (ATR). A diamond ATR crystal was used for the measurements (analysis dept 2.0 µm at 1000 cm⁻¹). The measurements were performed with 4 cm⁻¹ resolution using 16 scans in the range 4000 to 400 cm⁻¹. The ratio of the height of peaks at 997 cm⁻¹ and 972 cm⁻¹ (I_{997}/I_{972}) is a measure of the degree of isotacticity in PP (higher ratio higher degree of isotacticity) [2].

ICP-MS

Ahead of the ICP-MMs analysis (Inductively coupled plasma mass spectrometry), two parallels of each sample were decomposed with 5 ml TMAH in a Milestone Ethos microwave oven at 200 °C for 15 minutes. Tellur (¹²⁵Te) was then added as internal standard and analysed on an Agilent 8800 Triple Quadrupole ICP-MS (ICP-QQQ) with SPS 2 Autosampler. The samples were quantified against standards from Inorganic Ventures. The results reported are concentrations in mg/kg and relative standard deviation (RSD) in %.

5.2.7. Results

5.2.7.1. Melt flow index (MFI)

MFI was measured with load 2.16 kg at 230 °C, Table 51

Table 51 Measured MFI on produces samples.

Sample no	MFI [g/10 min]
Virgin	3
1	21
2	18
3	34
5	19
6	15
7	44*
8	22
9	19
10	†
11	51*
12	46*

*Inaccurate due to low viscosity

†Too low viscosity

The MFI results show a variation between the compounds with #3 showing the highest MFI. Apart from this, the MFI values are about in the target range for the application.

5.2.7.2. DSC

Crystalline features reflect polymer properties a chain regularity and chain length. In Figure 24 Heating thermograms of pure PP and compound #1 run for different times in the extruder, for #1 we see the tail of the melting peaks shift to lower temperature with increasing processing time.

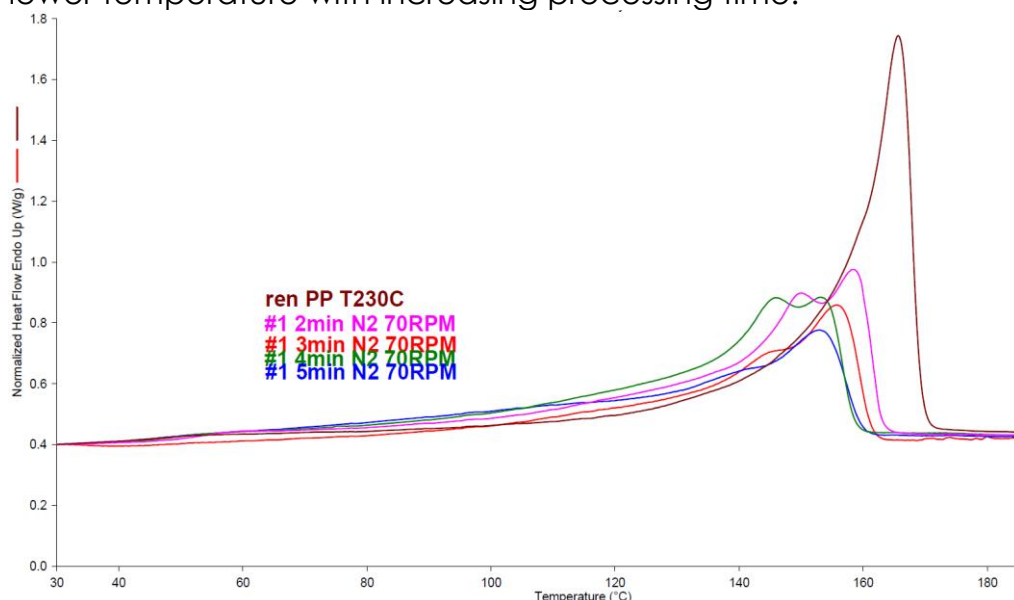


Figure 24 Heating thermograms of pure PP and compound #1 run for different times in the extruder

Relating the crystallinity of #1 to the MFI values we see no direct correlation, Figure 25. This may indicate that the differences between the heating diagrams in Figure 24 are due to irregularities introduced in the chain rather than chain scission.

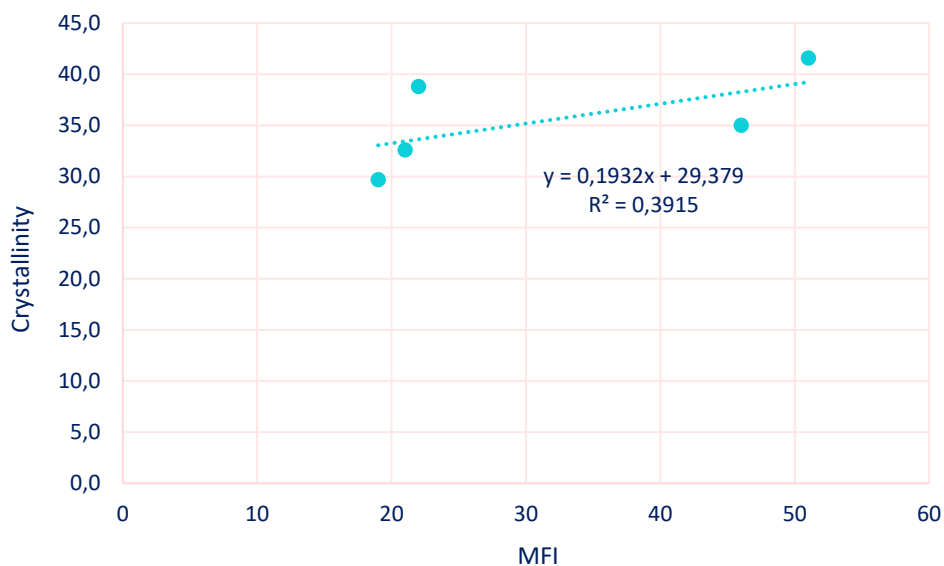


Figure 25 Relation between MFI and crystallinity for samples of #1

In the following figures we show DSC results for different samples of the three compounds.

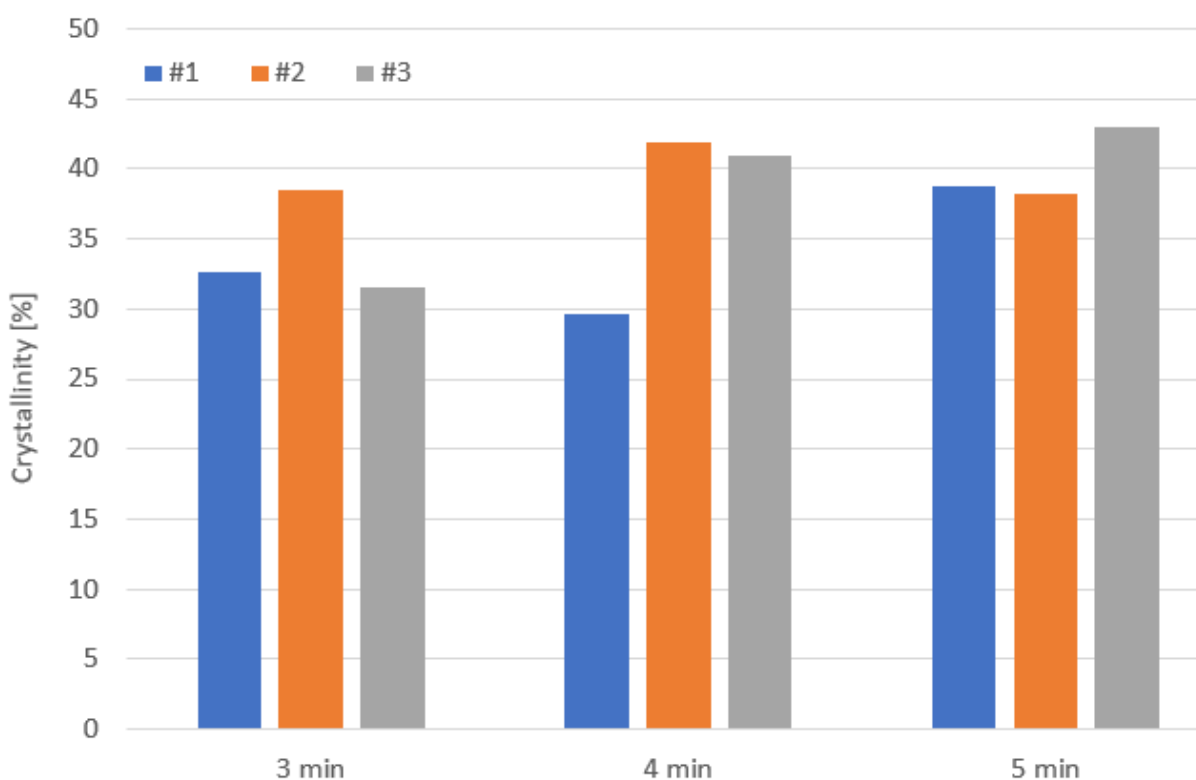


Figure 26 Crystallinity of the three compounds with different processing times

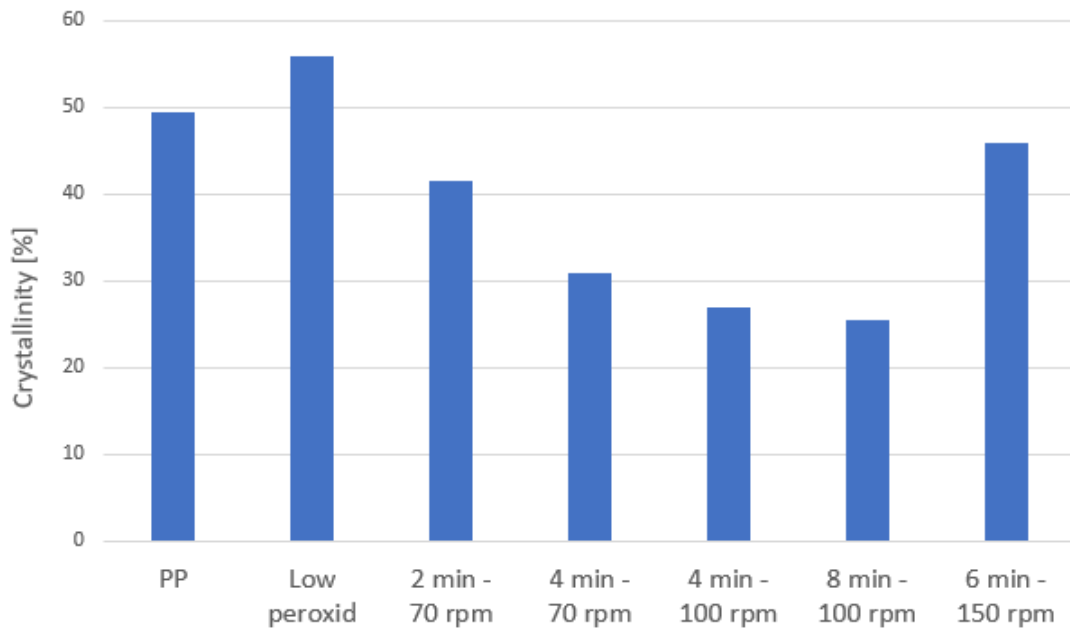


Figure 27 Crystallinity of #1 with different processing compared to reference PP and PP with peroxide

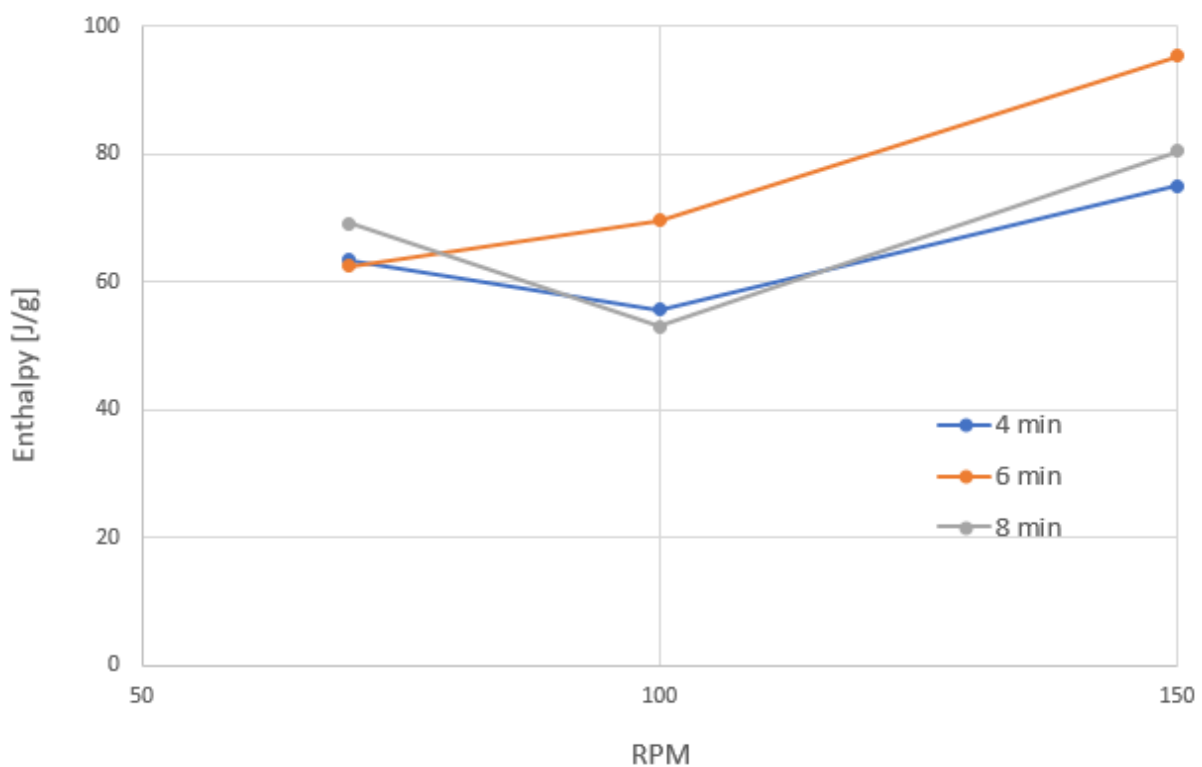


Figure 28 Crystallinity of samples from compound #1 processed at different rpm and residence times

From the results above, we are unable to deduce a clear trend which relates processing conditions to the crystallinity of the samples.

The best results achieved was for compound #1 processed at 100 rpm with crystallinity around 26 % which is approximately half of that of virgin iPP. The shifts with increasing processing time, seen for #1 in the melting thermograms in **Figure 24**, indicate a reduction in chain order. This does not, however, translate directly into reduced crystallinity.

5.2.7.3. FT-IR

Figure 29 shows the degree of isotacticity measured by FT-IR as compared to the degree of crystallinity measured by DSC for the different samples. No clear correlation between the degree of crystallinity and degree of isotacticity can be seen.

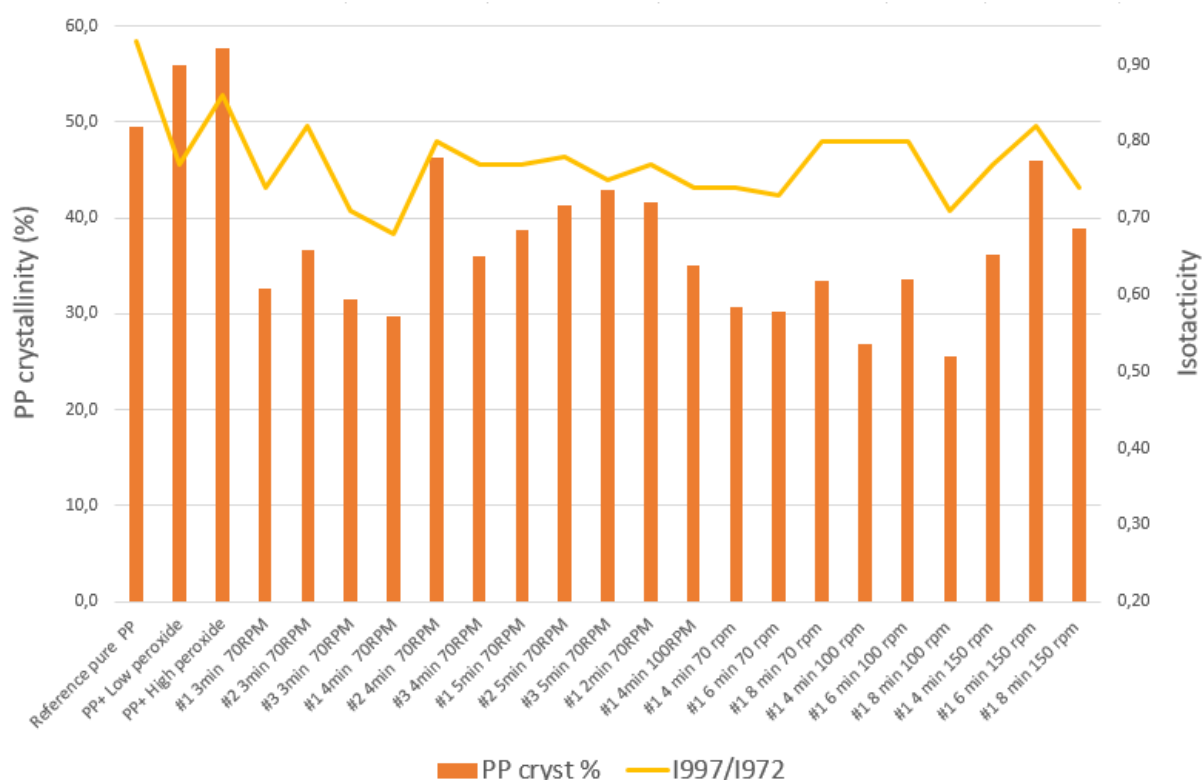


Figure 29. *PP crystallinity and degree of isotacticity for samples extruded with peroxide and NBS.*

Table 52 shows the results from degree of isotacticity measurements done both on the surface of extruded material and on cross section of extruded material. It is a clear that the isotacticity measured on cross sections of the extruded material is lower than for the isotacticity measured on the surface. This may indicate that some segregation of PP with different tacticity happens during extrusion.

Table 52. Degree of isotacticity measured on surface or cross section of extrudate, the ratios are an average of three measurements.

Sample	l ₉₉₇ /l ₉₇₂ surface	l ₉₉₇ /l ₉₇₂ cross section
#1 8 min 70 rpm	0.80±0.05	0.66±0.03
#1 8 min 100 rpm	0.71±0.02	0.63±0.03
#1 6 min 150 rpm	0.82±0.03	0.68±0.03
#1 8 min 150 rpm	0.74±0.01	0.68±0.02

5.2.7.4. ICP-MS – Metal content.

Metals may affect the functioning of NBS. Metals are likely found in rPP due to contamination. We therefore analyzed a post-consumer PP in addition to the virgin iPP material by ICP-MS, Table 53. The differences in metal content are striking.

Table 53 Metal content of rPP and virgin iPP [mg/kg]

PP grade	Fe	Zn	Ca	Si	Al	Ba	Cr	K	Mg	Mn	Na
rPP	342	56	1768	176	176	96	6,7	10	330	1,1	36
iPP	0,09	8,3	64	7,2	27	0,42	0,02	0,22	9,1	0,05	1,1

Table 54 Brom content in processed samples

Sample		Br	
ID	LIMS Number	mg/kg	RSD (%)
#1 - PP 230C / 70°C 3min	2019-5472 1	883	1,8
#1 - PP 230C / 70°C 3min	2019-5472 1	645	1,1
2 - Proplast PP + High peroxide	2019-5473 2	6	15,8
2 - Proplast PP + High peroxide	2019-5473 2	5	12,6
#3 - PP 230°C 70 rpm	2019-5474 3	491	1,3
#3 - PP 230°C 70 rpm	2019-5474 3	502	0,8

It is relevant to see if the Br remains in the compounds, Table 54, and results correlate well with the added Br in tested samples.

5.2.7.5. Conclusion – Reducing crystallinity

We have succeeded in reducing PP crystallinity to about half of the initial level. This level of crystallinity is still high compared to project goal which is a reduction of about 90 %.

By the compounding process we have described we modify chain regularity and chain length (from MFI). Generally, one can imagine that reducing chain regularity while maintaining chain length may could be a solution. Achieving this, however, will demand fine-tuning the process. Further testing of other extruder configurations will be part of this work.

References

- [1] G. R. P. Henry, X. Drooghaag, D. D. J. Rousseaux, M. Sclavons, J. Devaux, J. Marchand-Brynaert, V. Carlier, *Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 46, 2936–2947 (2008)
- [2] C. Longo, M. Savaris, M. Zeni, R. N. Brandalise, A. M. Coulon Grisa, *Materials Research*, 14(4), 442-448 (2011)

5.3. Estimating PE fraction in recycled PP

5.3.1. Summary

The presence of a PE fraction in PP will influence the processing as well as mechanical and thermal properties of a recycled polypropylene. The objective of this work has been to compare methods used to determine the fraction of polyethylene (PE) in recycled polypropylene (PP) establishing calibration curves for each method. The basis for the calibration curves were known blends of PE and PP. Characterization methods used were differential scanning calorimetry (DSC), FTIR spectroscopy, NMR and gel content measurement after peroxide extrusion.

We have applied the derived calibration curves to two different post-consumer recycled PP (rPP) in addition to a known 50/50 blend of PE and PP. DSC and FTIR give about estimates of the PE content, whereas the gel content approach gives a significant higher estimate.

5.3.2. Introduction

In recycling of PP, the general handling of the material and existing sorting technology does not yield pure PP. The same material sources will contain PE products and a PE fraction is expected to be present in recycled PP.

Quality assurance of recycled household plastic is necessary since the presence of small amounts of PP in HDPE or vice versa affects the performance of the material and determines whether the material can be used for high value applications [1]. For many applications, optimum properties of blends depend on the correct mixing of PE and PP. A significant negative synergy between PE and PP was found regarding yield strength, impact strength, tensile energy to break and tensile modulus [2]. Knowing the composition of these blends is therefore critical to recycling of polyolefins waste [3].

One candidate method of quantitative analysis of blends is measuring the melting enthalpies of compounds using differential scanning calorimetry (DSC). In interpreting results, one should be aware of previous observations where it was found that the presence of two polymers in the blend has influence on the crystallization of its components [4]. This could for example be due to the influence of one component on the nucleation of the other.

Several applications have been found for low-tacticity polypropylene, notably as hot-melt adhesives and bitumen modifiers [5]. New catalysts have reduced the amount of low-tacticity PP during iPP production, but low crystalline PP can be obtained from iPP. Recycled PP can be used rather than virgin PP, but the content of PE is expected to influence the results.

Methods using chromatographic techniques [6] (high-T gradient HPLC) and temperature rising elution and crystallization analysis fractionation (TREF) [7] have been presented. They demand non-standard equipment and high competence. Each of the methods (TREF, CRYSTAF) were shown to work best according to the exact type of PE or PP. For a general case, as for rPP, combinations of TREF and CRYSTAF should be used.

In the following we have tested several techniques by applying them to laboratory made blends of PE and PP, using different types of both polymers. The established calibration curves for each method are finally applied to two different rPP's and a known PE-PP blend. Studying PE-PP blends, one must consider the different commercial types of both PE and PP. There is PE with different branching and crystallinity and PP materials with varying ethylene content. We selected materials taking this into account.

5.3.3. Materials

Table 55 Materials included in the study

Polymer	Type [cc·mm/(m ² ·day)]	MFI [g/10 min]	Density [kg/m ³]
PP-1	Homopolymer	2,8-3,5 *	905-917
PP-2	Random copolymer	1,5 *	905
PP-3	Block copolymer	0,3*	900
PE-1	LDPE	7,5 ⁺	920
PE-2	MDPE	6,0 ⁺	934
PE-3	HDPE	0,25 ⁺	959
rPP-1	Recycled- Proplast	8,3*	912
rPP-2	Recycled- Derbigum	20,4*	970

* 230 °C, 2.16 kg

⁺190 °C, 2.16 kg

By inspecting the pellets, we see that rPP-2 consists of a mix of at least three different materials. Measuring density on pellets of different colour showed variations in the range 930-950. As we will see from the FTIR analysis, the material has an unidentified component which may influence the density.

5.3.4. Material compounding

The materials were processed on a DSM Midi 2000 15 cm³ batch extruder. Processing temperature for the PE-PP blends was 230 °C and cycle time for processing of pellets were 3 minutes with nitrogen flushing.

For samples extruded with 2 % peroxide, extruder start temperature was 200 °C during filling and then increased to 230 °C and processing then continued for 2 minutes with Nitrogen flushing.

5.3.5. Produced blends for testing

Table 56 PP and PE content in produced blends

PP	PE
100	0
95	5
90	10
85	15
70	30
50	50
25	75
0	100

Different series of blends were produced based on different combinations of polymers

- 1) SS-142: RTF-3 + Borsafe HE 3490-LS
- 2) SS-142: RTF-3 + Dow 740E
- 3) RB307MO + Borecene™ RM8343
- 4) RB307MO + PE mix (equal parts of each PE grade)
- 5) BA212E + Borsafe HE3490

In addition, a special blend was produced with equal parts of each the six polymers, thus with 50 % PE.

5.4. Characterization methods

○ DSC

Samples were run at Perkin Elmer DSC 8500. Heating rate was 10 K/min from 30 °C to 200 °C with isothermal steps at the start and stop to ensure instrument stability. Sample weights were about 5 mg.

For the data analysis, due to overlap of the melting peaks for PE and PP, we defined an upper limit for the PE peak. Then, based on the thermogram for pure PP, we estimated the contribution of PP to the thermogram below this temperature correcting for the PP fraction of the blend. Depending on the material grades, the estimated limit for the PE peak was in the range 127-135 °C.

○ FTIR

Measurements were performed with a Cary 670 FTIR spectrometer from Agilent Technologies using Attenuated Total Reflection mode (ATR). A diamond ATR crystal was used for the measurements (analysis dept 2.0 μm at 1000 cm^{-1}). The measurements were performed with 4 cm^{-1} resolution using 16 scans in the range 4000 to 400 cm^{-1} .

○ NMR Spectroscopy

The NMR spectroscopy experiments were performed at 11.7T (500 MHz proton resonance frequency) by using Bruker Avance III spectrometer, equipped with 4-mm and 3.2 mm solid-state probe. All the ^{13}C -NMR measurements were conducted at 298K at a MAS spinning rate of 10kHz with a cross-polarization magic angle spinning (CP/MAS) pulse sequence. The number of acquisitions was 2048. All the spectra were processed using TopSpin 3.2 software.

○ Gel content

Peroxides will cross-link PE while PP chains are cut. In compounds extruded with 2 % peroxide one will therefore expect to find a gel content depending on the PE fraction in the material. Compounds were then treated according to the standard ASTM D2765 [8] consisting of cryo-grinding using liquid N₂ in a Retsch Ultra Centrifugal mill ZM 200

with a 0.75 mm sieve. The resulting gel content is then related to the PE content of known blends.

5.4.1. Results and calibration curves

5.4.1.1. DSC

Due to the overlap of melting peaks, we defined a procedure to separately estimate the melting enthalpy for PE and PP.

By visual inspection the upper limit, T_{PE} , for the PE peak was identified with values in the temperature range 127-135 °C.

The PP contribution above T_{PE} was then calculated and subtracted from the total melting enthalpy. The PP part below T_{PE} was then estimated from the thermogram for the pure PP sample scaled by the PP content of the actual sample. This gave the total PP melting enthalpy.

The PP contribution was subtracted from the thermogram below T_{PE} to give the melting enthalpy of PE.

Below we show the melting thermograms of selected samples covering the three types of PP materials.

For series 4 – a PE mix blended with the random copolymer – we show the curves for 0, 50 and 100 % PP, Figure 30.

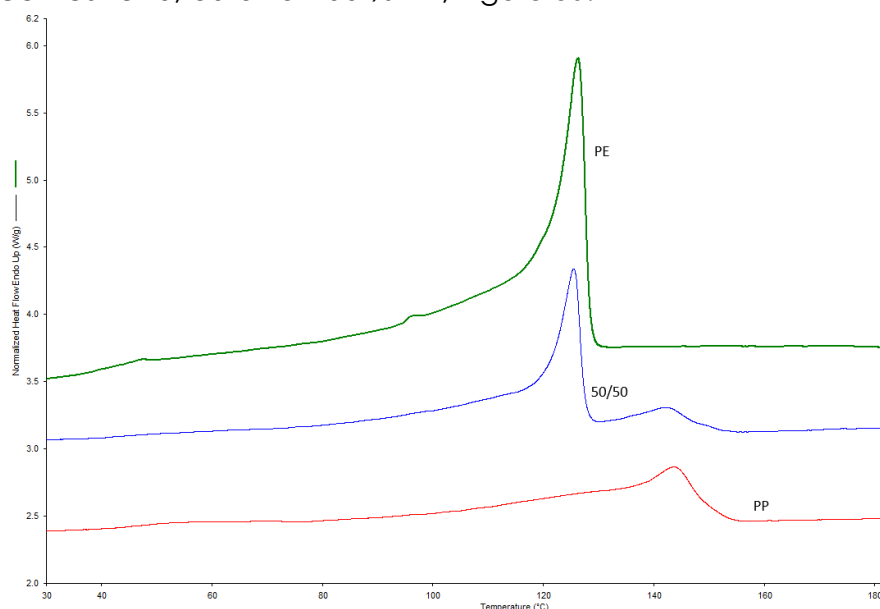


Figure 30 Melting thermograms of series 4 sample with 0, 50 and 100 % PP

For series 5 we show the curve with 15 % PE in Figure 31.

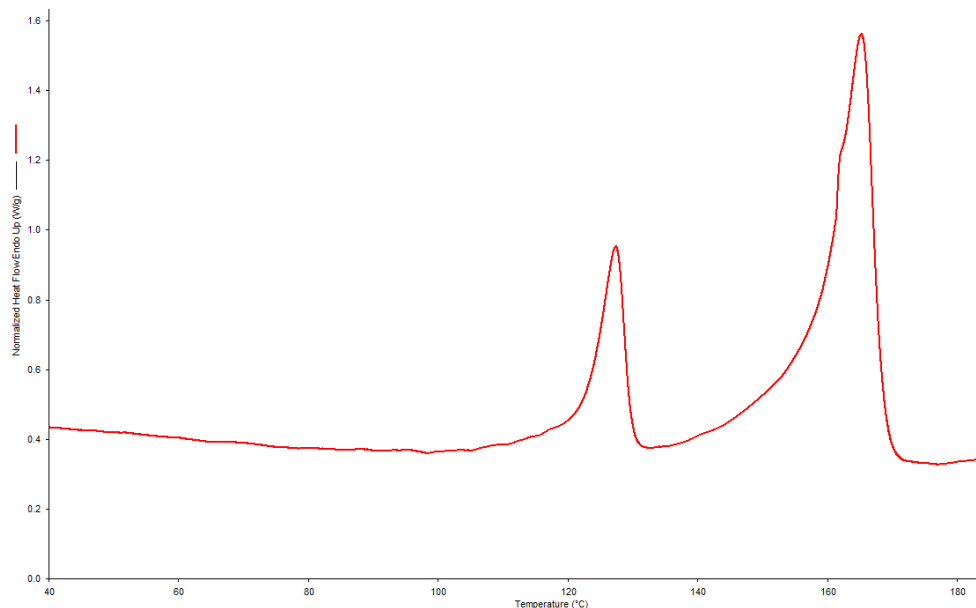


Figure 31 Melting thermogram of the series 5 sample with 15 % PE

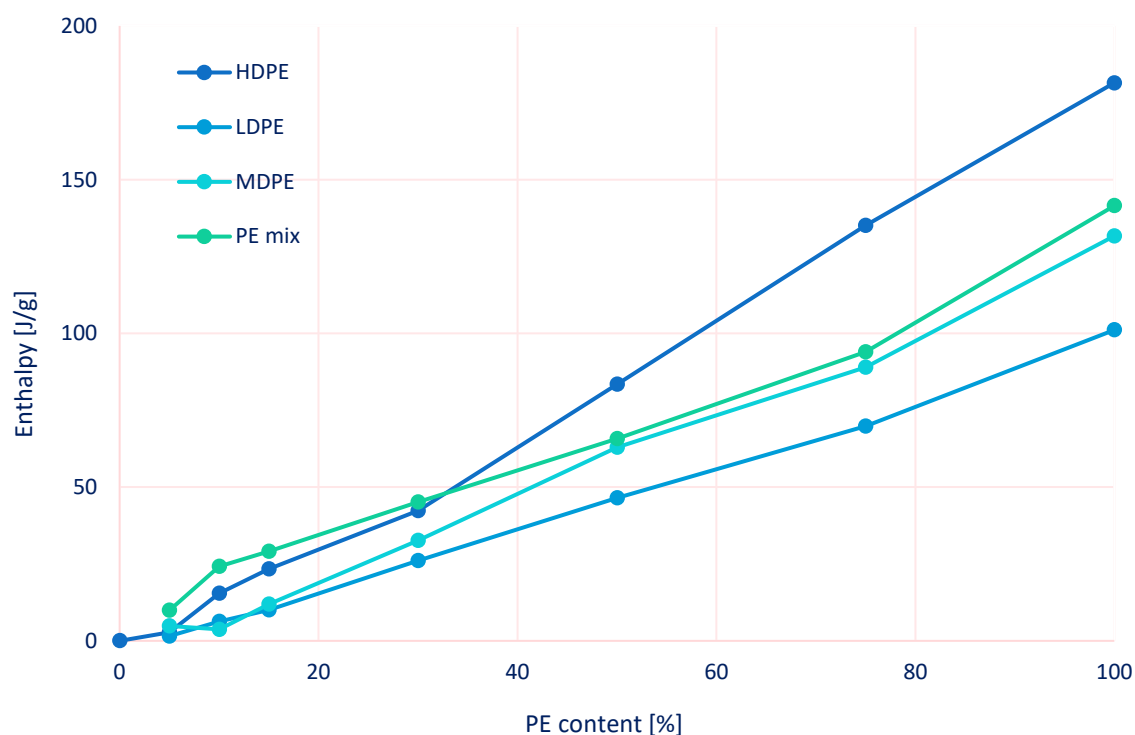


Figure 32 Melting enthalpy as function of PE content for different PE materials

In Figure 32 we see that the result varies with the type of PE material. In order to extrapolate a master curve to be applied to a general rPP, we use the results for the PE mix of series 4. This is plotted with the linear fit in Figure 33.

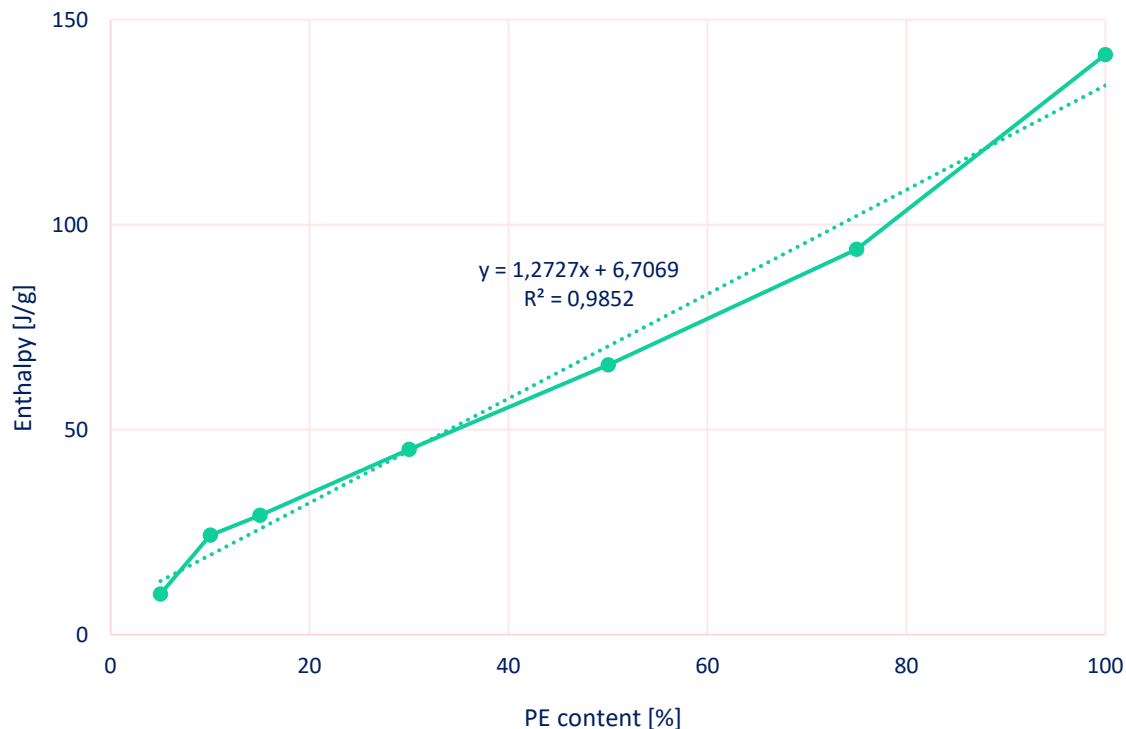


Figure 33 Data for series 4 - PE mix - with linear fit

We use the inverted trendline displayed in Figure 33 to estimate the PE content from the PE melting enthalpy in J/g, ΔH ,

$$PE = 0.7857 \cdot \Delta H - 5.3186 \quad (1)$$

5.4.1.2. FTIR

FT-IR analysis has been performed on five series of PP/PE blends with PP content from 0 to 100 %. Three different methods to prepare calibration curves for determination of PP content have been tried out based on the measurements PP/PE blends with known PP content. Camacho and Karlsson [1] describe a calibration curve based on the ratio of the heights of $1168 \text{ cm}^{-1}/(1168 \text{ cm}^{-1}+716 \text{ cm}^{-1})$ peaks. Agilent [3] describes a calibration curve from the ratio $1376 \text{ cm}^{-1}/1462 \text{ cm}^{-1}$ peaks, and Perkin Elmer [9] uses the ratio of the $719 \text{ cm}^{-1}/1376 \text{ cm}^{-1}$ peaks.

All calibration curves and tests of the different calibration curves to determine the PP content in a known blend and in two materials with unknown PP content are shown in the separately submitted Appendix.

It was found that the calibration curves based on the $1168 \text{ cm}^{-1}/(1168 \text{ cm}^{-1}+716 \text{ cm}^{-1})$ peaks gave the best results, see Figure 34. An example of one calibration curve is shown in Figure 35, and the results from testing the calibration curve are shown in Table 57.

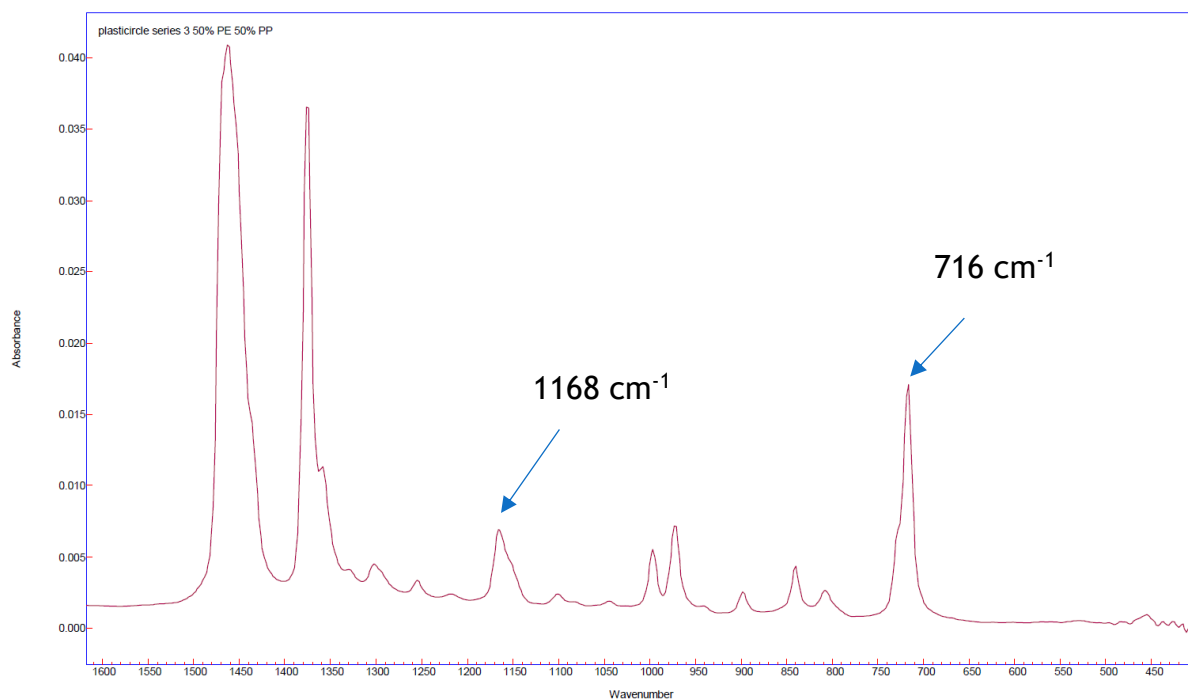


Figure 34. FT-IR spectrum of 50/50 PP/PE blend series 3. The two peaks used for making a calibration curve are marked.

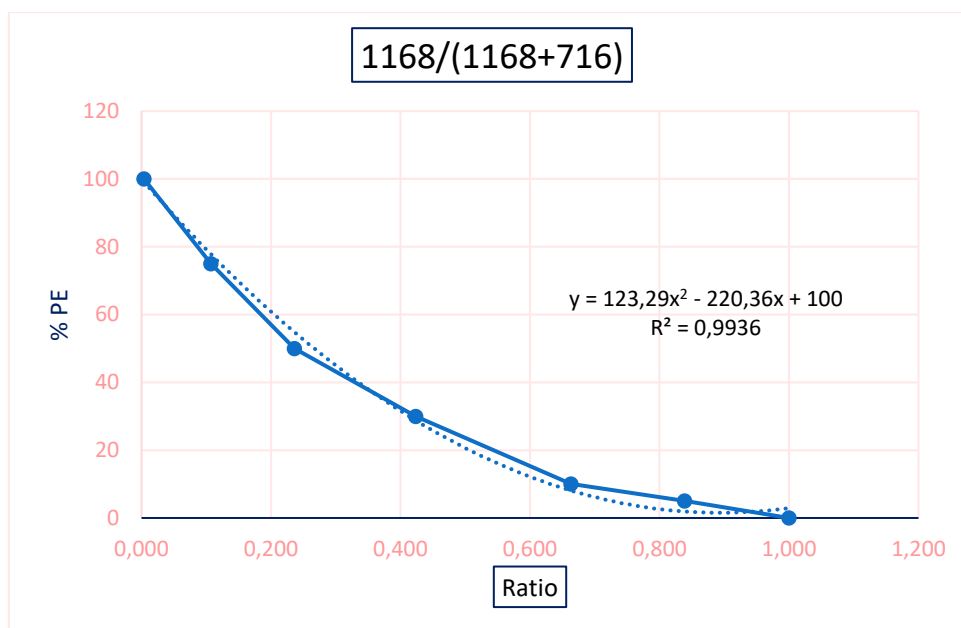


Figure 35. Calibration curve for 1168/(1168+716) peaks based on measurements on series 3 blends.

$$PE = 123.29 \cdot R^2 - 220.36 \cdot R + 100 \quad (2)$$

The final test of the calibration curves is given in Table 57.

Table 57. Determination of PE content in PP/PE blends using FT-IR calibration curves from 1168/(1168+716) peaks

Material	PE (%) Calibration curve series 3
Special blend 1	52
rPP-1	3
rPP-1 extruded with 2 % peroxide	3
rPP-2*	-

*Not possible to use the calibration curve because this PP has an unidentified broad peak overlapping the 716 cm^{-1} peak (see **Figure 36**)
 The special blend 1 has a known PE content of 50 %.

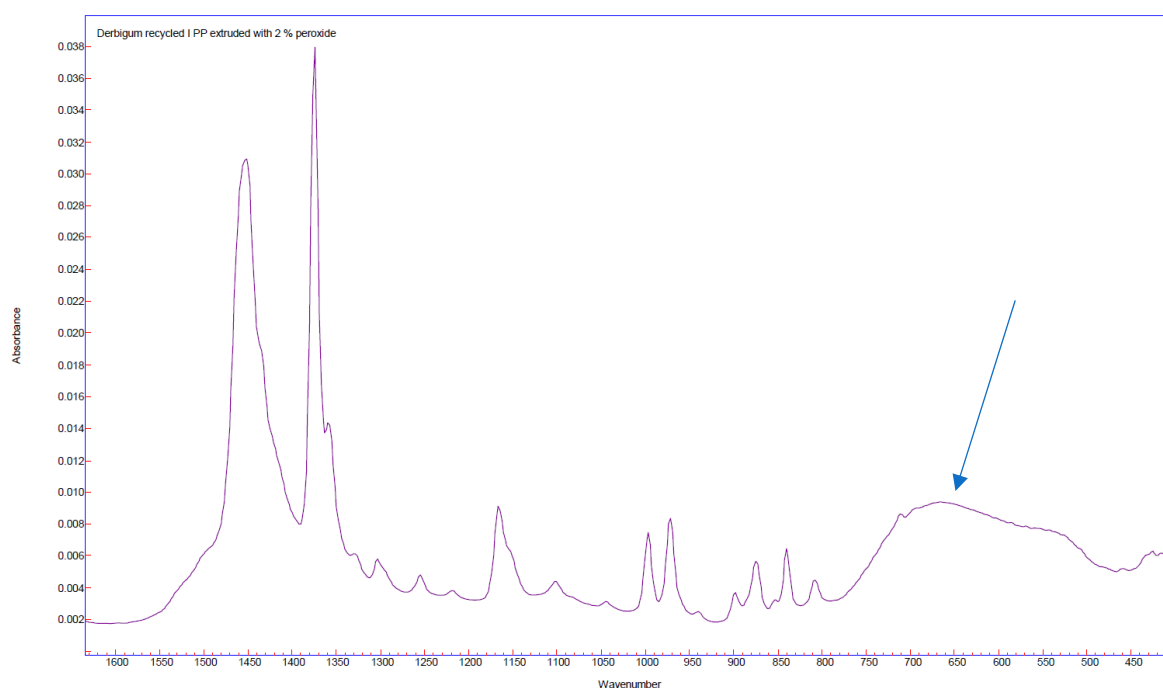


Figure 36. FT-IR spectrum off rPP-2 showing broad unidentified peak (marked with arrow) overlapping the 716 cm^{-1} peak.

5.4.1.3. NMR

We used series 1 and 4 in this study.

PE and PP show distinct peaks in the NMR spectra. Series 4 contains the mix of the three PE's in combination with the random copolymer, Figure 37. The ethylene component of the random copolymer is not visible in the spectrum of 100 % PP.

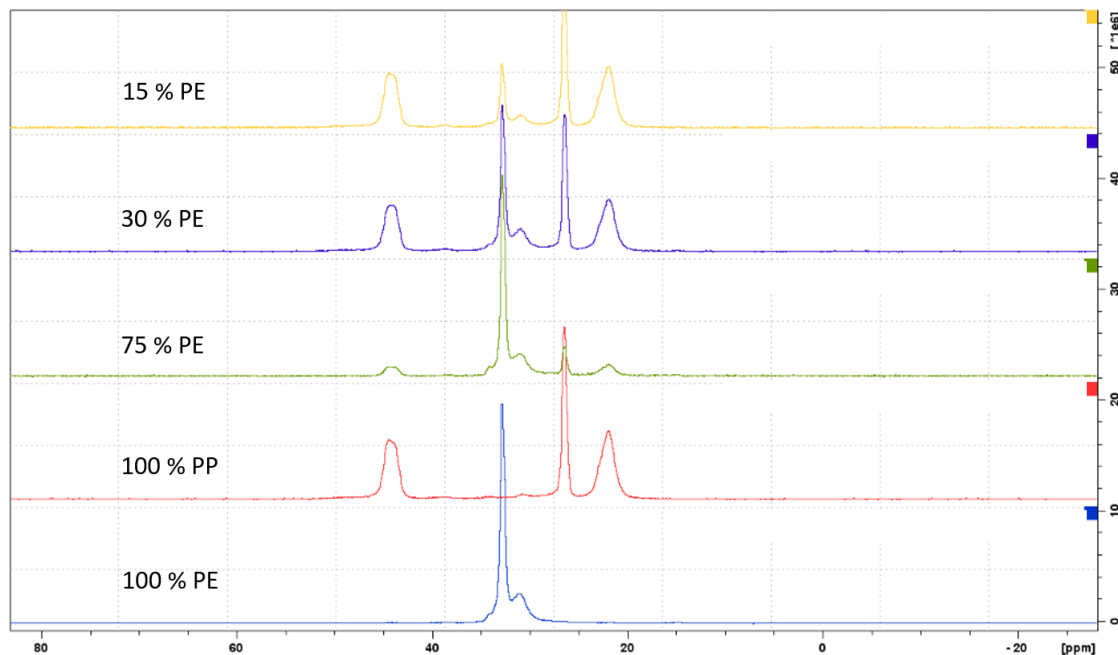


Figure 37 Series 4 spectra with PE fraction varied from 0 to 100 %

In Figure 38 and Figure 39 we show the calibration curves for the two series.

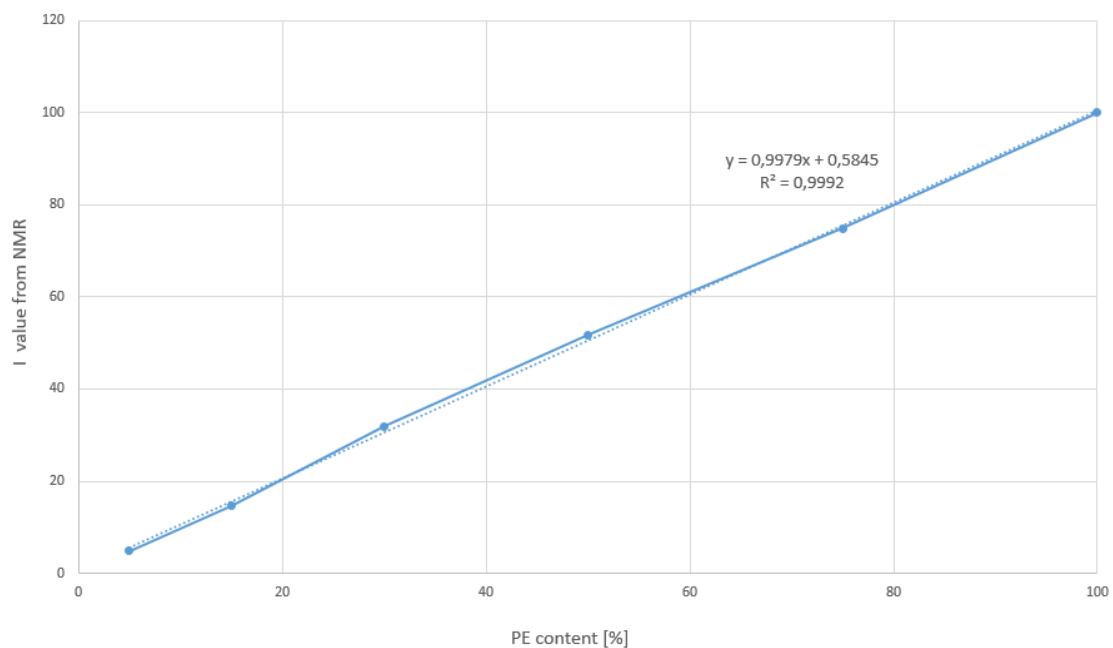


Figure 38 Calibration curve for Series 1 - PP homopolymer and HDPE

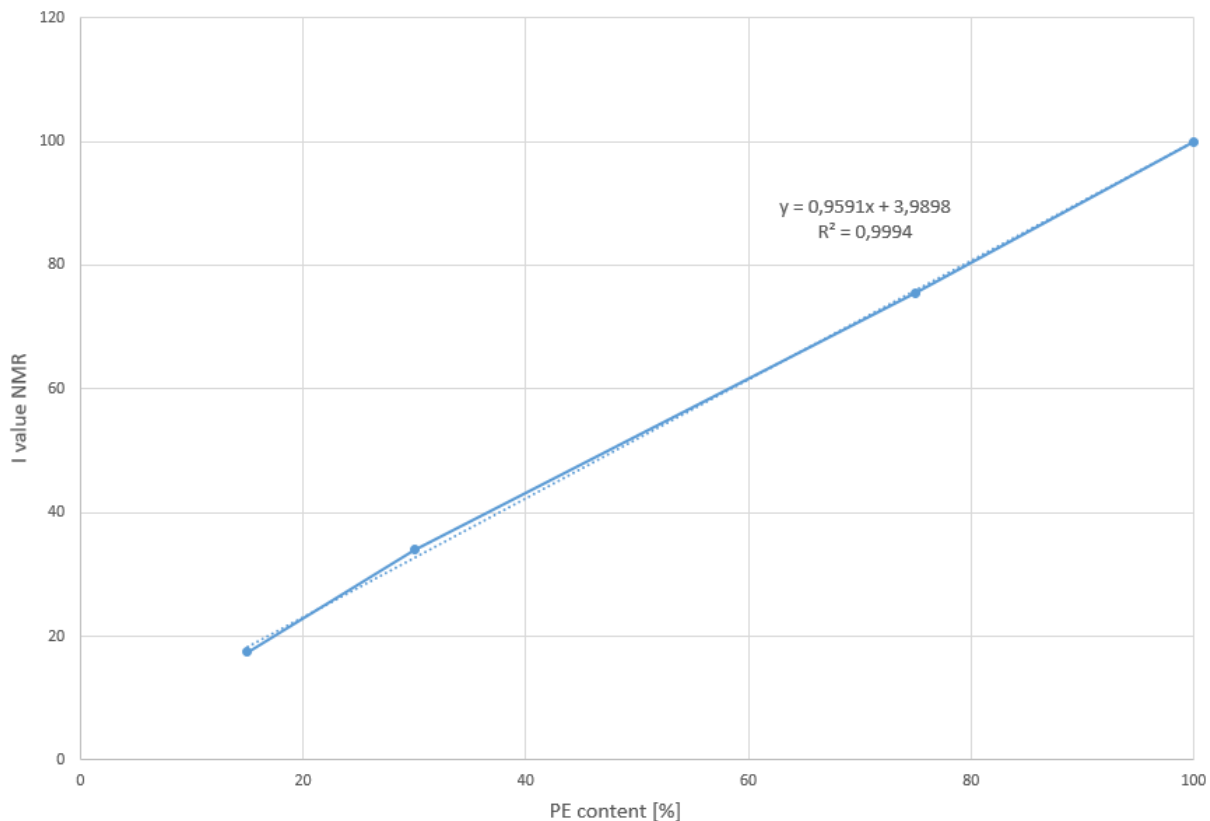


Figure 39 Calibration curve for Series 4 - PP random copolymer and PE mix

We suggest the calibration curve for series 4 is most relevant to use with a general rPP. For measured intensity, I , we have

$$PE = 1.0426 \cdot I - 4.1599 \quad (3)$$

5.4.1.4. Gel content

Table 58 shows the results for measurements of gel content. Two different PP and PE qualities and blends thereof have been studied. SS-142 RTF3 is a PP homopolymer and a gel content of 0 is measured as expected after extrusion with peroxide because PP do not form cross-links after extrusion with peroxide. HE 3490-LS is a bimodal PE which cross-links when extruded by peroxide (gel content approximately 50 %). Blends of these materials, PP/PE 90/10 and 50/50 gave a gel content of approximately 5 and 20 %, respectively.

RB307MO is a PP random copolymer, and a gel content of around 5 % was found after extrusion with peroxide due to cross-linking of the PE part of the copolymer. RM8343 is linear PE, and without added peroxide this polymer has a gel content near zero because cross-linking is not expected to take place, extruded with peroxide a gel content from 56 to 59 % was measured. The deviation between the two parallels may be explained by inhomogeneities in the blend. A 50/50 blend of RB307MO/RM8343 had a gel content of approximately 20 %.

Both rPP's has a gel content after extrusion with peroxide, indicating that the PP's contains some PE. The rPP-1 has a relatively large deviation in gel content between the two measurements, this may also be explained by inhomogeneous distribution of PE in the PP material.

Table 58 Gel content of PP/PE materials with peroxide

Material	Gel content (%), two parallels
SS-142 RTF3+ 2 % peroxide	- -
HE 3490-LS + 2 % peroxide	49.6 49.2
SS-142RTF3 90 %+HE3490-LS 10 % + 2 % peroxide	4.9 5.0
SS-142RTF3 50 %+HE3490-LS 50 % + 2 % peroxide	18.6 19.7
RB307MO +2 % peroxide	5.3 4.0
Borecene RM8343 without peroxide	1.0 0.5
Borecene RM8343 + 2 % peroxide	58.8 55.9
RB307MO 50 % + Borecene RM8343 50 % + 2 % peroxide	22.2 20.5
rPP1 + 2% peroxide	2.9 7.7
rPP2 + 2 % peroxide	6.4 7.6

Based on the gel content measurements two calibration curves were made for the two different PP/PE combinations in order to be able to estimate the PE content in unknown materials, see Figure 40 and Figure 41. The calibration curves show that the gel content increases linearly with increasing PE content, as expected.

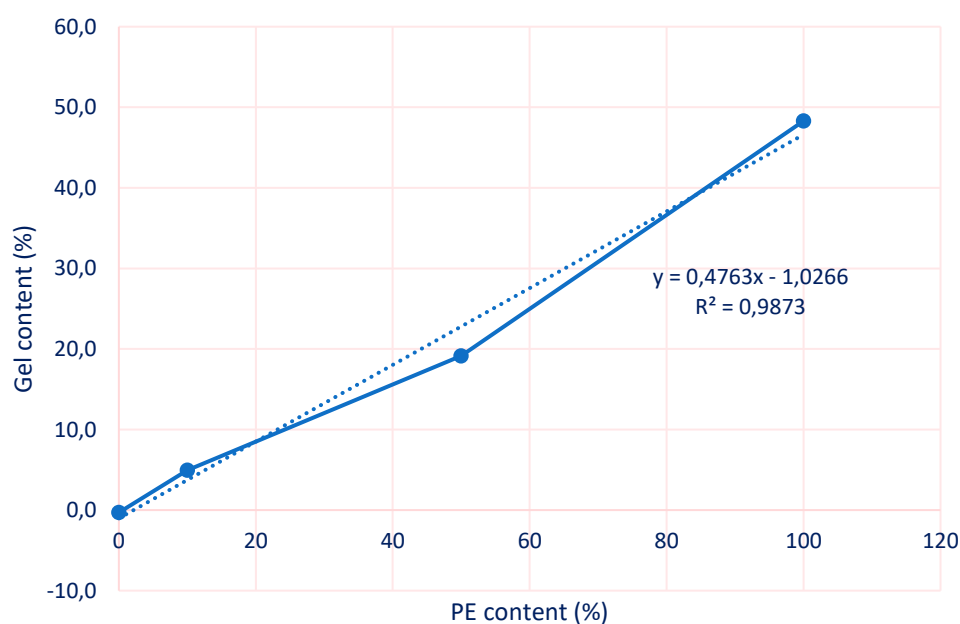


Figure 40. Calibration curve based on SS-142 RTF3 and HE3490-LS - Series 1

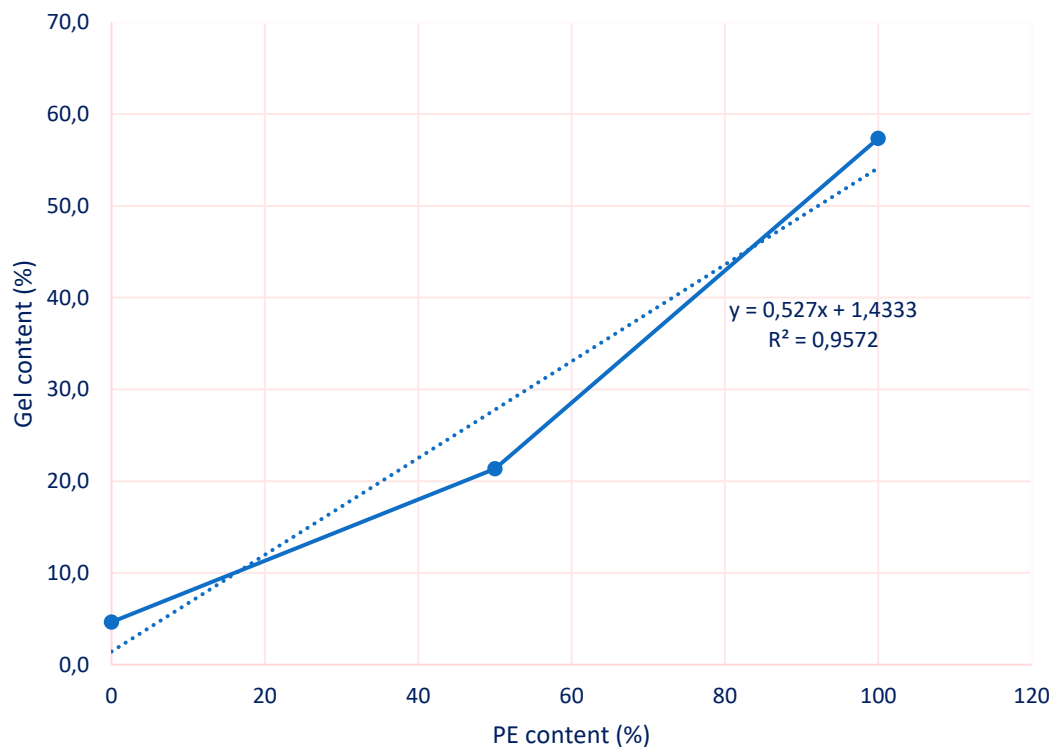


Figure 41. Calibration curve 2 based on RB307MO and Borecene RM8353 - Series 3

The calibration curves for the two series, where subscripts refer to the respective series, are:

$$PE_1 = 1.0426 \cdot G + 4.1599 \quad (4)$$

$$PE_3 = 1.8975 \cdot G - 2.7197 \quad (5)$$

5.4.2. Testing of characterization alternatives

To test the derived calibration curves, we selected two available rPP grades and included the 50/50 PE-PP blend in the study:

- 50/50 PE/PP
- rPP-2
- rPP-1

In Figure 42 and Figure 43 we display the thermograms of the two rPP's.

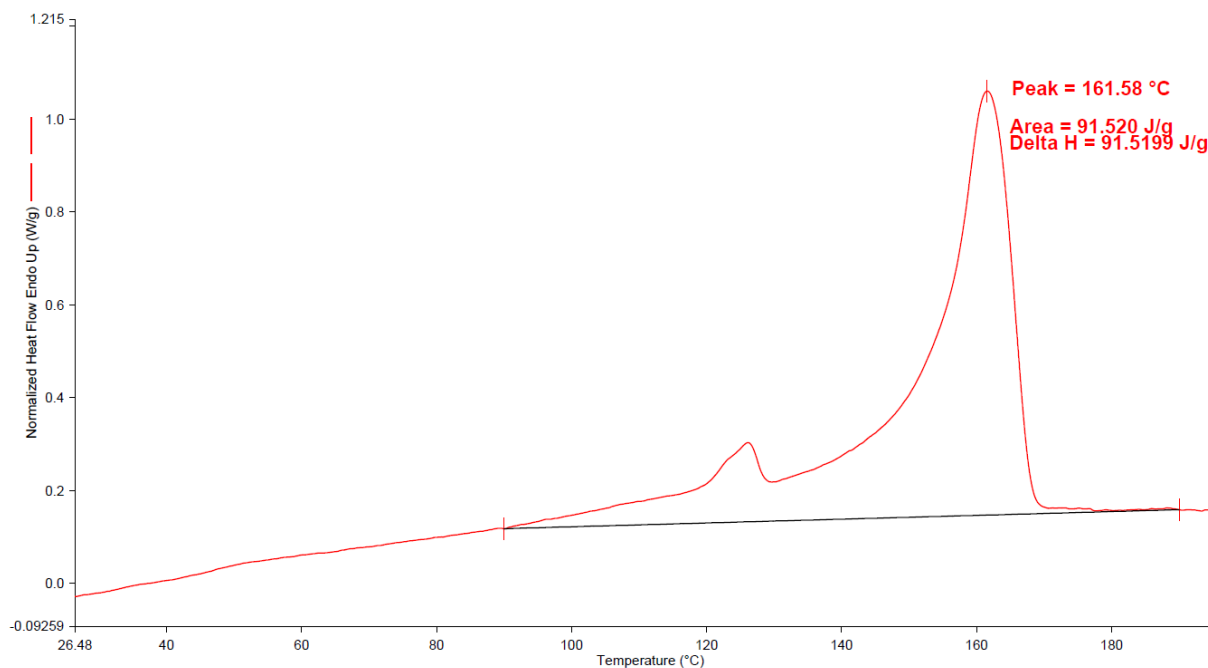


Figure 42 Thermogram rPP-1

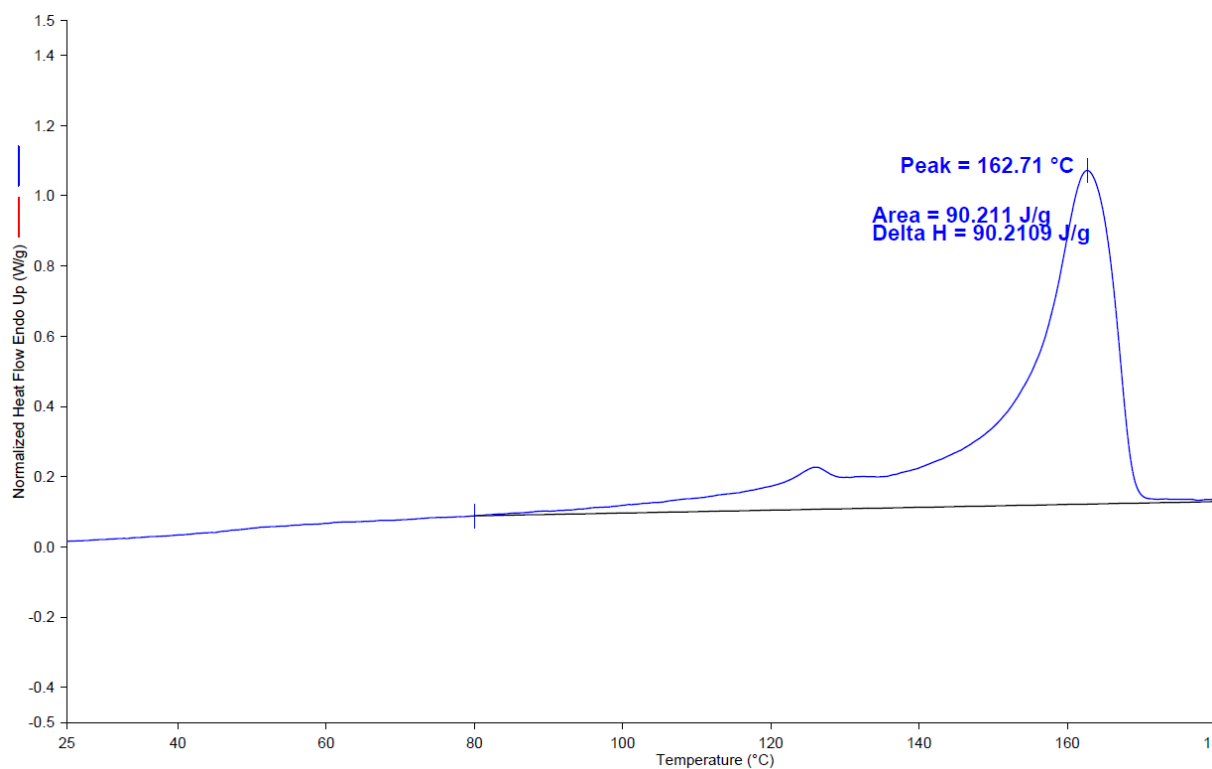


Figure 43 Thermogram rPP-2

From the thermograms, the PE peak is most pronounced for rPP-1 but the low-temperature shoulder of the PP peaks, overlapping the PE peaks, also differs. Using the derived calibration curves, we do a test by applying them to the two rPP's and to the 50/50 PE/PP special blend. Results are given in Table 59 (PE₁ and PE₃ refer to different calibration curves)

Table 59 Estimated PE content [%] in the two rPP's and the 50/50 blend

Material	DSC	FT-IR	NMR	Gel content
Special blend 1	42	52	46	-
rPP-1	4	3	3	-
rPP-1 extruded with 2 % peroxide		3		9 -PE ₁ 7 -PE ₃
rPP-2	4	-	3	-
rPP-2 extruded with 2 % peroxide		-		13 -PE ₁ 11 -PE ₃

5.4.3. Conclusion

Comparison of the four methods show agreement between results from DSC, FT-IR and NMR. However, the estimates based on gel content deviates. The respective calibration curves for the gel content were consistent, but the method may be less accurate for small PE content as is the case for rPP-1 and rPP-2.

The gel content of the Special blend will be tested in the next period for extra point for comparison.

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6. Refuse sacks

6.1. Background

Interval currently produce blown film products from recycled Low-Density Polyethylene (LDPE). The source of the material is primarily commercial and post-industrial films, with a level of agricultural films.

The interval plant uses a basic wash line to help remove dirt and labels, before the material is dried and extruded using a melt filter. This commercial and agricultural film differs greatly from post-consumer household films.

The household films are typically more contaminated, not only with other non-plastics like paper and metal, but also the film itself is often contaminated with Fats, Oil and Grease (FOGs). This means that a very different type of washing process is needed than the one currently in place.

6.2. Film processing

The washing of household films has been developed by several technology providers in Europe. The main providers of wash lines are:

- Sorema
- Herbold
- Lindner
- Amut

Household film can be washed cold or hot. Hot washing takes place at 80°C. In both hot and cold washing, detergents and caustic soda are used to help remove the Fats, Oils and Grease and any labels.

Firstly, the material is granulated with added water to liberate the loose, heavier contaminants attached to the packaging. Once granulated, the material is fed into a series of friction washers and washing tanks. Friction washers contain paddles that rotate at high speeds and jets of water, breaking down the fibrous contaminants on the packaging such as paper labels. From the friction washer, the material flows into a hot washing tank. The material is washed with a caustic solution (3 wt%) at 80°C to remove the residual FOGs from the packaging. The washed material is then fed through an additional friction washer to ensure thorough washing has been achieved. Following the washing stages there is a sink/float tank, where the denser contaminants are separated from the low density target material. The material flows in at the top of the tank, which is filled with water, and as the target material is less dense than water it floats but as the contaminants are denser than water, they sink. Amongst the dense contaminants, any of the remaining foil laminates (non-target material) are removed in this process stage.

The floating target film can be skimmed from the surface of the water and sent for drying. As a water treatment step, the wash water from the friction washers and from the sink float tank is filtered to recover the water and retrieve the contaminants for disposal.

The drying process of the post-consumer film occurs in two stages. Firstly, the material is mechanically dried, which operates similarly to a centrifuge but with screens to allow the water to drain and be recovered. Mechanical drying is capable of reaching moisture contents as low as 15%. Afterwards, the material is thermally dried by mixing the packaging with hot air, drying the film down to roughly 3% moisture content. **Figure 44** illustrates a simplified process of the washing line.

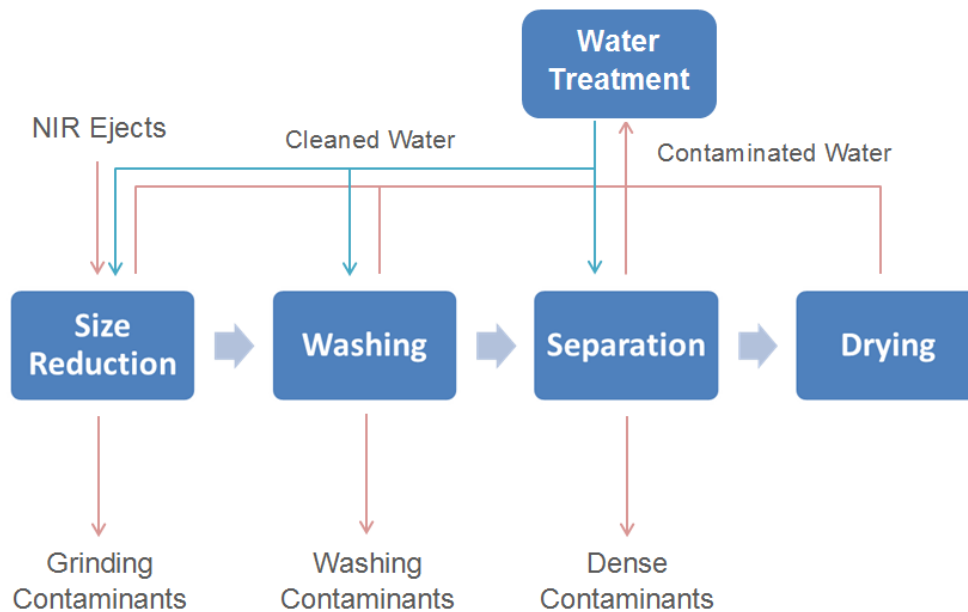


Figure 44 Wash line process flow diagram

The recirculation of the water is critical for the economics of the process. Process water must be reused as much as possible before being discharged. Any discharged water must then be topped up with fresh water.

Aside from washing, extrusion is a critical step. Mechanical washing of film will never on its own produce a suitable quality to be used back into film products. The purpose of the extrusion step is to:

- Remove trace levels of non-polymer contamination (i.e. metals, glass, paper)
- Remove moisture and volatiles from the polymer
- Mix the polymer to ensure it is more homogeneous
- Produce uniform pellets to aid the manufacture of new products

There are three main elements to the extrusion system:

- The mixing or compaction section
- The extruder barrel itself which carries out the degassing and creates a homogeneous mix
- The melt filter which removes the solid contamination (metal, glass, paper)
- The pelletiser to create a uniformed pellet.

There are several supplier of extrusion technology specialising in film, with the main ones being:

- MAS
- EREMA
- Amut
- Starlinger

The unit used for the post-consumer material was the INTAREMA equipped with a laser filter. **Figure 45** Error! Reference source not found. shows the EREMA INTAREMA extruder which has been specifically designed for film, with the key elements labelled.

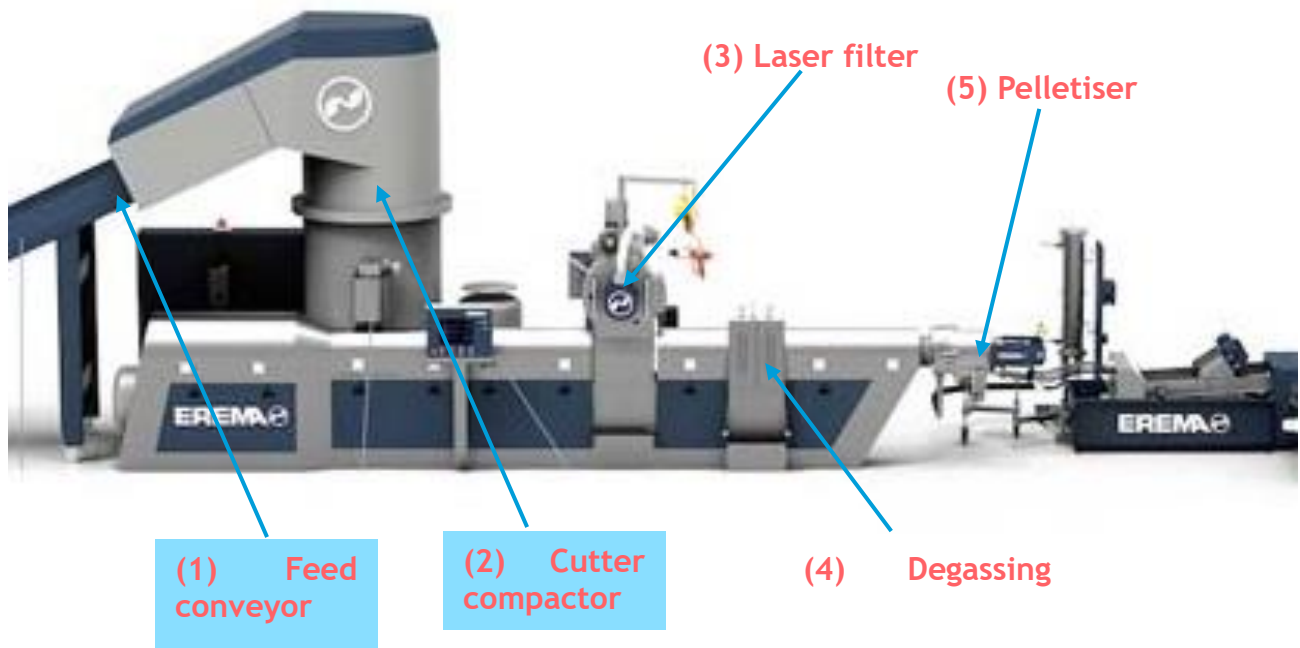


Figure 45 INTAREMA extruder

- (1) Material is fed into the cutter compactor via an inclined feed conveyor;
- (2) The cutter compactor size reduces and densifies the film using friction force, allowing it to be fed into the extruder;
- (3) The plastic is melted in the extruder screw and conveyed to the laser filter where contamination such as paper, high melt point polymers (for example PET and PA) and other residual contamination is removed;
- (4) Once filtered the molten plastic passes through a degassing vent where volatiles from inks, fats and oils are removed; and
- (5) The polymer is then extruded underwater where it cools and is cut into pellets.

There are three primary reasons why the EREMA is particularly suited to post-consumer film waste:

- The cutter compactor allows for very low bulk density material to be extruded at a commercially viable rate (the rate depends on the design of the unit and can range from several hundred kg to several tonnes per hour);
- The laser filter can process material with up to solid 5% contamination. The laser filter is a continuous filter which is self-cleaning to retain the design throughput; and
- The degassing is conducted after filtration. Much of the material removed by the filter would create gas if allowed to remain in the extruder. By removing the contamination mid-way through extrusion, it makes the degassing more effective.

Figure 46Error! Reference source not found. shows a diagram of the laser filter.

The filter allows for the processing of more contaminated material and produces a discharge which contains approximately 40% waste and 60% product. The filter is called a laser filter as the holes in the screen are cut using a laser.

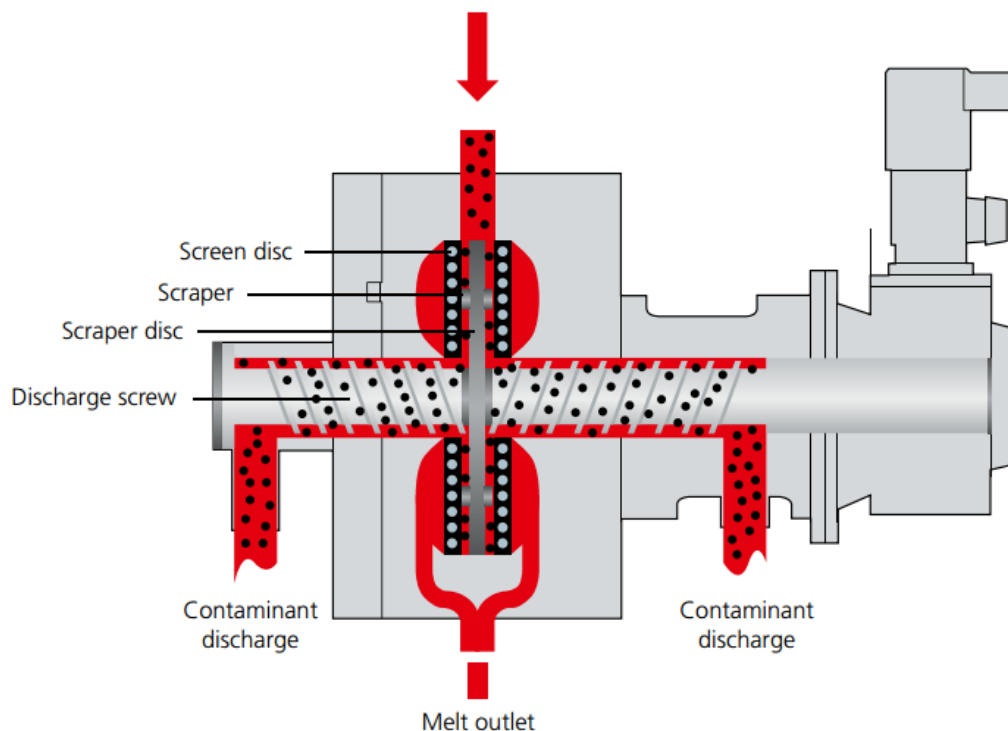


Figure 46 EREMA laser filter

Interval currently use an EREMA extruder, although to process post-consumer household film the filtration may need to be upgraded.

The technology for washing and extruding post-consumer films is reasonable well established, and a turnkey solution can be purchased and installed. However, there are relatively few plants in Europe running on only post-consumer household films. This is especially true as China is no longer accepting the cleaner commercial films which are remaining in Europe and can be purchased for a lower price.

6.3. PlastiCircle project plan

In the PlastiCircle project, the plan is to carry out a trial with Sorema to hot wash 500 kg of PE films. Film will be sourced from household Material Recovery Facilities (MRFs). The film will have been sorted from other recyclable materials into a "2D" fraction. This will be rich in PE film, but still likely to be contaminated with other polymers (such as PP) and paper.

The 2D fraction will be taken from the MRF and delivered to the Picvisa test center. Picvisa will sort the material to produce 500 kg of sorted PE film, with a target purity of >95%. This will be delivered to Sorema who will hot wash the film. At Sorema, a mass balance will be recorded to determine the level of contamination on the film. The dried fill will be transported to Interval who will extrude the material using a melt filter.

The extruded material will then be blown into new film. Interval products are a

single layer thick. Typically, when using recycled LDPE, especially from household waste, it is put into the middle layer of a three-layer structure. This reduces the risk of processing issues if there is a high level of gas or solid contamination.

The film blowing process involves extruding the polymer through a ringed shaped die to form a tube. The tube is then filled with air to “blow” the polymer, creating the desired thickness of the film. The blown film is then rolled up or cut into bags.

Once the film has been blown the properties can be measured. The tests performed to determine the mechanical properties of the film are:

- Melt flow rate of the polymer before extrusion
- Drop dart test
- Machine direction tensile strength
- Transverse direction tensile strength

These tests determine the strength of the film.

In addition to these tests, the gel content of the film can be measured. This is important for recycled material. Gels are areas of the film where the polymer chains have “clumped” together to form a dense gel in the film. This can make printing on the film difficult and can create localized weak points.

Gels are formed when PE is heated and extruded, and so is more prominent in recycled material. Gels cannot be removed using filtration as they can deform to pass through the filter. Additives can be used to reduce the level of gels. In **Figure 47**, the gels can be seen as the dark spots. This is an image of 100% recycled post-consumer PE blown into film.



Figure 47 Film made from 100% post-consumer recyclate

7. Outdoor furniture

7.1. Background

Hahn produce wood replacement products using intrusion moulding. Intrusion moulding is the process of filling a large mould with a molten polymer mixture and then allowing it to cool before releasing the mould.

This is different from extrusion or injection moulding where material is melted in a screw and then either pushed through a shaped die in the case of extrusion or injected into a shaped mould in the case of injection moulding. Intrusion moulding is in effect a combination of extrusion and injection moulding.

Intrusion moulding has the benefit of being able to handle more incompatible materials and also higher levels of contamination. This is because the dimensions of the mould are typically much larger than in injection moulding, so any incompatible materials can be dispersed within the compatible polymer matrix. This makes it ideal for lower quality plastics from household waste.

The process creates "boards" of a set dimension, which can then be used in the same way as lumber to make products such as fences, walkways, retaining walls and furniture. **Figure 48** shows one of the possible products that can be made using the intrusion moulded products.



Figure 48 Barrier made from Hahn product

The main opportunity for Hahn is to take the film fraction, which may be difficult or costly to sort and wash to a point where it is of sufficient quality for Interval.

Hahn currently process post-consumer material and are in the PlastiCircle project to demonstrate that virtually all polymer collected from households can be used in the manufacture of new products.

7.2. PlastiCircle project

The PlastiCircle project is constrained in the scale at which material can be sorted using pilot facilities. As a result, it has not been possible to test all the materials that could potentially be used in the Hahn process, as they can handle most polyolefin material.

Therefore, a focus has been places on comparing the cost and impact of using

cold washed PE film in a Hahn product against hot washed PE film in the Interval product.

Cold washing post-consumer household film will remove less of the volatile and organic materials, which means it cannot be used in the production of new film as the quality would be too low. However, the intrusion moulding process can tolerate higher contamination levels.

The benefit of cold washing the film is that it reduces the processing cost and also the environmental impact as less energy is required.

In the project, 500 kg of sorted PE film will be cold washed using the SOREMA test facility. The washed flake will then be agglomerated before being sent to Hahn. Agglomeration is used to increase the bulk density of the material by melting it into a crumb. Agglomeration also has a lower cost and energy requirement than extrusion, but it is not possible to melt filter the polymer to remove contamination.

Figure 49 shows a flow diagram for the work to be undertaken for Hahn.



Figure 49 flow diagram for Hahn process

No additives will be added to the polymer. Again this is so that the cost and impact of the product is kept to a minimum.

7.3. Conclusions

Work in WP5 is ongoing and there are still tasks to complete.

There is a very clear idea of what the issues are and the requirements of each of the manufacturing partners.

There is still likely to be a significant challenge surrounding PET thermoforms. This is a known issue in the industry however, a new facility has recently opened in the Netherlands which could provide further insight into how this material can be recycled.

There is little recycling of household film across Europe. These materials are often contaminated so proper washing technology must be used to meet demands from processors.

The PlastiCircle project will unlock new markets for recycle from post-consumer household packaging, complimenting the existing end markets.



The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant Agreement No. 730292.

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