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Compatibilized PC/ABS blends from solvent recycled PC and ABS polymers from electronic equipment waste

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ABSTRACT

This study encompasses the development of high-performance PC/ABS blends utilizing recycled PC (r-PC) and recycled ABS (r-ABS) polymers from waste electric and electronic equipment (WEEE) fractions heavily contaminated by flame retardants (FRs). Upgrading of mechanical properties was facilitated by addition of virgin ABS and additives. In total three different WEEE fractions -containing high concentrations of bromine, chloride and phosphorous were purified from polymers other than PC and decontaminated from halogenated contaminants by dissolution-precipitation CreaSolv® Process. In two studied cases the WEEE fractions were optically pre-sorted for PC before purification and decontamination. Gas chromatography (GC-ECD) and X-ray fluorescence (XRF) analyses were performed to validate efficient removal of contaminants from r-PC.

The targeted mechanical properties of polymers to upgrade are notched impact strength and elastic moduli. Upgrading was achieved by using the suitable compatibilizers, and, optionally by a chain extender. First, small-scale laboratory screening test series were conducted for three compatibilizers and different ABS polymers based on micro-compounding experiments. Upscaling test series based on the pre-screening data was then organized on a conventional bench scale twin-screw extruder.

SEM microstructural characterizations of the blend morphology and fractured surfaces are done to correlate structure to the mechanical properties.Dynamic mechanical analysis (DMA) and Rheological Dynamic Analysis (RDA) and Gel permeation chromatography (GPC) provided some insight to the chain branching and molecular weight distribution of r-PC, respectively. Moreover, melt rheology and solid-state mechanical properties of the compatibilized r-PC/ABS blend were thoroughly investigated.

Addition of virgin ABS polymer and a suitable compatibilizer enhance the properties of the recycled PC/ABS 60/40 blends towards virgin-like, allowing easily >55% r-PC content, or in favourable cases much higher than 75% recycled polymer content when applying significant concentration of recycled ABS from CreaSolv® together with some virgin ABS.

1. Introduction

PC/ABS blends of polycarbonate and polyacrylonitrile-butadiene-styrene (PC/ABS) are commonly applied in automotive parts as well as housings of electronics and household appliances. Popularity of the blends stem from the synergistic balance of good thermomechanical properties and high impact strength of PC, combined with the attractive cost and easy injection moulding of ABS [17,18]. In thicker injection moulded parts PC/ABS blend has several advantages over neat PC; for example, notch sensitivity of neat PC can be overcome by blending with ABS [2].

Due to the global transition to circular plastics economy, there is an increasing demand for high quality recycled technical plastics such as ABS, PC, and their blend PC/ABS. End-of-life (EoL) PC/ABS, however, may cause issues in mechanical recycling as material reprocessing inevitably changes the mechanical properties of recycled PC/ABS. This has been demonstrated in early studies [3–5]. In many cases, the observed degradation of properties such as elastic moduli, tensile strength, fracture toughness or thermomechanical properties in PC/ABS re-processing has not been dramatic [21], as confirmed also in a recent study by Orzan *et al.* (2021) [1]. However, according to private communications with household appliance original equipment

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manufacturers (Advisory board of EU-Nontox project, 2020) the most compromised technical property for many applications of the recycled plastics is mostly their weak notched impact strength. Degradation of impact properties may be traced back to several factors: First, when applying recycled polymers with fluctuating origin, composition, and properties, then the melt viscosity ratio between PC and ABS is not fully consistent. This variance has a negative effect on the melt blending process, blend morphology, and hence compromising the consistency of impact properties in blends with high recycled content. Moreover, increased rubber particle sizes [6] and aging/cross-linking of rubbery segments of ABS from WEEE streams are generally factors reducing impact properties [7]. Finally, small amounts of contaminations such as polyamide [5], and trace amounts of other incompatible polymers acting as mechanically weak points or cavities, and the halogenated flame retardants (FRs) and catalytic metal compounds may potentially trigger several polymer degradation mechanisms, such as by acid hydrolysis of PC and thermo-oxidation of ABS at elevated temperatures.

From eco-design perspective, the preservation of the impact strength is essential, as it enables circularity of recycled polymers in durable appliances. Thus, recycling of PC/ABS typically necessitates the addition of virgin polymers (PC, ABS or both polymers) or a well compatible elastomeric impact modifier such as polybutadiene rubber, MBS core-shell rubber particles or styrenic thermoplastic elastomer, such as SEBS [16] into the recycled blend. Industrially acceptable performance level in the impact strength of ABS and PC/ABS plastics in common small domestic appliances is typically in the range of Charpy notched 25 kJ/m^2 (OEM interviews in Nontox project, 2020) while retaining the stiffness of the virgin material. Moreover, beyond the thermal and mechanical requirements, and aesthetics, such as colour, gloss, and haze, also the melt flow properties of recycled material must be tuned over wide range according to the application and converting process, such as injection moulding, extrusion-thermoforming, which require quite different melt rheology.

Furthermore, feedstocks for recycled ABS, PC and PC/ABS exhibit a significant heterogeneity since they contain mixed low viscosity injection moulding and high viscosity extrusion grade PC and ABS plastics. Variability of melt viscosities of blend components makes it technically challenging to reproduce blend melt viscosity and mixing conditions. Since there is always an inter-batch fluctuation in the composition and melt flow properties of recycled polymers, reproducibility of recycled blends is typically poor compared to virgin polymer blends (both having typically 60–70% of PC in the blend). However, suitable compatibilization can effectively improve the mixing of the PC and ABS polymers in the melt [29], and yields more consistent mechanical properties of the recycled blends. Since compatibilizers effectively reduce the interfacial surface energy of the polymer phases in the melt, they facilitate mixing and stability of melt homogeneity, and they also allow more versatile viscosities of the blend components to be used. Consequently, assuring favourable mixing conditions may potentially enable increased recycled content in the blends. Suitable compatibilizers of PC/ABS are styrenic copolymers, such as styrene acrylonitrile (SAN), or rubber modified polystyrene (HIPS) [24] or slightly polar functionalized acrylic ester (EMA) [8], which are all polymers partly immiscible with the ABS. Adhesion to PC directly, or to inorganic fillers, such as organoclay or silica, is best achieved by compatibilizers. Commercially available, effective, and highly efficient compatibilizers for PC/ABS are rigid random copolymers of styrene with polar monomers such as maleic anhydride (SMA), which is the subject of this investigation, or styrenic copolymers with glycidyl methacrylate (GMA), of grafted ABS-*g*-MA or EVA-*g*-MA [9].

Moreover, end-of-life (EoL) management of PC/ABS in real life suffers from the fact that the use-related waste streams, such as end-of-life-vehicles (ELV), or waste electric and electronic equipment (WEEE), contain only minor amounts of the polymer blend. Therefore, other waste components are prioritized in recycling like metals or polymers with higher shares, whereas EoL PC/ABS is treated as a side stream and mostly wasted. As recently shown, PC/ABS can be enriched in specific fractions of WEEE plastic recycling plants, the so called “heavy fraction” with densities higher than 1.1 g/ml [11]. However, in these fractions ABS and PS co-exist, both equipped with brominated flame retardants (BFR) with some of these BFR listed as persistent organic pollutants (POP). That requests an efficient sorting of PC/ABS which is highly challenging, especially when considering that materials in such heavy fraction are often black. As a result, sorted PC/ABS may contain up to 5% of foreign polymers including both, compatible impurities like ABS or PC and incompatible materials like PS or POM. Furthermore, residues of BFR or phosphorous based flame retardants (PFR) may be present and enhance the above-described heterogeneity of feedstocks with respect to viscosities [25,26].

To overcome the above discussed challenges in sorting EoL PC/ABS and re-compounding of undefined PC/ABS ratios dissolution-based recycling has been proposed as an alternative treatment route. Such approaches apply selective solvents to dissolve target polymers from plastic waste and separate undissolved non-target materials and polymers from the dissolution [10]. After separation and re-circulation of the solvent, a purified polymer is recovered. The dissolution technology CreaSolv® even enables the purification of co-dissolved molecules, as exemplified for HBCD containing expanded polystyrene (EPS) [11] or BFR equipped WEEE plastics [10,12] or other legacy additives from waste plastics [13]. With respect to PC/ABS, the dissolution approach may target for the blend only, as published earlier [11]. As it has been recognised, that specific process condition allows separation of ABS from the PC/ABS blend, an alternative approach may dissolve ABS in a first step and PC from the undissolved matter of step one. This is especially interesting, when using the above-mentioned heavy fractions after simple pre-sorting as a feedstock. These may contain amongst others ~5% of BFR equipped ABS and PC items [10]. A separate recovery of ABS and PC enables purification of legacy additives on the one hand and a re-blending ABS and PC in defined ratios on the other. However, depending on the process parameters, the solvent-based purification may also reduce levels of stabilizers, impact modifiers and compatibilizers. In these cases, re-compounding of solvent based recycled ABS and PC requires an optimized additive package.

This study investigates the blending of dissolution based recovered ABS and PC with different mechanical properties and related virgin grades to upgrade the blend properties by enhancing the notched impact strength and thermomechanical properties. This is demonstrated by using the combination of suitable compatibilizers and epoxy chain extender. Small-scale laboratory screening test series for three compatibilizers and different ABS polymers produced by micro-compounding is shown first. Upscaling test series based on the pre-screening is then organized to demonstrate the mechanical properties on the best blends generated using conventional bench scale twin screw compounders which can be further upscaled to industrial scale processing equipment. Microstructural characterizations of the blend morphology and fractured surfaces are done to correlate structure to the mechanical properties.

2. Experimental

2.1. Materials

Recycled PC batches 9.8 g/10min (260 °C/2.16 kg) (PC Creasolv1), MFI 19.8 g/10min (PC Creasolv2), MFI 6.7 g/10 min (PC Creasolv3), and recycled ABS MFI 23 g/10 min (+220 °C/10 kg) (ABS Creasolv) were produced on a small-technical CreaSolv® pilot line using diverse WEEE sources. The first batch separated PC/ABS from a heavy fraction (density >1.1 g/ml) of small domestic appliances (SDA) and information & communication technology (ICT) after pre-extraction of HIPS and ABS, both containing brominated flame retardants as described in detail by Strobl *et al.* (2021) [10]. The two later PC batches were produced by optical sorting to pre-concentrate PC from the heavy fractions followed by the same CreaSolv® Treatment as for PC Creasolv1. In case of PC Creasolv2 the feedstock contained SDA, flat panel displays (FPD) and cathode ray tube (CRT) equipment and therefore a higher share of large-scale housing plastics, however in PC CreaSolv3 again SDA and ICT heavy fractions were used. The recyclates were received from Fraunhofer IVV, further dried and compounded at VTT. Polymers were used without further stabilization. The screening experiments were carried out with the firstly prepared small laboratory sample (PC Creasolv1) having the highest level of residual halogen concentrations (see XRF results) - and lowest melt stability, as compared to the two subsequently delivered batches used in the upscaling experiments (PC Creasolv2 and PC Creasolv3).

High impact strength virgin grade ABS EX58F from Sabic (Melt Flow Rate 4 g/10 min, +220 °C/10 kg) was used.

Commercial styrene-maleic acid (SMA) -terpolymers Xibond® 315 (random terpolymer of styrene, maleic anhydride and N-Phenylmaleimide, Compatibilizer A) and Xibond 160® (random copolymer of styrene and maleic anhydride) from Polyscope, and an elastic Lotader 8840 (ethylene-ethylacrylate-GMA terpolymer, Compatibilizer C) from Arkema were tested as compatibilizers in the PC/ABS (60/40) blends.

Low molecular weight epoxy functionalized chain extender Joncryl 4400 (BASF) was added to some formulations. The studied material compositions are listed in Table 1. Between 4.3 and 5.0 wt-% SMA or EEA-GMA compatibilizer, with or without the addition of 0.7% chain extender.

3. Methods

3.1. Screening experiments

All the material formulations studied in the screening experiments are shown in Table 1. Between 57.5% and 59.5% Recycled PC from CreaSolv® Process (PC REF1 Creasolv1) was compounded with 37.5%–39.7% virgin ABS (S1–S6 in Table 1) and 4.3%–5% compatibilizers. Three different compatibilizers A, B and C were studied. For some samples (PC REF2 and S4–S6), 0.7% epoxy functional chain extender was added. Samples S7 to S10 contained 37.5%–39.5% ABS from CreaSolv®. Samples S11 to S13 contained 17.5% ABS from CreaSolv® and 20% virgin ABS.

Polymers were mixed using DSM Xplore micro-compounder, with mixing volume of 15 cm^3, and barrel temperature of +230 °C with mixing time 3–4 min.

ThermoHaake Minijet pneumatic ram injection moulding machine was used in the preparation of 80 × 4 × 10 mm^3 Charpy test samples. Injection barrel temperatures was set to +240 °C and the mould temperature was in the range +70 °C to +80 °C. The samples were notched according to ISO 179 1eA.

3.2. Upscaling experiments

The three selected formulations S2, S3 and S5 from the screening experiments showing significantly improved notched impact strength were upscaled. Polycarbonate samples from CreaSolv® Process, from a different batch than in the screening trials and recovered from different batches of recyclates from small domestic appliances were also tested for comparison (PC Creasolv2 and PC Creasolv3). Additive package of stabilizers was used in each case.

The upscaled samples are hereby designated by postfix, S2_u, S3_u and S5_u, respectively. These upscaled samples also contain virgin ABS. Moreover, a new reference sample without compatibilization was prepared (ref_u) using the PC Creasolv2 (Table 1). Upscaled samples were generated using Thermo Prism co-rotating twin screw compounder (D16mm, L/D 25), melt temperature +230 °C, extruder speed 300 rpm) was used for compounding. Engel 60-ton injection moulding machine was used to produce tensile test and impact test samples.

3.3. Dynamical mechanical analysis (DMA)

Approximately 9.00 × 3 × 4 mm^3 samples were cut from injection moulded slabs. Mettler DMA SDTA 861e in tensile mode was used. Tension was applied in the direction of melt flow orientation. 10 Hz test frequency was used, and temperature range from 0 °C to +220 °C was investigated.

3.4. Scanning electron microscopy (SEM)

Fractured surface of the injection moulded Charpy impact tested samples was imaged using JEOL JSM 6360-LV SEM and with few nm thick sputtered Au surface coating (Bal-tec SCD 050, Balzers, Switzerland).

3.5. Notched Charpy impact strength

Edgewise Charpy impact strength of the notched samples in room temperature was determined according to ISO-179 standard. Ceast Resil 5.5 Impact Strength Machine (CEAST S.p.a., Torino, Italy) was applied. For the initial screening of the compatibilizers and PC Creasolv1 samples, impact testing was made for minimum of three replicate samples

Table 1

Screening test series for r-PC/ABS 60/40 blends. Composition of and Impact strength of the laboratory scale compounded and IM samples (N = 3).

	r-PC CreaSolv®	virgin ABS	r-ABS CreaSolv®	Comp A	Comp B	Comp C	Chain extender	Charpy Impact Notched @ RT
	%	%	%	%	%	%	%	kJ/m^2
PC REF1 (Creasolv1)	100							6.2
PC REF2 (Creasolv1)	99.3						0.7	6.1
ABS REF*(Creasolv)			100					6.2
ABS EX58F		100						28*
S1	57.5	37.5		5				10.3
S2	57.5	37.5			5			23.9
S3	57.5	37.5				5		13.8
S4	57.5	37.5		4.3			0.7	7.4
S5	57.5	37.5			4.3		0.7	15.7
S6	59.65	39.65					0.7	10.1
S7	57.5		37.5	5				8.0
S8	57.5		37.5		5			4.6
S9	57.5		37.5			5		12.8
S10	59.65		39.65				0.7	8.0
S11	57.5	20.0	17.5		5			13.3
S12	57.5	20.0	17.5			5		14.6
S13	57.5	20.0	17.5				0.7	10.8

* Injection moulded using 60-ton IM machine.

generated using micro-compounder. The test specimens were kept in standard conditions (23 °C, 50% relative humidity) for at least five days before testing. For the upscaled material, a minimum of six replicate samples generated using a larger 60-ton injection moulding machine were measured.

3.6. Gas chromatography (GC-ECD)

Flame retardants were determined by gas chromatography (GC) combined with electron capture detection (ECD), which combines high sensitivity to halogenated compounds (comparable to GC-MS) and high stability to co-extracted oligomers that may affect the performance of GC-MS systems. Granules of the produced recyclate were extracted by dissolution in tetrahydrofuran (p.a., Merck, Kenilworth, NJ, USA) and precipitation of the polymers in ethanol (p.a., Merck). The filtered extracts were analysed by gas chromatography coupled to an electron capture detector (GC-2010, Shimadzu, Kyoto, Japan). Samples were injected at +270 °C in split mode and separated on a RTX-5 (15 m × 0.25 mm x 0.1 m, Restek) using following oven program: +120 °C, 2 min, 20 K/min to +320 °C (10 min). Measurements were calibrated using certified standards of hexa-through deca-BDEs, HBCDD, TBBPA, and BTBPE from Wellington Laboratories Inc. (Guelph, Ontario, Canada).

3.7. Gel permeation chromatography (GPC)

A solution with the concentration of 5000 μg/g in THF was prepared from each sample to be tested using about 50 mg of dry material. The samples were then kept at rest for 12 h. If this solution was not completely dissolved, it was tempered in a heating oven for 2 h, which should completely dissolve the polymer. Before each measurement, the solution was filtered through a 0.22 μm PTFE splash filter. Distilled THF was used as the chromatography mobile phase. A 600 mm long column with a diameter of 8.0 mm and a particle size of 5 μm (PSS SDV Linear M, 600 mm, 5 μm) served as stationary phase. The measurement took place at a flow rate of 1 ml/min and at a temperature of 40 °C. Polystyrene dissolved in THF was used as the calibration standard.

3.8. X-ray fluorescence (XRF)

Total concentrations of bromine, chlorine and phosphorous were determined by energy dispersive XRF (SPECTRO XEPOS) using the Turboquant method that corrects matrix effects. Samples were homogenized by pulverization and analysed in triplicate.

4. Results and discussions

4.1. Screening of compatibilizers

An evaluation of screened compatibilizers was done by based on the notched impact strength and retention of elastic modulus of the blend samples in elevated temperatures near glass transition of ABS. These two properties were prioritized, as according to industrial manufactures (EU-Nontox project, 2020) these are the two most relevant mechanical parameters in recycled PC/ABS in most technical applications, and particularly the impact strength often being deteriorated in recycled materials.

Epoxy chain extender increases the melt viscosity of both the recycled PC and the PC/ABS blends, as evidenced by the large increase of the mixing screw torque in the micro-compounding (data not presented). This increase in viscosity was later validated by MFI measurements of the upscaled formulations. This implies that the PC is reactive with the epoxy groups and therefore the chain extender increases the molecular weight of recycled PC significantly. Whether the chain extension increases the linear chain length or happens by branching remains unclear due to the unknown origin, feedstock heterogeneity, aging history of the PC sample. However, in the case of chain extended recycled PC the increased melt viscosity did not have the common connection to the improved notched impact strength.

Comparing to the neat, recycled PC and recycled ABS polymers, even blend samples without compatibilizers, namely S6, with virgin ABS, and S10, with recycled ABS both had higher notched impact strength. This implies that blending PC and ABS is a viable approach in upgrading the otherwise compromised impact properties of recycled PC.

The data in Table 1 shows that the compatibilizers have very distinct effects on the notched impact strength of the r-PC/ABS (60/40) blends. Moreover, effectiveness of compatibilizers in improving the impact properties depends on the type of ABS used, for example the virgin ABS or the recycled ABS material from CreaSolv® show their best behavior with different compatibilizers. The origin of the varying impact properties between the samples are not clearly deducible from the SEM micrographs of the fractured surfaces (Fig. 2). However, DMA analyses (Fig. 1) show differences in the elastic moduli, which can be linked to the rubber content and the elasticity of the rubber phase. For example, S3 with elastic compatibilizer C (EA-GMA) has approximately 20% lower modulus over the entire studied temperature range. S4 with compatibilizer A (SMA-PBI) and the chain extender has significantly higher modulus compared to the other samples, plateauing at temperature range from +40 °C to +60 °C. This effect, however, is not manifested in the glass transition temperature range of neither ABS nor PC, located at in the range of +105 °C and at +145 °C, respectively.

Compatibilizer B (SMA) is superior for the PC/ABS 60/40 blends containing the virgin ABS, providing four-fold notched impact strength compared to the recycled PC and ABS recyclates from CreaSolv®. Whereas, in contrast, the elastic compatibilizer C provided the highest impact strength for the sample containing ABS from CreaSolv®. Clearly, the properties of the ABS polymer have a major influence on the blend impact properties. This effect is depending not only on the degradation of the rubber phase in the recycled ABS [6], but also the mixing, homogeneity, and phase stability of the blend, all factors which are facilitated by appropriate melt viscosity ratio between the dispersed ABS and continuous PC phases. The blends S2 and S5 having the Compatibilizer B showed increased in the glass transition temperature of the PC at +150 °C and suppression of the tan(δ) peak, which implies that the SMA changes the bulk properties of the recycled PC, but less clearly affecting the properties the of ABS (T_g at around +105 °C) (Fig. 1).

Main outcome of the small-scale screening experiments was that only the samples with the high virgin ABS content (37.5%) and with consistently high impact strength (S2, S3 and S6) were upscaled, as those were likely to reach the targeted 25 kJ/m^2 in the upscaled batches.

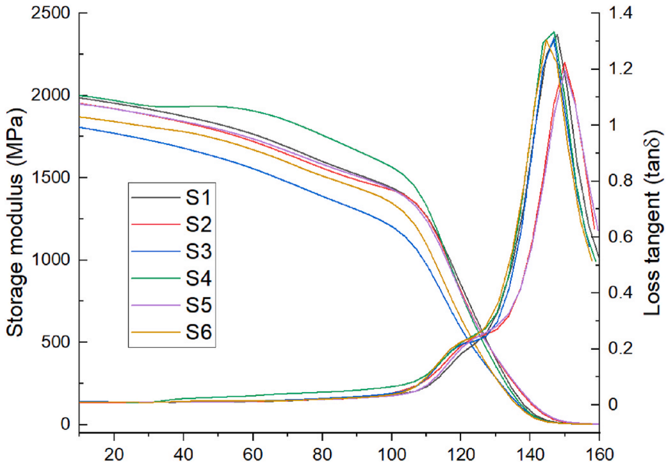

Fig. 1. DMA screening test series for r-PC/ABS 60/40 blends. Storage modulus and tan(δ) recorded in tension mode at 10 Hz test frequency.

4.2. Molecular weight distribution of r-PC

Table 2 summarizes the GPC data of the three Creasolv® PC batches. In all cases the M_w was in the 50000 g/mol range and polydispersity index between 2 and 3, which are typical numbers for industrial polycarbonates. Clearly, the first sample has higher polydispersity (2.7) and higher M_w than the two other batches. The presence of a higher molecular weight fraction in the batch Creasolv_1 is also manifested in the low MFR (3.8 g/10 min) measured at +240 °C temperature. However, thermal stability of the Creasolv_1 sample was clearly compromised in higher temperatures, evidenced by the large irreversible increase of the MFR already at +260 °C. Polydispersities of the two latter PC batches were low, implying that they were indeed of highly uniform origin, possibly from injection moulding grade plastics having very similar molecular weight distributions. The second batch has the lowest M_w and the highest MFR, which might be due to partial degradation. Polydispersity index was not significantly changed in the Creasolv® process.

4.3. Removal of halogens, phosphorous and FRs from the recycled PC

Fig. 2Abelow shows the total concentration of elemental bromine, chloride and phosphorous from the three studied WEEE fractions before and after the CreaSolv® Process. Halogen concentration in the input feedstock material was high, particularly in the Creasolv1 sample which had >12000 ppm bromine from FRs. In all cases the removal of halogens by the CreaSolv® Process is very efficient; residual level of all three elements drops well below 500 ppm. However, according to XRF, small amounts of bromine were detectable in the sample after the decontamination process. As described in Ref. [10] removal of halogenated additives in CreaSolv® Processes occurs stepwise and thus, residual bromine may be further reduced if required, however at higher process cost.

GC-ECD analyses (Fig. 2B) of the input samples and products reveal 4,4′-(Propane-2,2-diyl)bis(2,6-dibromophenol) (TBBPA), 1,2-bis (tribromophenoxy)-ethane (TBPE) and 1,1′-Oxybis(2,3,4,5,6-pentabromobenzene) (DecaBDE) levels in the feedstock and significantly reduced levels in the products. In agreement with earlier studies [10] removal by 99% and higher is visible. In case of PC Creasolv1, a even higher degree of removal is calculated, which is due to the effect, that larger amounts ABS and HIPS with brominated flame retardants have been present in the feedstock sample, as no sensor based pre-sorting has been applied. All cases, however, show practically complete removal down to <10 ppm level of the three targeted BFRs. ECD method was also calibrated for hexa-through nona-brominated PBDE congeners, which were not detected at levels higher than 10 ppm in feedstock or products. In conclusion, for the sum of all PBDE levels below 500 ppm, as requested by the lately revised POP directive, are safely achieved.

Table 2
GPC data before and after Creasolv® process and MFR of the studied r-PC samples.

	M_n (g/mol)	M_w (g/mol)	Polydispersity index	MFR [g/10 min] (240 °C, 5 kg)/(260 °C, 2.16 kg)
PC Creasolv1 Input	20700	54000	2.61	
PC Creasolv1 recyclate	18700	50600	2.71	3.8/9.8
PC Creasolv2 Input	20700	37700	1.82	
PC Creasolv2 recyclate	20600	41300	2.01	15.3/19.8
PC Creasolv3 Input	19100	40200	2.12	
PC Creasolv3 recyclate	22500	49500	2.20	6.5/6.7

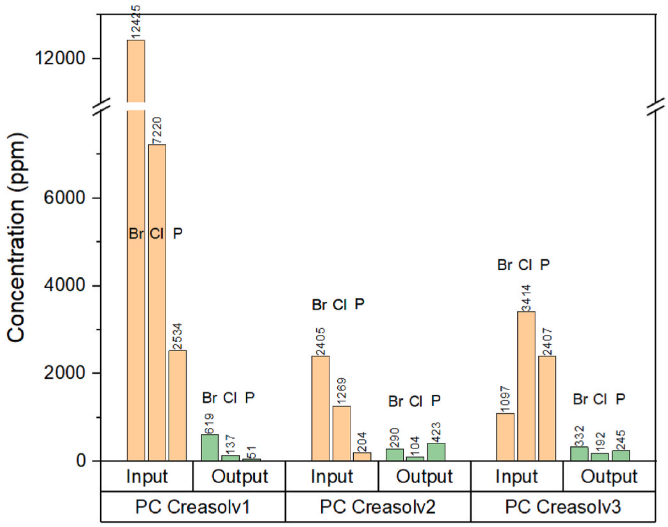

Fig. 2A. XRF total bromine, chlorine and phosphorous concentrations in the three PC batches before and after the CreaSolv® de-contamination process.

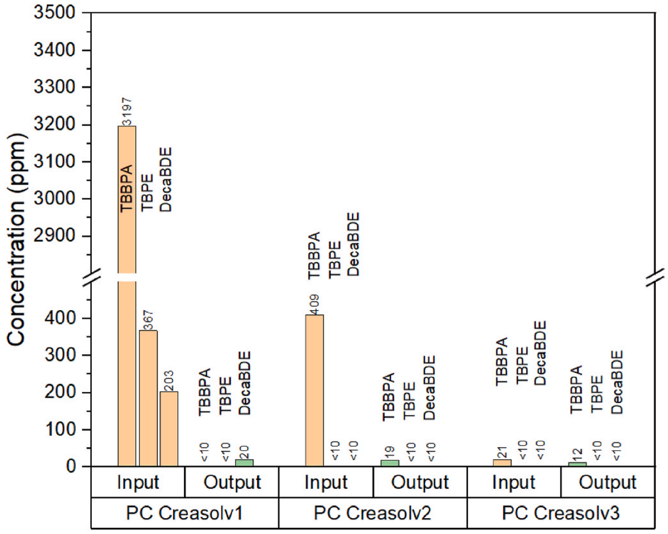

Fig. 2B. XRF total bromine, chlorine, and phosphorous concentrations in the three PC batches before and after the CreaSolv® de-contamination process.

It should be noted that the GC-ECD method used measures only volatile and semi volatile compounds. Bromine and chlorine levels derived from XRF suggest the presence of other brominated compounds in addition to the detected BFRs. These may come from oligomeric BFRs, traces of printed circuit boards that contain reactively bound and thus non-extractable BFR, or degradation product of BFRs like brominated phenols, which were not targeted in the GC analysis.

Chlorine levels in SDA, ICT, FDP and XRT materials are usually not attributable to chlorinated flame retardants. Therefore, it is most likely that chlorine levels origin from PVC and/or PVDC coatings in the feedstock.

4.4. Morphology of the r-PC/ABS blends

Fig. 3 shows the fractured surfaces of the screening test r-PC/ABS samples and the reference r-PC sample. The fracture surface was generated in the notched Charpy impact test at room temperature.

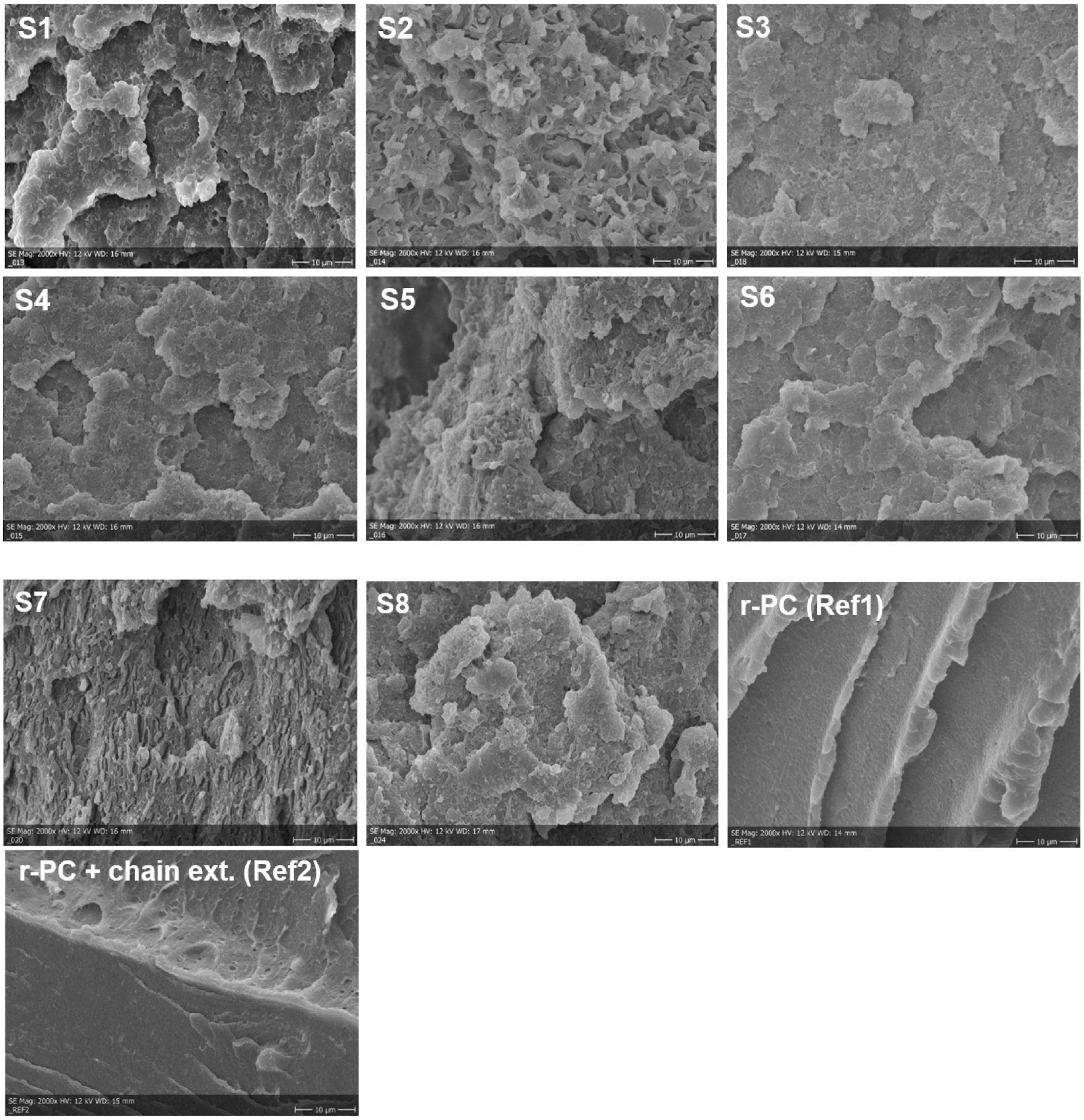

Fig. 3. SEM micrographs of fractured surfaces screening test samples after Notched Charpy test at room temperature.

Overall, according to the SEM and the optical micrographs (Fig. 3) the PC/ABS blends S1–S6 containing the virgin ABS and different compatibilizers look similarly homogeneous. The optical micrographs of Fig. 4 show the fine black particle originating from the recycled PC. These are black pigment particles and fine dust particles from handling. Both these contaminations are laborious and expensive to remove from the solvent or by melt filtration. Practically this is not even necessary, however, as these small particles are expected to have only a minor effect on the mechanical properties of the blend.

The impact test sample S2 with SMA compatibilizer B with the highest notched impact strength (24 kJ/m^2) shows notable plastic deformation on their fractured surfaces, and some detachment of the PC and ABS phases. In contrast, the corresponding sample S5 with the SMA compatibilizer B and with added chain extender had less plastic deformation, lower impact strength (15.7 kJ/m2) than the S2, and, in fact, more similarly cohesive fractured surface and impact as compared to the rest of the samples. This implies that the addition of the chain extender changes the cohesiveness of the blend significantly, the effect stemming from several factors, for example, by increasing the molecular weight of the r-PC and continuous phase melt viscosity, thus improved mixing conditions, or by acting synergistically with SMA and thus improving the compatibility of PC and ABS phases.

Chain extender was present also in the S4 – S6 and the r-PC reference (ref2) samples, and the comparing to the corresponding samples without the chain extender, it could be deduced that the cohesion of the fractured surface in those samples was increased. The higher impact strength of sample S1 over the chain extended S4 and the sample S2 over the chain extended S5 could hypothetically be linked the a priori existing micropores seen in the SEM micrograph of the blend samples. Indeed, microcellular structure has been earlier shown to improve fracture toughness of PC/ABS [14], and shown to induce a transition from brittle to ductile behavior in PC [15]. Similarly, low concentrations of nano powders or micron-sized fillers such hollow glass microspheres [20] (and references therein) with and without strong adhesion to the matrix (PC) may improve the impact strength of PC/ABS blends. As some of those fillers act basically as microscopic voids or cavities, the explaining factor is the different fracture mechanism leading to crazing between the filler particles, and thus wider distribution of the impact

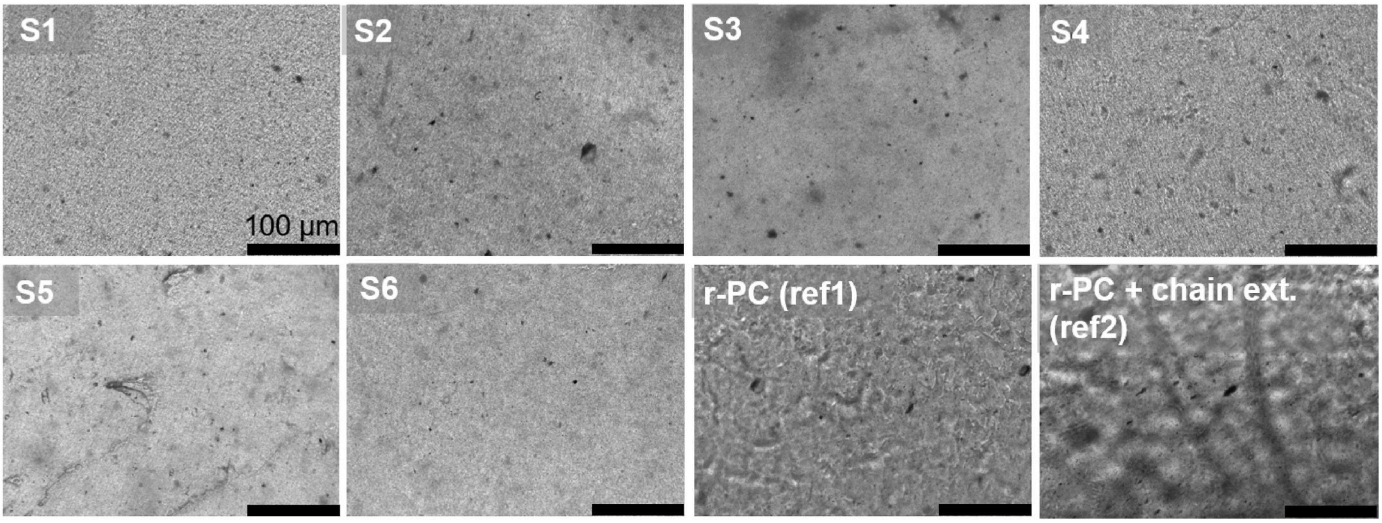

Fig. 4. Transmission optical micrographs of screening test samples molten on microscope glass slides. Black dots are traces of colour pigments from the r-PC, and which cannot be easily removed by either solvent treatment or by melt filtration during compounding. Scale bar 100 μm.

energy in micron-scale. Noteworthy, it is well known that epoxy chain extenders can compensate for some of the degrading effects of residual moisture and volatiles during compounding, which might hypothetically also contribute to the improved mechanical properties.

Fig. 5 shows the fractured surfaces of the upscaled r-PC/ABS samples. ABS phase is shown as droplets and partly co-continuous ribbons having thickness of few hundred nanometers, which can be considered a landmark of a good polymer dispersion. The reference sample (Ref_u) without any compatibilizer has similar phase morphology as the compatibilized samples - dispersed phase “droplet size” or the short dimension or the ribbon is in the sub-micron scale in all cases. However, fracture surface of S2_u_C3 appears less cohesive, which interestingly correlates with the high impact strength of that sample.

4.5. *Properties of the upscaled r-PC/ABS blends*

DMA thermograms for the upscaled samples are presented in Fig. 6. The quantification of T_g from DMA, results of the tensile testing, and melt flow index (MFI) are summarized in Table 3 below.

Storage moduli from DMA of the upscaled compatibilized blends is in general higher than the moduli of the corresponding screening samples. This can be explained by more optimal mixing conditions in bench scale twin screw compounding extruder versus the micro-compounder.

The elastic moduli derived from tensile test and the storage moduli from DMA data are well in accordance (Table 3). Noteworthy, DMA data from the screening test shown in Fig. 1, and the bench scale test (Fig. 6) show consistent order between those sample blends generated with the same recipes (S2, S3 and S5), but utilizing two very different r-PC batches (C1 and C2).

DMA tan (δ) curves indicate that glass transition (T_g) temperature of both ABS and PC, at +105 °C and +147 °C, respectively. The presence of two T_g temperatures indicated immiscible (two phase) polymer blend, as expected. In the compatibilized blends the detected $T_{g,ABS}$ and $T_{g,PC}$ both were shifted to slightly higher temperature. This implies reduced chain

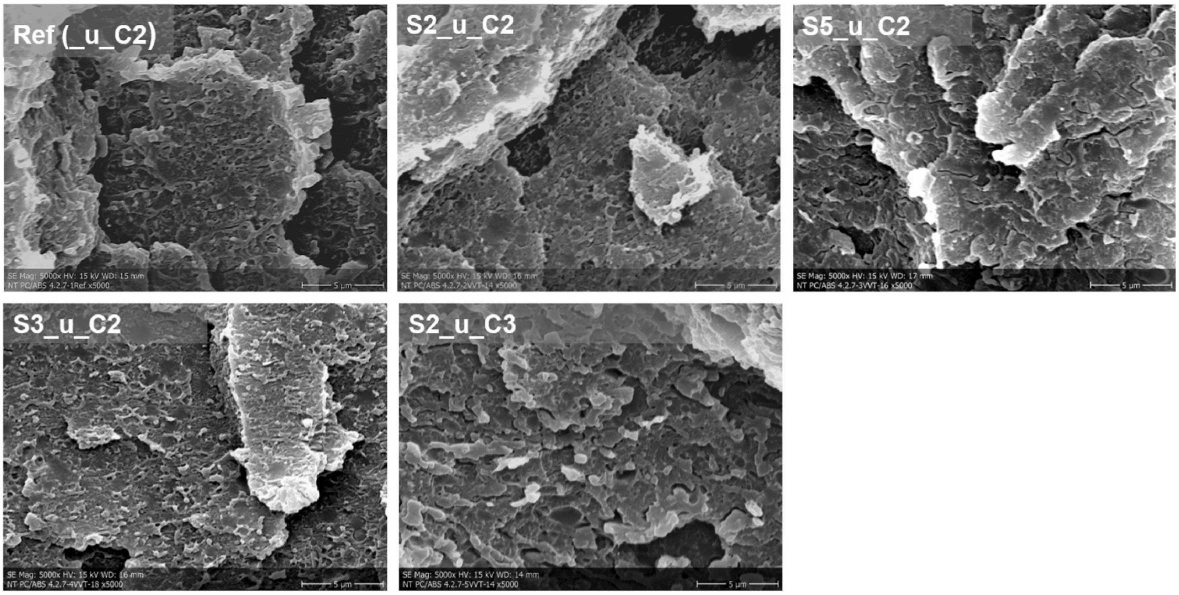

Fig. 5. SEM micrographs of the fractured surfaces of the upscaled r-PC/ABS blend samples. Reference sample is without compatibilizer. Suffix _u denotes the sample upscaled sample generated by 16 mm 25D twin screw extruder, based on the original composition from the screening experiments with small scale batch mixer providing longer residence time but less intensive mixing.

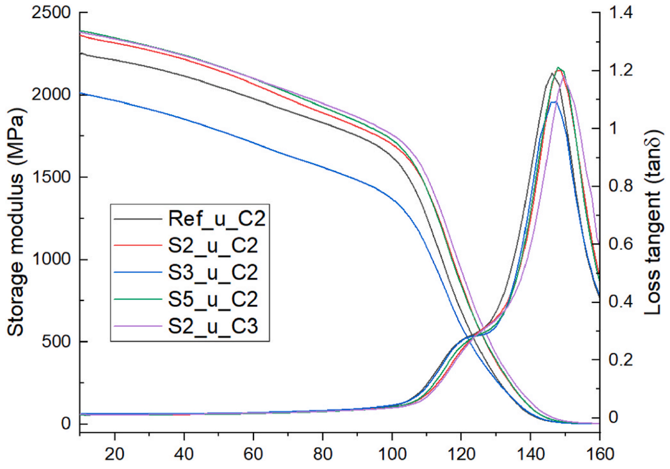

Fig. 6. DMA test series for r-PC/ABS 60/40 upscaled blends. Storage modulus and tanδ recorded in tension mode at 10 Hz test frequency.

mobility in both phases, and the result of chain interactions with the compatibilizer and with the chain extender. The mechanisms of those interactions are discussed in more depth the following chapter dealing with melt rheological properties. The blend with higher molecular weight PC (PC_Creasolv3) component has the highest $T_{g,ABS}$ and $T_{g,PC}$ or the studied samples. This shows that the higher molecular weight PC_Creasolv3 provides the best thermomechanical stability of the blend.

However, the effect of the compatibilizer is more ambiguous. Firstly, glass transition temperatures of the PC and ABS both increase slightly by the effect of compatibilizer B, as compared to the non-compatibilized reference (ref_u_C2), the sample with (rubbery) compatibilizer C (S3_u_C2), and compared to all of the screening test samples (S2, S3 and S5). This implies that storage modulus increases due to the partial miscibility and reactivity of the compatibilizer B to both PC and ABS, decreasing the polymer mobility in the bulk of both phases, or it could be stemming partly from the improved interfacial adhesion and better mixing and differing blend morphologies.

4.6. Rheology and flow behaviour

Flow characteristics of the upscaled samples, such as complex viscosity derived from RDA frequency sweeps and MFI are shown in Fig. 7 and the MFI data in Table 2. The MFI results and the complex viscosity at low frequency are in good agreement. The non-compatibilized blend (Ref_u_C2) has the lowest viscosity of all the studied sample. Addition of compatibilizers consistently increases viscosity of the blend. It is noteworthy that the sample with the PC Creasolv3 content (S2_u_C3) with intermediate complex viscosity and loss tangent has the best notched impact strength, highest glass transition temperature, high DMA storage modulus (Fig. 6) and the best tensile properties (Table 3).

The tan (δ) curves in Fig. 6 portray well the networking of polymer

Table 3

DMA and tensile mechanical properties of the upscaled PC/ABS blends summarized: tensile elastic moduli and tensile strength at room temperature, glass transition temperature of PC and ABS (10 Hz), Charpy notched impact strength measured at room temperature, and MFI of the upscaled samples.

Basis recipe from μ-compounder[a], ref. Table 1	Upscaled recipe PC/ABS (60/40%) CreaSolv® batch/ Compatibilizer (B or C, E[f])	Charpy Notched @RT/(kJ/m[b])	E-modulus/ tensile strength at break @RT (MPa)		Glass temp. T_g ABS[d]/ PC[e] (CELS)		MFI +260 °C/2.16 kg (g/10 min)
Ref_u_C2	Creasolv2-(Add[c]) none	14.4	2378	51.4	104	146	12.5
S2_u_C2	Creasolv2- Comp B	22.5	2427	52.9	105	148	7.0
S5_u_C2	Creasolv2- Comp B-E[f]	23.4	2423	55.6	105	148	1.6
S3_u_C2	Creasolv2 - Comp C	21.9	2103	46.2	103	147	3.8
S2_u_C3	Creasolv3- Comp B	36.2	2433	53.5	107	150	3.9

[a] DSM Xplore μ-compounder.
[b] with Thermo Electron Prism 16 mm TSE, +230 °C, extruder speed 300 rpm.
[c] Add = stabilization package added to all samples.
[d] from onset of E′.
[e] from tanδ peak.
[f] epoxy chain extender.

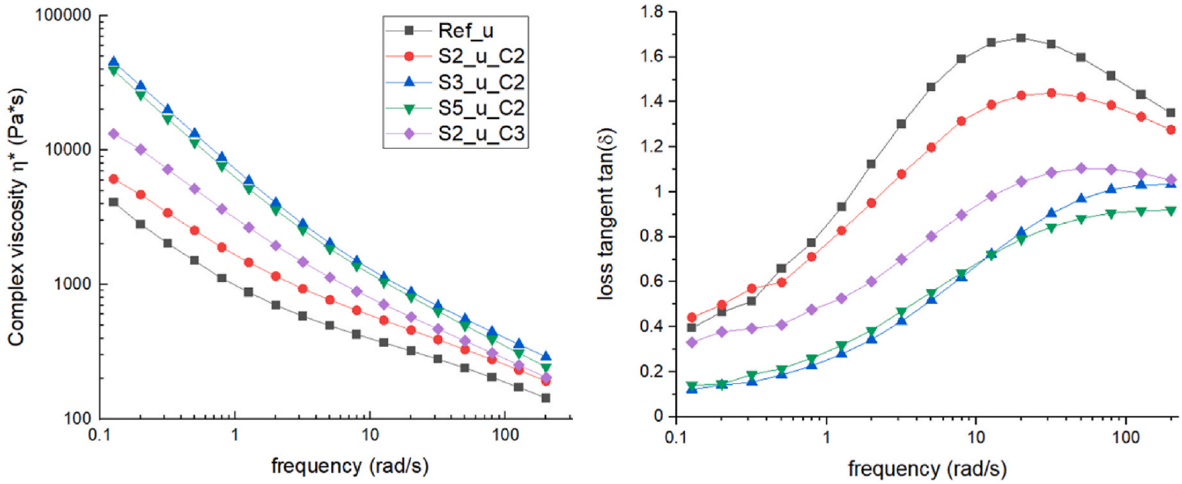

Fig. 7. Rheological Dynamic analysis of upscaled samples: Complex viscosity η* and loss tangent Tan (δ)at +260°C.

chains in the molten phase, which is deducible from the data in the low frequency range. Networking or the interaction of polymer chains in the melt is increased by factors such as longer polymer chains and side branches. The tan (δ) = G’‘/G′ is the ratio of the loss and elastic moduli, and thus represents the viscoelastic damping of the melts. Non-crosslinked linear short chains depart from a G” ≫ G and networking in a polymer melt is manifested by a G’ ≥ G″ or when tan (δ) ≤1 [23]. Therefore, distinct levels on tan (δ) values at certain low frequency portray the increased interactions at the blend microstructural level because of the compatibilization. It could also be hypothesized that the self-reaction of epoxy groups of glycidyl methacrylate functional groups could play a significant role in the viscosity increase from the molecular weight perspective, or alternatively, from enhanced interactions from the newly formed structures. Lower tan (δ) relative to the higher G’ and lower G” can be the result of the increased polymer chain length and/or the development of short side branches [27]. Additional hypothetical explanations to the observed rheological behaviour could be an enhanced compatibility with the polyether bonds emerging from the self-reaction of epoxy groups, or covalent interaction between the epoxy groups and degradation species of the polycarbonate from the thermo-oxidation such as aldehydes end-groups [19]. The chain extension of PC is broadly discussed in patent and technical literature; however, it is important to point out that a careful explanation cannot be found in scientific literature. Therefore, it cannot be stated from this work the clear nature of the interactions that lead to the interesting enhancement of properties presented. This fact constitutes a gap to be studied in detail in later studies.

Based on these premises, all blends including the starting sample (Ref_u) show a high degree of networking that could emerge from undetermined covalent or non-covalent interactions. Furthermore, it is possible to hypothesize that the actual microstructures of S3_u_C2 and S5_u_C2 may have a configuration comprising short branches, some degree of chain extension or alternatively being the result of secondary, non-covalent, interactions resulting in a more elastic response. On the other hand, S2_u_C3 (the optimal configuration) may comprise longer branches than the reference (Ref_u) or alternatively being the result of secondary, non-covalent, interactions resulting in a more viscous response.

4.7. *Notched impact strength*

Clearly, the effect of the compatibilizer on the impact strength of the blend depends on both the properties of the ABS (Table 3) and the native properties of the recycled PC matrix. For example, SMA (compatibilizer B) was remarkably effective in increasing the notched impact strength of the blend of the PC-Creasolv1 sample with the virgin ABS polymer (S2) in both screening test, and particularly in the upscaled blends. On the other side, when the recycled ABS from CreaSolv® was used in the blend, then only the elastic terpolymer (compatibilizer C) provided good impact properties. In contrast, compatibilizer B (SMA) had a negative effect on the notched impact strength of recycled PC blended with the recycled ABS (S8). According to SEM micrographs this contradiction is not due to any significant difference in the dispersion or blend morphology between the samples. The two factors explaining the results are the elastic properties of the ABS in the different cases and interfacial adhesion. The brittle fracture mechanism sometimes observed in samples containing recycled ABS is indeed characteristic to the thermo-oxidatively aged material [3]. Our results also confirm that a severe loss of impact strength of the highly degraded ABS can be only compensated by adding virgin ABS and/or by adding rubber, or rubbery compatibilizer.

5. Conclusions

Mechanically strong PC/ABS blend were prepared from PC recyclates originating from mixed WEEE plastics streams from dismantled small household appliances. The best r-PC samples had undergone both optical sorting and de-contamination by CreaSolv® solvent-precipitation process. CreaSolv® process has been recently adapted for the recovery of PC and ABS plastics from complex mixtures of polymers, which are often heavily contaminated by thousands of ppms of bromine and phosphorous from flame retardants. According to GC-EDC analysis of their corresponding thermal degradation products the three targeted brominated flame retardants (TBBPA, TBPE and DecaBDE) were completely removed by CreaSolv®. XRF shows <500 ppm levels of bromine, chlorine and phosphorous remaining in the sample after the process, which is considered uncritical.

Addition of virgin ABS polymer and a suitable compatibilizer enhance the properties of the recycled PC/ABS (60/40%) blends towards virgin-like, allowing easily >57% recycled PC content, or in favourable cases even much higher (75%) recycled PC and ABS polymer content.

Small-scale screening tests with a small laboratory scale micro-compounder showed that the severe notch sensitivity of the r-PC was significantly improved by the addition of any ABS, virgin and/or recycled, and technically attractive mechanical properties of PC could be recovered in the reactively compatibilized r-PC + virgin ABS (60/40) blends. Particularly the combination of virgin ABS (37%) and a 5% styrene-maleic anhydride (SMA) reactive compatibilizer provided four-fold improved Charpy notched impact strength and as compared to the initial properties of neat r-PC or neat r-ABS.

Further improvements in the mechanical properties of the blends were achieved in upscaling experiments, were performed in up-scalable continuous co-rotating 16 mm twin screw extruder. The SMA and E/EA-GMA compatibilizers (4–5%) significantly increased the melt viscosity of the blends. More than two-fold improved notched impact strength was achieved compared to the thermally stabilized blend without compatibilizer. Addition of 0.7% epoxy chain extender increased the viscosity of the compatibilized r-PC/ABS blends further. Combination of 4.3% SMA and 0.7% epoxy chain extender resulted in even higher elastic modulus of PC/ABS (60/40) blends and better retention on modulus at the glass transition range of ABS near +105 °C. However, increased stiffness of the blend by the chain extender was linked to somewhat lower impact strength.

Compatibilized blends had intermediate melt viscosities useful for various injection moulding and extrusion processes, as evidenced by the melt flow rate measurement and RDA, while maintaining the mechanical stiffness and retention of high modulus of the PC/ABS near glass temperature transition of ABS (DMA and tensile test). The results of the micro-compounding screening test for finding the optimal compatibilization are aligned with the results from up-scaling using bench scale processing. This is also providing good perspectives for further upscaling to higher outputs in larger commercial scale compounding extruders.

To summarize, full development path in the r-PC/ABS blend formulation from screening to upscaling experiments was described. The study highlighted the practical characteristics of formulating good PC/ABS blends from heavily contaminated and mixed recycled WEEE feedstocks with brominated and phosphorous flame retardants, which -show markedly variable initial properties between production batches, due to variation in input materials and changes in the recycling processes.

CRediT authorship contribution statement

Jani Pelto: Conceptualization, Writing – original draft, Writing – review & editing, Visualization, Formal analysis, Investigation. **Carlos Barreto:** Writing – review & editing, Project administration, Methodology, Validation. **Hany Anwar:** Data curation, Investigation, Formal analysis. **Laura Strobl:** Data curation, Investigation, Formal analysis. **Martin Schlummer:** Methodology, Writing – review & editing, Resources, Funding acquisition, Investigation, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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