D4.1 Production of pellets for demonstrator production

Deliverable no./title:	D4.1 Production of pellets for demonstrator production
Lead beneficiary:	TCK
Nature of deliverable:	Report
Dissemination level:	Public
Due date:	31.05.2022

Grant Agreement number:	820477
Project acronym:	CREAToR
Project title:	Collection of raw materials, Removal of flAme reTardants and Reuse of secondary raw materials
Funding scheme:	H2020-SC5-2018-2019-2020
Coordinator:	FRAUNHOFER GESELLSCHAFT ZUR FOERDERUNG DER ANGEWANDTEN FORSCHUNG E.V.
Project Website:	www.creatorproject.eu

CREATOR CONSORTIUM

PARTICIPANT NUMBER	ABBREVIATION	ORGANISATION
1	ICT	Fraunhofer-Gesellschaft für angewandte Forschung – Institut für Chemische Technologie
2	VLB	Volbas S.A.
3	MOS	Machinefabriek Otto Schouten BV
4	CLR	Coolrec BV
5	REL	Relight SRL
6	GKR	Fundacion Gaiker
7	TCK	Transfercenter fur Kunststofftechnik GmbH
8	RMA	Erema Engineering Recycling Maschinen und Anlagen Ges.m.b.H
9	CTB	Centre Scientifique & Technique De L'industrie Textile Belge
10	MAI	Maier S. Coop.
11	DAW	DAW SE
12	CYC	Cyclefibre S.L.
13	CID	Fundacion Cidaut
14	KLU	Kuhne Logistics University GmbH
15	OVM	Openbare Vlaamse Afvalstoffenmaatschappij
16	RWE	RWEnergia Robert Wudarczyk
17	ITB	ITRB Group LTD

DOCUMENT HISTORY AND CONTRIBUTION OF THE PARTNERS

Table 1: Version management

VERSION NR	REVISER	CONTENT
1	TCK	Author
2	MAI	Review
3	ICT	Review
4	TCK	Revision
5	ICT	Submission

Table 2: Partners' contribution to the deliverable

PARTNER	SHORT NAME	ROLE IN THE WP	CONTRIBUTION TO THE DELIVERABLE
Transfercenter fur Kunststofftechnik GmbH	TCK	Participant WP4	recycling test on the raw materials, testing the material properties, evaluating the data, production of pellets, writing the report
Coolrec BV	CLR	Participant WP4	providing raw materials
Maier S. Coop.	MAI	Lead WP4	providing feedback on material quality

ABBREVIATIONS

ABS	Acrylonitrile butadiene styrene
B&C	Building and construction
C&D	Construction and demolition
E-modulus	Elastic modulus
HDT	Heat deflection temperature
ISO	International Organization for Standardization
MFR	Melt flow rate
NADES	Natural deep eutectic solvent
RT	Room temperature
$Sc\text{-}CO_2$	Supercritical CO_2
TiO_2	Titanium oxide
VST	Vicat softening temperature
WEEE	Waste electrical and electronic equipment

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1 INTRODUCTION

The EU-funded project CREAToR focusses on process development and demonstration (to TRL 5) to remove hazardous, already banned bromine-containing flame-retardants from waste streams using continuous purification technologies (supercritical CO_2 and cost-effective solvent-based processes using natural deep eutectic solvents (NADES)) in twin-screw extruders. CREAToR covers the whole value chain, starting from collecting thermoplastic waste streams from construction and demolition waste (C&DW) and from waste electrical and electronic equipment (WEEE). Recyclers and sorters of both industries are part of the CREAToR consortium. The project is implementing ways to collect secondary raw materials, identify the presence of hazardous flame retardants, remove these contaminants and finally reuse the materials. As case studies the materials will be reused as valuable secondary raw materials for new building and construction (B&C) insulation panels (creating a circular economy), for automotive interior application, and for producing 3D printed parts for aerospace applications. The end user partners for each sector are also part of the CREAToR consortium. To further increase the economic feasibility of the approach, an optimised logistic concept and a harmonised material quality classification scheme is being developed and applied.

The use of sustainable materials is one of the current demands from automotive OEMs, so MAI's customers are looking for new grades and formulations based on recycled materials. These recycled materials need to have the same performance (the technical and aesthetical properties of recycled materials rarely meet the requirements defined by OEMs for added-value parts) and the same cost as the virgin ones.

In the deliverable "D4.1 Production of pellets for demonstrator production", the production of pellets from bromine-free ABS recyclate flakes is described. The pellets are intended for the production of 2D and 3D demonstrators for automotive interior application. The objective is to find a material for the demonstrator that consists of at least 7 wt.% recyclate material. The focus lies on the pretreatment of the recyclate flakes, their compounding with virgin material, and the testing of the different materials after compounding. Before producing the pellets needed to produce the demonstrator, preliminary studies with different amounts of recycled ABS were conducted. The aim was to find out how much virgin ABS can be replaced by recycled ABS while still meeting the requirements for the material. Based on the values from the material tests, it emerged that even the plain recyclate could be suitable for the production of the demonstrators. However, impurities posed a challenge that had to be overcome with an additional processing step: melt filtration.

The requirements that the material for the 3D demonstrator has to fulfil are listed in Table 3. In addition to the requested material properties, the demonstrator must be an aesthetic interior part of a vehicle and should not contain impurities, bubbles, streaks or injection flux.

Table 3: Requirements for the material for 3D demonstrator from MAI.

PARAMETER	UNIT	VALUE (REQUEST)
Density	g/cm³	1.05
Melt volume-flow rate	cm³/10min	25
Tensile modulus	MPa	2400
Yield stress	MPa	47
Yield strain	%	2.5
Charpy notched impact strength	kJ/m²	7

Charpy notched impact strength (-30 °C)	kJ/m²	17
Temperature of deflection under load	°C	98
Vicat softening temperature	°C	101

2 MATERIALS AND METHODS

2.1 MATERIALS

In the CREAToR project two grades of ABS recyclate flakes were used to produce pellets to develop a material for the production of the demonstrators. The two grades were:

- ABS recyclate flakes (white) from fridges by CLR [ABS30009]
- ABS recyclate flakes (black) from WEEE/small domestic appliances by CLR [ABS30005].

The white fraction from fridges is obtained from components such as drawers, trays, handles and fridge cabinet outer tops. The black fraction is mainly obtained from plastic parts of the casing of appliances, for example covers from vacuum cleaners, coffee machines, conditioning devices and backcovers from monitors (s. Figure 1).

Figure 1: White (left) and black (right) ABS recyclate flakes.

The recyclate materials were blended with a virgin ABS grade:

- ABS virgin (black) from MAI.

2.2 METHODS

2.2.1 MATERIALS PROCESSING

The various material mixtures were compounded, injection moulded and then characterised. The pure materials (i.e. 100% virgin material and 100% recyclates) were processed in the same way to ensure comparable results.

2.2.1.1 COMPOUNDING

The compounding was carried out in a co-rotating twin-screw extruder (Prism). The processing parameters for the preliminary material tests were kept the same for all materials and compounds, and are listed in Table 4. The production of pellets for the demonstrator was carried out on a co-rotrating twin-screw extruder (Leistritz) with additional melt filtration. The processing parameters are listed in

Table 5. The material was processed into granules using strand pelletising. After pelletising, the materials were dried in dry-air driers prior to injection moulding (s. Figure 2).

Table 4: Parameters for compounding for the preliminary tests with different material compositions.

PARAMETER	VALUE
Screw diameter	24 mm
Processing length	40 L/D
Nozzle	3 hole
Rotational speed	300 rpm
Throughput	12 kg/h
Processing temperature	260 °C

Table 5: Parameters for compounding the material for the demonstrator.

PARAMETER	VALUE
Screw diameter	27 mm
Processing length	40 L/D
Nozzle	3 hole
Rotational speed	350 rpm
Throughput	22 kg/h
Processing temperature	50 °C
Melt filatration (mesh size)	150 µm

2.2.1.2 INJECTION MOULDING

The pellets were injection moulded to universal testing specimens in accordance with ISO-3167. Specimen geometry was in accordance with ISO-527 for mechanical testing on a conventional injection moulding machine (Engel 330/80). The parameters are given in Table 6. The universal test specimens were stored at 23 °C and 50 % relative humidity for at least 96 h prior to testing.

Table 6: Parameters for injection moulding the pellets to universal test specimens.

PARAMETER	VALUE
Mass temperature	250 °C
Mould temperature	40 °C
Cycle time	49 s

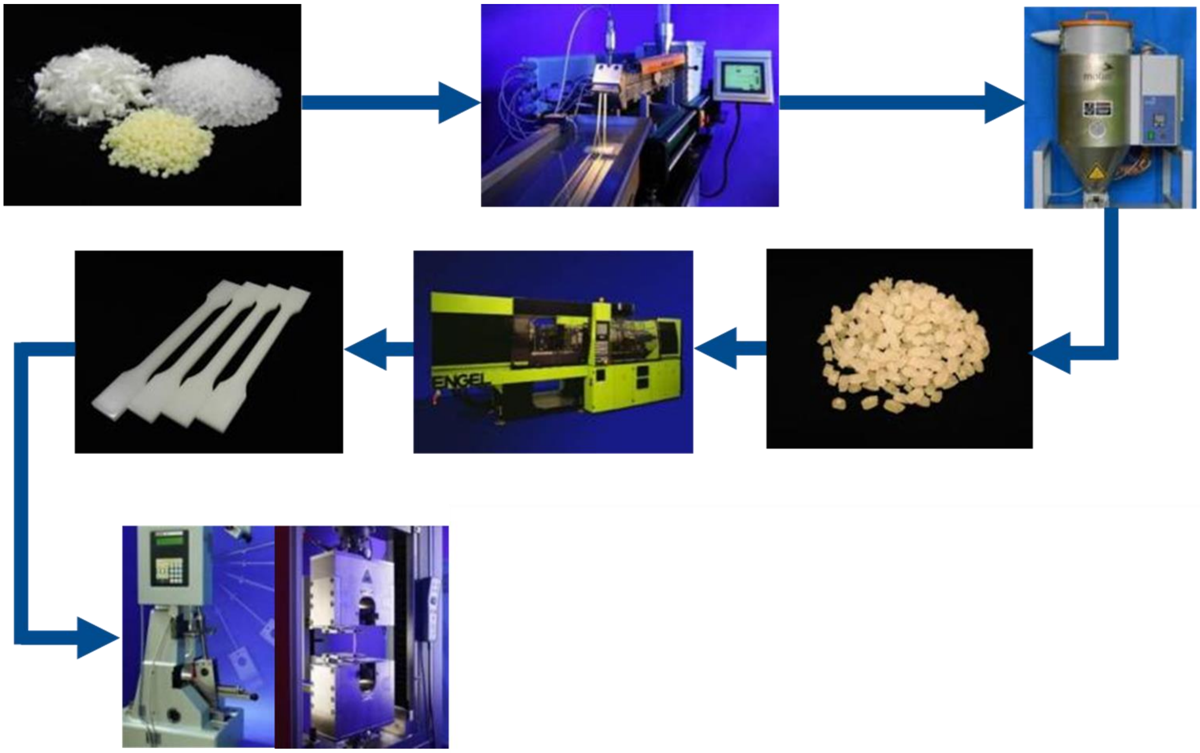

Figure 2: Schematic of compound production: The input material is compounded, pelletised, dried, injection moulded into universal test specimens and characterised.

2.2.2 MATERIALS TESTING

2.2.2.1 DENSITY

The density was measured on laboratory scale using a density kit. Parts of universal test specimens were cut off, weighed in air and submerged in ethanol. The density of the samples was then calculated from these values.

2.2.2.2 MFR

The melt flow rate (MFR) gives an indication of the flowability of a plastic at a certain temperature and load. Granules of the compounds were used for the measurements. The MFR of the samples was determined at a temperature of 220 °C with a load weight of 10 kg.

2.2.2.3 TENSILE TEST

Tensile testing for elastic modulus and tensile strength in accordance with ISO-527 was carried out on a universal testing machine (Zwick Roell Z020) with a crosshead speed of 1 mm/min to measure the elastic modulus and subsequently with 50 mm/min until the samples broke. For each series, five replicates were tested.

2.2.2.4 CHARPY NOTCHED IMPACT STRENGTH

Impact testing was carried out on a pendulum impact tester (Zwick Roell 5113.300) for notched Charpy impact strength after punching out the prismatic specimen (80x10x4 mm³) from the universal test specimens and notching them with a precision circular saw. The tests were carried out at room temperature (23 °C) as well as at -30 °C. 10 replicates per series and temperature were used.

2.2.2.5 HDT/VST

Heat deflection temperature (HDT) was measured to determine the thermal stability of a sample under a certain load. HDT was was tested according to ISO75-2 with a heating rate of 120 k/h. Vicat softening temperature (VST) was measured in accordance with ISO306 with a heating rate of 50 k/h.

2.3 PRELIMINARY TESTS

In preliminary tests, different amounts of recyclates were added to virgin ABS and the properties of the materials obtained were evaluated according to the requirements for the material given in Table 3. Both grades of recyclates (white and black) were compounded in various proportions from 0 to 100 wt.% with virgin ABS (black). The exact composition of the materials produced in the preliminary studies can be found in Table 7 and Table 8.

Table 7: Materials produced with ABS recyclate (white).

wt.%	Material 1	wt.%	Material 2
100	ABS virgin black	0	
0		100	ABS recyclate white
93	ABS virgin black	7	ABS recyclate white
75	ABS virgin black	25	ABS recyclate white
50	ABS virgin black	50	ABS recyclate white

Table 8: Materials produced with ABS recyclate (black).

wt.%	Material 1	wt.%	Material 2
0		100	ABS recyclate black
95	ABS virgin black	5	ABS recyclate black
93	ABS virgin black	7	ABS recyclate black
85	ABS virgin black	15	ABS recyclate black
75	ABS virgin black	25	ABS recyclate black
50	ABS virgin black	50	ABS recyclate black

The recyclates were found to contain metal. The recyclate flakes were therefore examined in a metal separator prior to compounding. Metal-containing particles were separated from the rest, as metals can cause severe damage to plastic processing machines and reduce the properties of the recyclate. Figure 3 shows that most ejected pieces were coated by a thin metal paint (or a galvanised layer), and there were no full metal pieces. The pieces removed in sorting had a size of 5-10 mm and were predominantly white and grey. The amount can only be roughly estimated, as the metal separator not only removes the metal containing particles but also surrounding ones. It is assumed that about 1-2 pieces with metal coating can be found in one kilogram of ABS recyclate, which is definitely less than 0.1 %.

Figure 3: Metal-containing parts removed from ABS recyclate.

2.3.1 RESULTS

There were no major issues in the processing of the materials, even those with high recyclate content, compared to virgin ABS. Figure 4 shows the pellets produced from 100 wt.% recyclates. The materials were subjected to various tests and the results of the recyclate-containing materials were compared among each other and with the virgin ABS in each case. An overview of the requested values, and the values of the virgin ABS and the two recyclates is given in Table 9.

Figure 4: Pelletised recyclates white (left) and black (right).

Figure 5 shows that the **density** of the recyclates (both white and black) is slightly higher than the density of the virgin material. Hence, density increases linearly with increasing recyclate content. The difference between the recyclates and the virgin ABS can be due to the fact that the density of ABS can vary depending on its composition. In addition, the white material could contain TiO_2 as a filler or pigment, which leads to higher density, as TiO_2 exhibits higher density (4.2 g/cm³) than the ABS (1.03-1.07 g/cm³)[1].

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[1] Baur et al., „Saechtling Kunststoff Taschenbuch", Carl Hanser Verlag, 31. Ausgabe, München (2013)

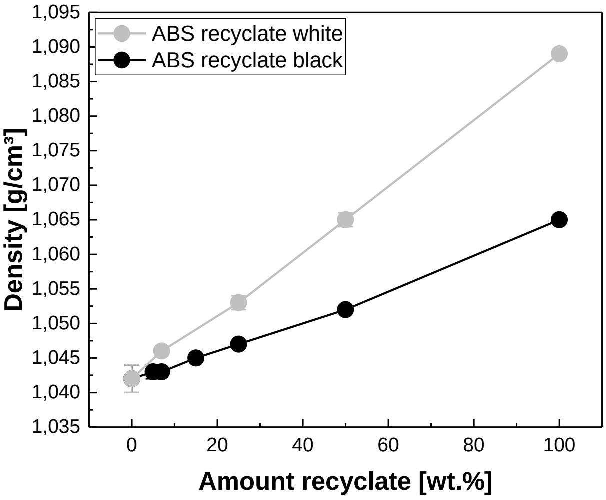

Figure 5: Density of the compounds depending on the recyclate content.

The **melt flow rate (MFR)** of the samples is given in Figure 6. As is clear from Figure 6, the MFR of the white ABS recyclate (21.05 g/10min) is lower, and the MFR of the black ABS recyclate (30.15 g/10min) is higher than the MFR of virgin ABS (25.60 g/10min). This is due to the different ABS grades exhibiting different MFR values, as can be seen from the values at 100% recyclate. Although there are differences, both recyclate grades can be used as injection moulding materials. The change in MFR according to recyclate content for both recyclates is almost linear.

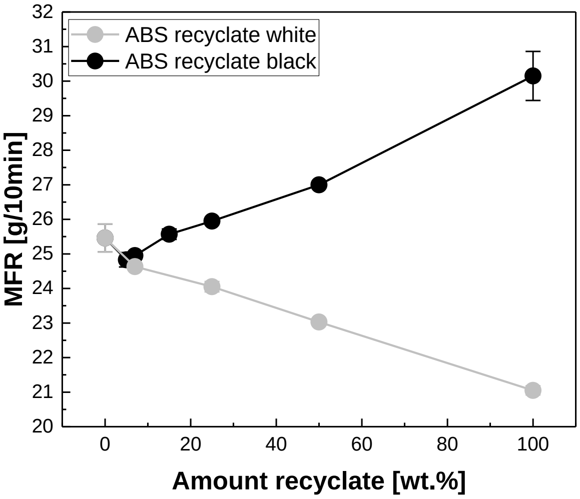

Figure 6: Melt flow rate (MFR) of the compounds depending on the recyclate content.

The results of the **tensile tests** are given in Figure 7. The elastic moduli (**E-moduli**) of both recyclates are higher than the modulus of virgin ABS. An almost linear increase of the E-moduli can be observed for the compounds. The difference between the compounds with white and black ABS is small. In **tensile strength**, however, the recyclates differ from each other as well as from the virgin ABS due to the composition, but the differences are very small and can be neglected in technical terms. **Yield strain** decreases little with increasing recyclate content for both recyclate grades. Again, this is due to the different ABS compositions and, as is the case for the tensile strength, the differences are not significant.

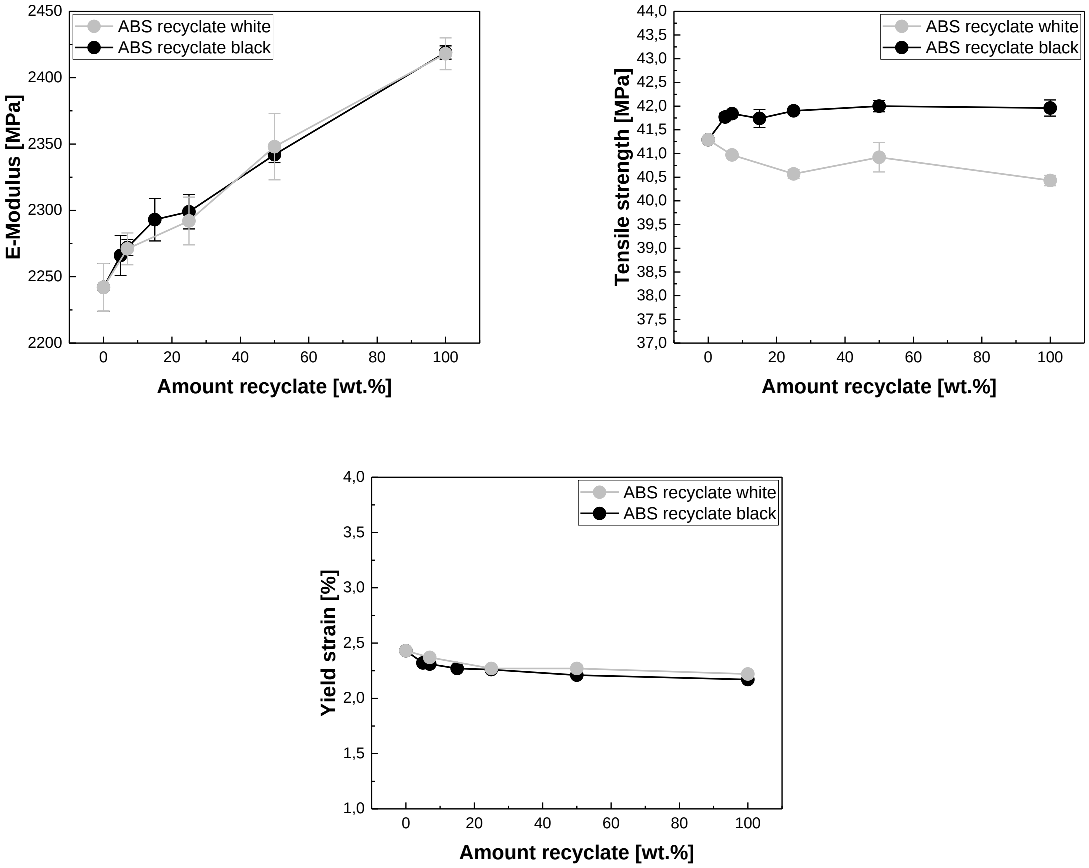

Figure 7: E-Modulus (top, left), tensile strength (top, right), and yield strain (bottom) of the compounds depending on the recyclate content.

Notched impact strength was determined at 23 °C and at -30 °C. Figure 8 depicts the curves of both measurements. The measurements show that the notched impact strength of 100 % recyclates is lower than for the virgin ABS, which can also be attributed to the composition, i.e. with a lower butadiene content, the modulus is higher, but the impact strength will be lower. The impact strength for the recyclate containing compounds stays practically the same within the 0-20 wt.% and slightly decreases with higher recyclate content. The trend for the measurements at -30 °C is similar to the measurements at RT, however the drop of the curve is not linear, as it is at RT.

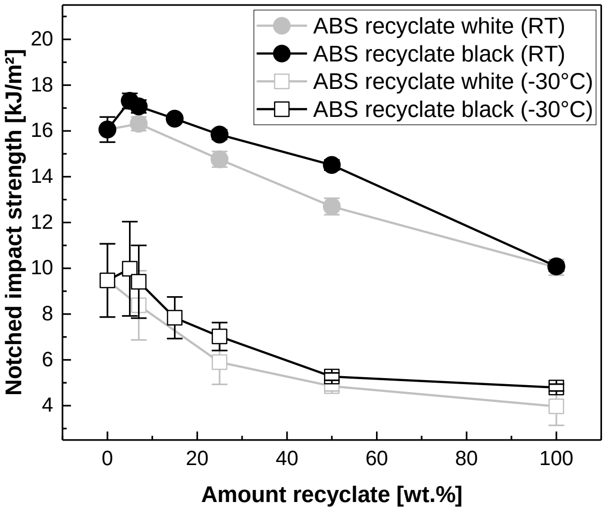

Figure 8: Notched impact strength of the compounds depending on the recyclate content.

The thermal stability of the materials was evaluated by measuring the **vicat softening temperature** (VST) and **heat deflection temperature** (HDT). Figure 9 shows that the VST is lower for the recyclates and recyclate-containing compounds than for virgin ABS. The values for the black recyclate are even lower than for the white grade. HDT measurements show a similar trend and therefore slightly lower values for the recyclates than for the virgin ABS. A possible explanation for the decrease of VST and HDT of the recyclates compared to virgin ABS is that these recyclates already have a life cycle behind them, which means that the materials have already been processed once before and had to endure certain stresses, which gives rise to a minor reduction of these values.

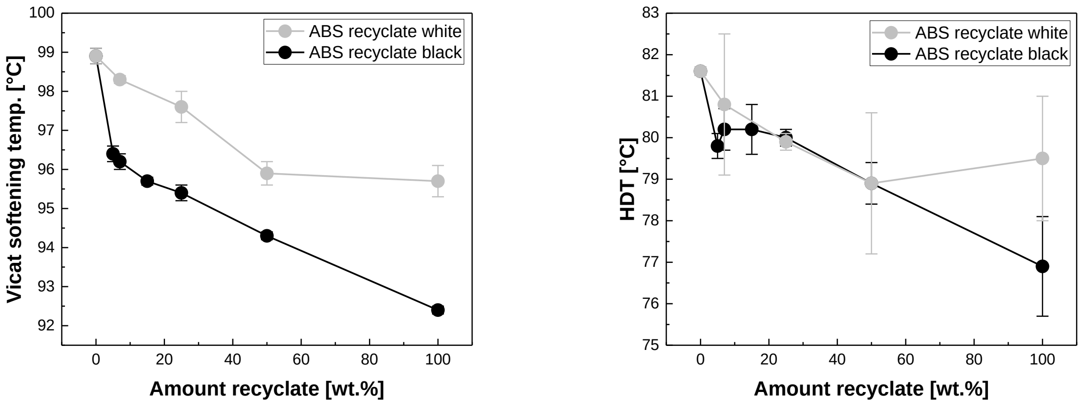

Figure 9: Vicat softening temperature (left) and heat deflection temperature (right) of the compounds depending on the recyclate content.

Table 9 compares the values of the mechanical and thermal tests with the requirements for the material for the 3D demonstrator. It can be seen that both recyclates are within the range of requirements and comparable to the virgin ABS, though there are slight deviations in density and MFR. The tensile moduli of the recyclates fulfil the requirements even better than virgin material. Yield stress and yield strain requirements cannot be achieved by all the materials, including virgin ABS. The requirements for Charpy notched impact strength at -30 °C and at RT are achieved with the virgin material, but not exactly with the recyclates. The HDT and VST of the recyclates do not quite reach the required values, but have almost minor deviations from the virgin ABS. This means that the recyclate ABS grades perform comparably to the virgin grade – with some small deviations. The work was therefore continued. Especially the critical values, i.e. elastic modulus, MFR and impact behaviour of the recyclates seemed well suited for the application.

Table 9: Comparison of the requirements for the material with the material properties for 100 wt.% recyclate material.

PARAMETER	UNIT	VALUE (REQUEST)	VIRGIN ABS	ABS RECYCLATE (WHITE)	ABS RECYCLATE (BLACK)
Density	g/cm³	1.050	1.042	1.089	1.065
Melt volume-flow rate	cm³/10min	25	25.60	21.05	30.15
Tensile modulus	MPa	2400	2261	2418	2419
Yield stress	MPa	47	40.82	40.43	41.96
Yield strain	%	2.5	2.31	2.22	2.17
Charpy notched impact strength	kJ/m²	17	18.20	10.04	10.08
Charpy notched impact strength (-30 °C)	kJ/m²	7	9.75	3.97	4.79
Vicat softening temperature	°C	101	97.8	95.7	92.4
Temperature of deflection under load	°C	98	79.5	79.5	76.9

2.4 PRODUCTION OF PELLETS FOR THE AUTOMOTIVE DEMONSTRATOR

MAI injected and tested all compounds produced in the preliminary tests with a 2D demonstrator. Promising results were obtained for injected 2D demonstrators even with the plain recyclates. For this reason, 200 kg of pellets from 100 wt.% white and black ABS recyclate materials were produced at TCK. As in the pre-trials, the recycled material was passed through a metal separator. The plain recyclate flakes were compounded in a co-rotating twin-screw extruder. After compounding and pelletising, they were dried and sent to MAI for demonstrator production.

MAI found particles and imperfections in the first moulded parts. These particles are in the recyclate material and do not originate from manfacturing. The recyclate flakes can only be tested for metal content at TCK, and metals are the only foreign particles that can be removed in advance via sorting. The contaminants MAI found mostly came from rubber particles and other impurities.

In an attempt to remove these particles from the material, the black ABS reyclate was compounded using melt filtration. The parameters of compounding can be found in

Table 5 in 2.2.1.1 Compounding. A sieve pack with a smallest mesh size of 150 µm was used, as a compromise between throughput and the filtration quality. 150 µm is smaller than impurities found in the demonstrators, and filtration pressure increases exponentially with reduced sieve size. Also, the shear brought into the material should not be too high, as the butadiene component of the ABS is rather sensitive to shear and oxidation, which can lead to a reduction of the impact strength. A balance must therefore be found between filtration efficiency and material properties. As evident from Figure 10, the particles and impurities could be significantly reduced through melt filtration and the quality of the material was improved. Injection moulding to produce a 3D demonstrator will be carried out at MAI.

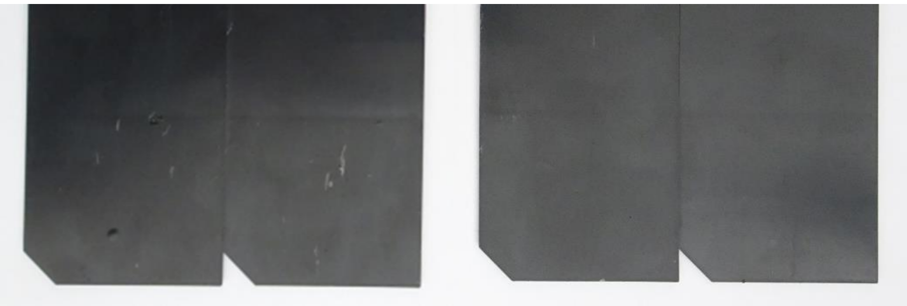

Figure 10: Injection moulded plates produced with the pellets from black ABS recyclate before (left) and after (right) melt filtration with a 150 µm sieve.

3 CONCLUSION

To produce the pellets for the demonstrator, two different grades of ABS recyclate were compounded in different proportions with virgin ABS. The mechanical and thermal characteristics of these compounds and plain recyclates were determined. In most cases, the addition of recyclate to virgin ABS alters the properties linearly according to the recyclate content. Based on the results with the materials from the preliminary tests, MAI decided to demonstrate production with the plain recyclate and thus with 100 % recyclate content. Impurities made melt filtration necessary. A melt filtrated compound was produced at TCK and shipped to MAI for 3D demonstrator tests.

4 OUTLOOK

MAI has received the melt filtrated pellets for the 3D demonstrator production. They will inject the new recycled black melt filtrated pellets into the 3D demonstrator. This new pellet batch will be compared to the previous one.