



## Research article

# Compatibilization of HIPS/ABS blends from WEEE by using Styrene-Butadiene Rubber (SBR)

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## ARTICLE INFO

## Article history:

Received 29 September 2017

Received in revised form

6 March 2018

Accepted 29 March 2018

## Keywords:

Blend compatibilization

Plastic WEEE

Recycling

HIPS

ABS

SBR

## ABSTRACT

The aim of this work is to develop compatibilization strategies for High Impact Polystyrene (HIPS)/Acrylonitrile-Butadiene-Styrene (ABS) blends from WEEE in order to add value to these recycled plastics by improving their mechanical performance. Results from a screening study of HIPS/ABS blends compatibilization by the addition of Styrene-Butadiene Rubber (SBR) are presented. Two different weight proportion of HIPS/ABS physical blends were analyzed, 80/20 and 20/80, with three different concentration of SBR: 2, 10 and 20 wt%. Compatibilization efficiency was analyzed from an accurate thermal and mechanical analysis, by comparing each physical blend and corresponding compatibilized blends with SBR. Results were discussed relating glass transition changes with mechanical performance, both aspects were interpreted in terms of blend morphology. Phase and fillers dispersion and distribution as well as SBR amount and its interaction with each phase were accurately analyzed.

Compatibilization of HIPS/ABS blends from WEEE with the addition of SBR is effective in blends with HIPS as main component. With the addition of 2 wt% of SBR, strength and toughness have notably increased respect to the corresponding physical blend, 244% and 186% respectively. From this screening study is possible to infer that SBR is a sustainable and efficient compatibilizer of HIPS rich blends allowing to obtain a final blend that can be used as a replacement material of separated resins from WEEE.

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## 1. Introduction

Waste from Electrical and Electronic Equipment (WEEE) is a waste stream which grows continuous and exponentially fast, mainly because the increase of high technology and short useful life products consumption (European Union, 2012; Namias, 2013). WEEE management is complex as this stream includes several kinds of materials. It contains both, elements of high intrinsic value that can be recovered with economic benefits (precious metals, glass, plastics, etc) and hazardous substances like mercury, bromine, heavy metals, among others (Baldé et al., 2015). Within WEEE, plastics are not considered the most relevant material because they are not highly dangerous and their cost are relatively low against precious metals like gold. However, they occupy lot of space in final disposal because of their low density, shape, low

compressibility and resilience. Around 18 wt% of WEEE are plastics, generally thermoplastic then they can be easily recycled by reprocessing (Baxter et al., 2014, 2016; Chagnes et al., 2016). In addition, statistical reports predict that worldwide amount of WEEE generated in 2016 was about 46 million tons (Mt). It means that 8.5 Mt of plastic WEEE were produced in that year expecting to reach up 9.5 Mt in 2018 (Baldé et al., 2015; Magalini et al., 2015; Zeng et al., 2017).

In order to diminish the disposal of WEEE as hazardous material, different kind of regulations are being implemented in several parts of the world (Stevens et al., 2013). They promote separation and special disposal for toxic and dangerous components of WEEE. With the rest, regulations mainly incentive reuse and recycling first to final disposal. In the European Union (EU) there are specific directives for WEEE management which involves responsibilities from the producer to final consumer. Their purpose is to prevent further increasing in WEEE, promote different types of recovery and enhance environmental treatment of all areas involved in WEEE generation (European Union, 2012; Ongondo et al., 2011). Also, directives regulate concentration ranges of bromine in plastic

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WEEE as well as, other hazardous materials in order to promote safe WEEE management in all steps, including recycling (European Union, 2011). Particularly in USA, IEEE Standard 1608 recommends to manufacturing industries of electrical and electronic devices housings to use at least 25 wt% of certified post-consumer material (IEEE Standard, 2006). This standard enhances the incoming of plastic WEEE to main manufacturer locations like China, Vietnam or Taiwan from the rest of the world, mainly third world countries (Namias, 2013). Usually, plastic WEEE are exported chopped and separated by type but, their sorting by type using automatic methods is very difficult as their composition is similar (Beigbeder et al., 2013; Campolina et al., 2017; Maris et al., 2015). In this way, manual sorting is the most popular method although it involves higher labor costs and unsafe and unhealthy labor conditions for workers (Ceballos et al., 2014). It is important to note that complete manual separation cannot be guaranteed since is typically made by color and source and, eventually separated resins could contain others plastics (Bernardeau et al., 2018). Consequently, the added value of recycled resins and recycler's profits decrease.

An alternative for diminishing the above problems and to increment added value of plastics from WEEE is avoid sorting by type and recycling them together by melt blending. However, it is well known that direct blending of two or more thermoplastic resins in appreciable proportions causes phase segregation, low interfacial adhesion and consequently mechanical properties deterioration. Then, an adequate compatibilization process is essential to increase phase adhesion, reduces the interfacial tension, stabilizes morphology by inhibiting droplet coalescence and consequently, improves mechanical properties (Davis et al., 2000; Elmendorp et al., 1991; Utracki, 1991; Wu, 1982). Main compatibilization methodologies involve a third component as a compatibilizer. In one of them, the compatibilizer is generated by a chemical reaction directly in the interphase during melt blending. This "in-situ compatibilization" is the most efficient because all the reactive generated acts as compatibilizer but it is not adequate for its use with recycled resins. The main reason proceeds from the possible variation in recycled resins composition and their additives that could affect chemical reaction efficiency. On the other hand, the most practical compatibilization methodology able for plastic recycling is the direct addition of a copolymer as compatibilizer during melt blending. This method involves the migration of the compatibilizer to the interphase. For this reason, compatibilizer molecules should contain similar segments to initial materials to better interact with them and then, improve load transfer and phase adhesion (Utracki, 2002). Please note that, despite it is less effective than in situ compatibilization, its efficiency is less affected by components composition and additives then it is not worker-dependent and friendly for them. In this sense, the challenge is to obtain materials with similar performance to recycled WEEE separated resins by blending them together with an adequate compatibilization strategy.

WEEE plastics are copolymers with complex morphologies which contain additives/mineral fillers like calcium and magnesium carbonate, silica, brominated substances, carbon black, among others. Then, they are composite materials which contain a very complex copolymer blend as matrix, multiple minerals as fillers and several additives (Arnold et al., 2009; Vazquez and Barbosa, 2016). The major fraction of plastic WEEE stream (71 wt%) is composed by ABS (Acrylonitrile-Butadiene-Styrene), HIPS (High Impact Poly-Styrene), and Polypropylene (PP), while Polycarbonate (PC), Polyamides (PA), Polymethylmethacrylate (PMMA), among others, represent the minor fraction (29 wt%). ABS and HIPS are two of the most common and abundant plastics in this waste stream, representing 29 wt% and 22 wt% of the total amount of plastics (Maris et al., 2015; Martinho et al., 2012). Their mechanical

properties are highly dependent of Butadiene (Bu) phase and also both, HIPS and ABS, are themselves mixtures of several components and their morphology highly depends on relative compositions, additives/fillers amount, and phase segregations (Hirayama and Saron, 2018; Bisio and Xanthos, 1995).

Considering that, HIPS and ABS are the major components of plastic WEEE and they are the most difficult to separate because of their physicochemical similarity, the selected system for this study includes blends of these plastic resins from WEEE. In literature, there are some works that studied HIPS/ABS blends compatibilization mainly on virgin resins. Peydro Raserio et al. (2015) considered SEBS (Styrene-Ethylene-Butylene-Styrene) to improve ductility of virgin HIPS/ABS blends for having similar polymeric segments to them. Their results showed an increment in elongation at break with tensile strength decrement. Also, Arnold et al. claims that in HIPS/ABS blends from virgin and WEEE plastic resins, properties suffer a deterioration respect to the corresponding base materials and consequently, final blend has poor added value (Arnold et al., 2010). However, as it was demonstrated in a previous work, plastic WEEE far differs from their correspondent virgin resins because of the fillers and additives presence (Vazquez and Barbosa, 2016). Taking into account that both, fillers and additives influence final blend properties and compatibilizer effect, it is necessary to find specific compatibilization methodologies for blends of HIPS/ABS from WEEE.

The aim of the present work is to develop compatibilization strategies for HIPS/ABS blends from WEEE in order to increase added value of these recycled plastics by improving their final mechanical performance. Styrene-Butadiene Rubber (SBR) was selected as compatibilizer for having similar molecular segments either to ABS or to HIPS, as well as for its low cost. In this sense, two different weight proportion of HIPS/ABS WEEE physical blends were selected, 80/20 and 20/80, and in order to perform a screening study three SBR concentration were used, one very low (2 wt%), one higher enough (20 wt%) and another one in the middle (10 wt%). The influence of SBR content for each relative HIPS/ABS WEEE proportion was analyzed. Results were discussed relating glass transition temperature changes with mechanical performance and, both were interpreted in terms of morphological aspects. Dispersion and distribution of polymeric phases and fillers as well as SBR interaction with each phase were also analyzed accurately.

## 2. Experimental

### 2.1. Materials

HIPS and ABS from e-scrap were used as initial materials of blends. They were kindly provided in powder form by Ecotécnica del Pilar S.R.L. Each plastic WEEE material sample used in this work were obtained by mixing 10 powder portions of 500 g from different places of a 25 kg commercial bag in order to have a representative sample of each initial plastic e-scrap. SBR ARPOL 1502 from Petrobras was used as compatibilizer of WEEE blends.

### 2.2. Blending

HIPS(80 wt%)/ABS(20 wt%) and HIPS(20 wt%)/ABS(80 wt%) physical blends from WEEE were prepared under nitrogen atmosphere, in a batch mixer (*Brabender Plastograph W50*) at 180 °C and 30 rpm for 10 min (Brennan et al., 2002; Utracki, 1991). From this point, HIPS and ABS mean HIPS WEEE and ABS WEEE. Each initial ABS and HIPS as well as compatibilized blends were processed in the same batch mixer under the same condition as physical one. In order to make a screening test, three different concentration of compatibilizer were chosen. In this way, 2, 10 and 20 wt% of SBR

were added to both physical blends. Table 1 summarizes the characteristics of all blends prepared.

### 2.3. Characterization

#### 2.3.1. Glass transition

Glass transition temperatures ( $T_g$ ) of all initial materials and blends prepared were determined by *Modulated Differential Scanning Calorimetry (MDSC)* in a Discovery DSC from TA Instruments (Gill et al., 1993). Initial scanning was performed to erase thermal history followed by a cooling step and a second heating. The oscillation amplitude was 1.25 °C, oscillation period and resolution were 60 s and 6.00, respectively. Heating and cooling rate were at 1 °C/min from 60 °C to 180 °C.

#### 2.3.2. Mechanical properties

Flexural tests of processed initial materials and all blends were performed at room temperature in the *Universal Testing Machine Instron 3369*. Specimens were cut from plates prepared by compression molding at 180 °C. Test conditions and specimen dimensions were determined according to *ASTM D790-03* standard for plastic. Eight specimens for each sample were measured. Modulus, ultimate strength, elongation at break and toughness were comparatively assessed from stress–strain curves.

#### 2.3.3. Blends morphology

Blends morphology analysis were performed by *Scanning Electron Microscopy (SEM)* in a LEO EVO 40 XVP electron microscope (operated at 10 kV) equipped with an *X-ray Energy Dispersive Spectrometry (EDS)* microanalyzer (Oxford, X-Max 50) to sense the local distribution of elements (Goldstein et al., 1992; Sawyer and Grubb, 1996). Samples were cryofractured by immersion in liquid nitrogen, mounted on bronze stubs and then, coated with a gold layer (~30 Å), using an argon plasma metallizer (sputter coater PELCO 91000).

## 3. Results and discussion

A complete characterization of initial materials was performed and described in previous works (Vazquez and Barbosa, 2016, 2017). It was concluded that ABS and HIPS contain calcite, dolomite, silica, carbon black, talc and titanium dioxide. This fact was assessed through a combined study including different analytical techniques like X-ray Diffraction, X-ray Fluorescence, Infrared Spectroscopy and Thermogravimetric Analysis. The total amount of fillers is 8.8 wt% for ABS and 4.6 wt% for HIPS. These results confirm that final blends mechanical performance will depend on the interaction between fillers and rubbery phase (Bu) present either in ABS or in HIPS. Also, in the same paper was proved that in each WEEE initial material bromine content satisfied European regulations (European Union, 2011; Hennebert and Filella, 2018).

**Table 1**

Names and concentration of all blends prepared.

Name	HIPS/ABS (wt%/wt%)	SBR (wt%)
<i>Physical Blends</i>		
H80/A20	80/20	0
H20/A80	20/80	0
<i>Compatibilized Blends</i>		
H80/A20-2SBR	78.4/19.6 (80/20)	2
H80/A20-10SBR	72/18 (80/20)	10
H80/A20-20SBR	64/16 (80/20)	20
H20/A80-2SBR	19.6/78.4 (20/80)	2
H20/A80-10SBR	18/72 (20/80)	10
H20/A80-20SBR	16/64 (20/80)	20

Regarding relative proportions of acrylonitrile (AN), Bu and styrene (St) in base copolymers, they are 35.6/30.8/33.6 for ABS and 6.30/63.5/30.2 for HIPS. St amount in HIPS is twice of ABS for similar amount of Bu while, ABS contain similar amounts of AN, St and Bu. A presence of 6 wt% of AN in HIPS evidenced that there is not neat separation of plastics by type. This characterization is important since mineral fillers/rubber phase/compatibilizer proportion determines final mechanical performance of blends.

In the present work, dispersion and distribution of mineral fillers in initial materials was assessed using scanning electronic microscopy with EDS X-ray analysis. Fig. 1 shows a SEM micrograph (5000x) of ABS cryofracture surface with the corresponding EDS X-ray spectra. Also, three elemental mapping which correspond to magnesium (Mg), calcium (Ca) and titanium (Ti) were included in this figure. From this data, the presence of C, Mg, Ca, O, Si and Ti, which proceeds from mineral fillers, is clear. Additionally, from the mapping images, an overall idea of relative homogeneous dispersion and distribution of mineral fillers in initial ABS is evident.

Regarding initial HIPS, cryofracture surface SEM image (5000x) along with EDS X-ray spectra and mapping images is presented in Fig. 2. Clearly, mineral fillers in HIPS contains C, O, Ca and Ti and are well dispersed and distributed on the overall surface. Also, the presence of bromine is evidenced in the spectra. The relative low intensity of Br signal agrees with the small quantity of this additive detected in previous work (Vazquez and Barbosa, 2016).

Glass transition temperature ( $T_g$ ) changes gives the first evidence of compatibilization in polymer blends. In compatibilized blends it is expected that  $T_g$  values of each component, tends to match each other when phase interaction is enhanced (Utracki, 1991).  $T_g$  of WEEE initial materials and all blends prepared are presented in Table 2. It is possible to note that blend with major content of HIPS (H80/A20) has a single  $T_g$  of 94.2 °C, between the corresponding  $T_g$  of initial HIPS and ABS. This fact could indicate an improvement in phase interaction and then, an effective compatibilization. On the other hand, blend with ABS as major component presents two glass transition temperatures, one at 94.9 °C and other at 101.2 °C. The first one, between correspondent HIPS and ABS  $T_g$ , seems to indicate interactions between styrene phase of each matrix. However, the second transition could suggest a decrease in phase interaction. The greater  $T_g$  could be related with the coalesce of AN domains (present in ABS) during blending, and consequently manifest the AN transition by itself (Zhang et al., 2011). However, this last fact does not indicate that compatibilization is not effective. In this sense, mechanical properties analysis allows to obtain the best evidence of blend compatibilization efficiency.

Mechanical properties measured at high strain allow to better appreciate phase interaction and conclude about phase adhesion (Nielsen and Landel, 1994). In this sense, changes in ultimate strength ( $\sigma_u$ ) and elongation at break ( $\epsilon_b$ ) give a measurement of compatibilization effectiveness because they evidence increments in strength and ductility. Toughness, that is the necessary energy to material breaking, is also very sensitive to compatibilization because of the same reasons aforementioned. Meanwhile, Elastic Modulus (E), that is a zero-strain property, gives an idea of material stiffness. For this reason, this last property does not give a measure of phase interactions in blends, E only depends on the internal structure of each specie and its relative proportion. Then, a combination of thermal and mechanical behavior analysis with phase morphology study allows to conclude about compatibilization efficiency.

Flexural mechanical properties (E,  $\sigma_u$ ,  $\epsilon_b$  and toughness) for initial materials as well as for all physical and compatibilized blends are shown Table 3. It is possible to note that ABS has higher stiffness and strength (higher E and  $\sigma_u$ ) and lower ductility (lower  $\epsilon_b$ ) than

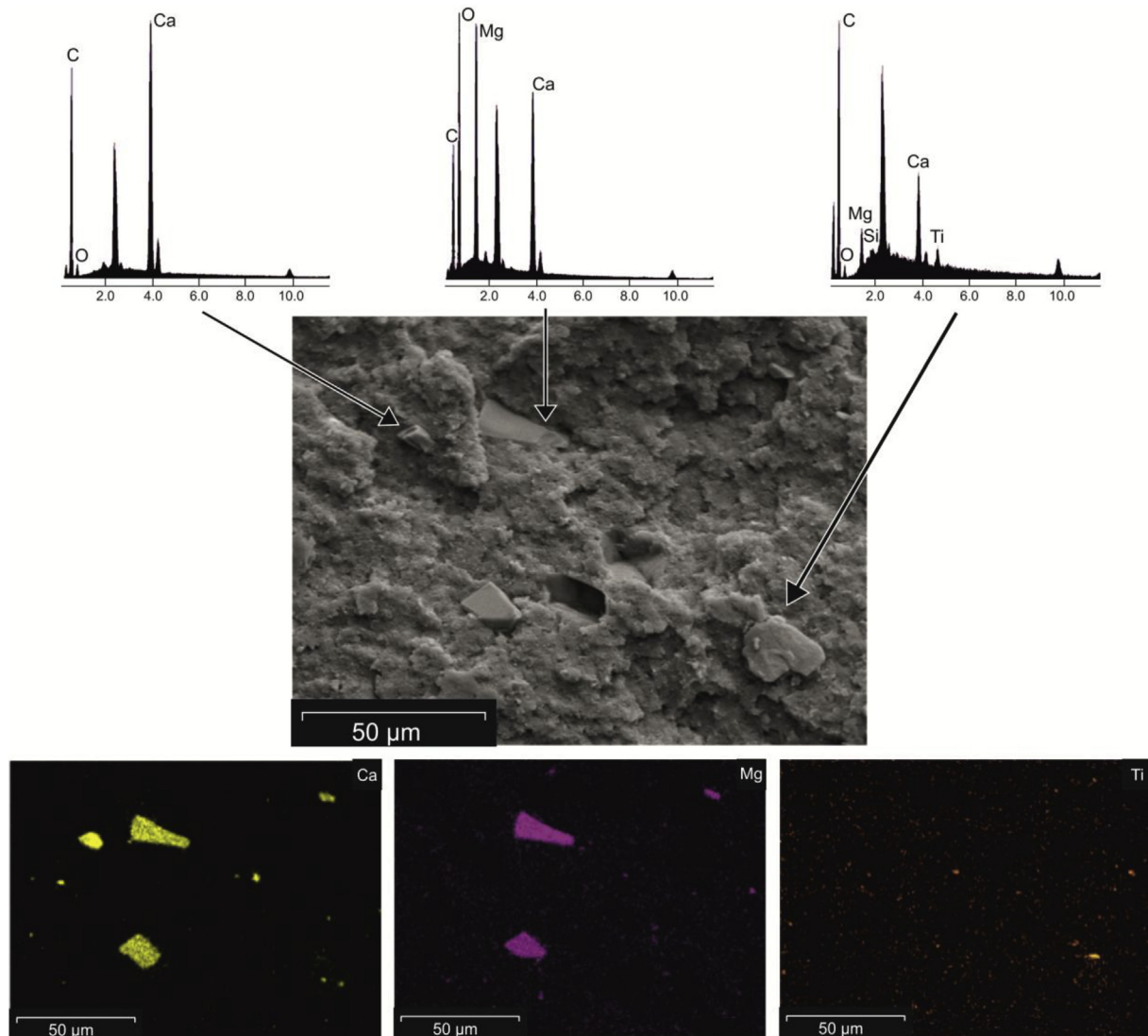


Fig. 1. Cryofractured surface SEM micrograph (5000X) of ABS along with EDS spectra and mapping images.

HIPS and then, lower toughness. This behavior is directly related with the higher content of fillers and AN in ABS. Regarding physical blends, when HIPS is the major component E presents a slight negative deviation of the rule of mixtures despite values remain within experimental error (Utracki, 1991). This is an unexpected behavior because a stiffer material (ABS) has been added. However, the increased rigidity evidences a strong interaction between fillers, AN, and Bu which could indicate that (during blending) rubbery phase (Bu), AN, and fillers have suffered a redistribution and then, for example, fillers were encapsulated by Bu phase. The others mechanical properties of H80/A20 blend present the expected variations respect to initial materials. On the other hand, when ABS is the major component (H20/A80), a small increment in  $E$ ,  $\sigma_u$  and  $\epsilon_b$  respect to ABS is evidenced. This indicates that material has been stiffened by AN phase redistribution during blending which is consistent with the presence of two glass transition temperatures observed in thermal analysis. Beside this, it is important to note that, phase interaction improvement is evidenced since H20/A80 blend is more ductile than ABS (major component of this blend).

In order to corroborate all assumptions made from mechanical properties analysis, a morphological study was performed. Fig. 3

presents SEM micrographs (20000x) of physical blends cryofracture surface. Particularly, Fig. 3a shows H80/A20 blend cryofracture surface in which at least three kinds of domains can be appreciated: rubbery ones folding along the interphase (solid circle), domains that exhibit a neat fracture together with the matrix (dash circle) and pulled out domains with a “smooth” surface (dash dot circle). Also, besides this blend contains around of 5 wt% of fillers (Vazquez and Barbosa, 2016, 2017), they are not evident in Fig. 3a. This observation agrees with the claim that fillers are encapsulated within rubbery domains with folding edges. Respect the other domains, those with neat fracture contain the typical salami structure of HIPS which is the main component in this blend. Finally, pull out domains evidence the intrinsic low adhesion with matrix. They can be associated to the AN phase included by ABS. The low adhesion of this stiff domains is the responsible of the diminishing in ductility of this blend respect to HIPS.

On the other hand, cryofracture surface which allows to appreciate H20/A80 blend morphology, is presented in Fig. 3b. Brittle fracture edges corresponding to a stiff material are evident and also, different kinds of domains can be observed. Pull out big ones with smooth surface and neat fracture (dash dot circle) correspond to AN phase. Their bigger size agrees with the

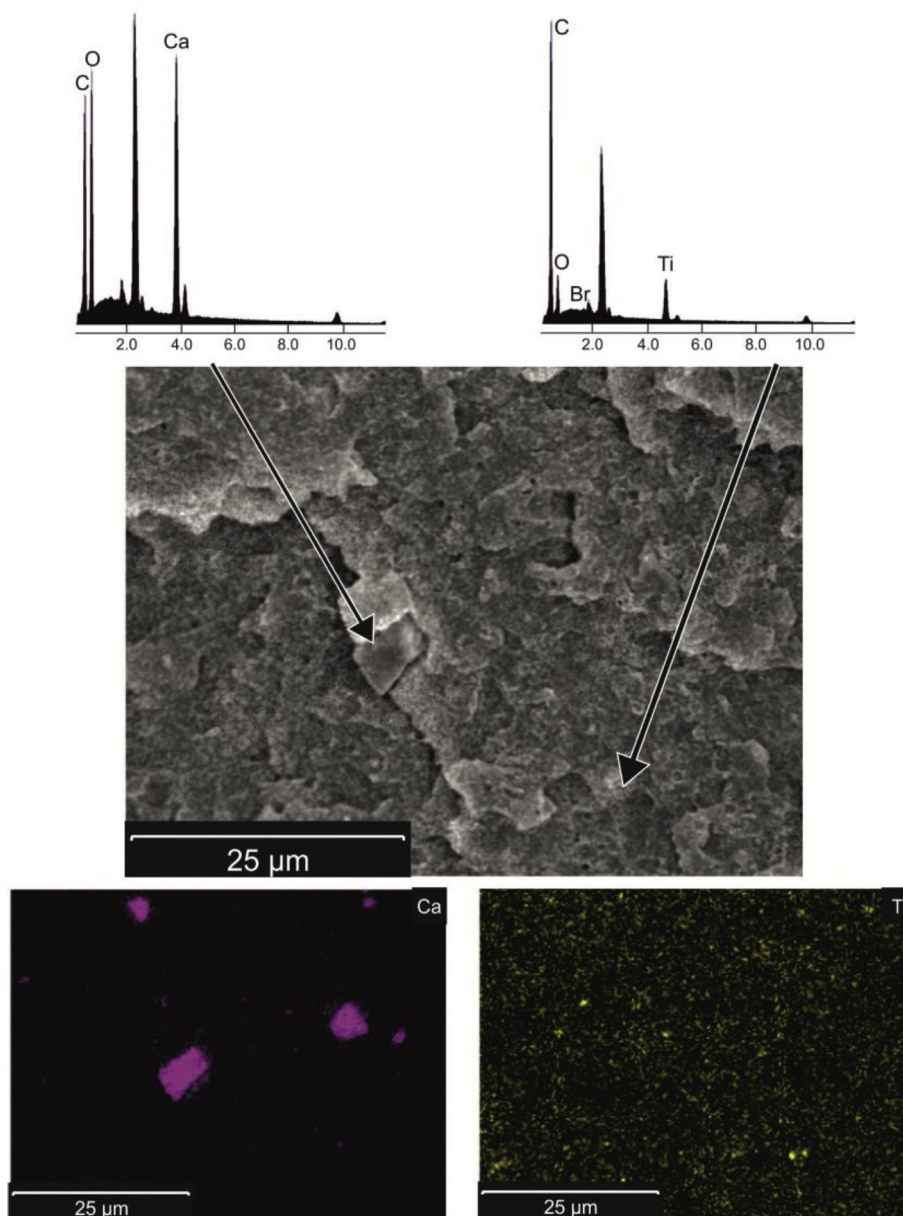


Fig. 2. Cryofractured surface SEM micrograph (5000X) of ABS along with EDS spectra and mapping images.

**Table 2**  
Glass transition temperatures of all blends prepared.

sample	T <sub>g</sub> (°C)	T <sub>g</sub> <sup>2</sup> (°C)
HIPS	93.7	–
ABS	95.2	–
H80/A20	94.2	–
H20/A80	94.9	101.2
H80/A20-2SBR	94.4	–
H80/A20-10SBR	95.2	–
H80/A20-20SBR	95.5	–
H20/A80-2SBR	95.4	–
H20/A80-10SBR	96.4	–
H20/A80-20SBR	96.6	–

**Table 3**  
Flexural mechanical properties (E, σ<sub>u</sub>, ε<sub>b</sub> and toughness) of WEEE initial materials and all blends prepared.

Sample	E (MPa)	σ <sub>u</sub> (MPa)	ε <sub>b</sub> (%)	toughness (J/m <sup>3</sup> )
HIPS	2068 ± 208	35.6 ± 1.6	6.96 ± 0.26	2.25 ± 0.16
ABS	2339 ± 29	43.4 ± 1.7	2.44 ± 0.16	0.63 ± 0.07
H80/A20	1946 ± 112	37.4 ± 2.0	5.90 ± 0.33	1.81 ± 0.15
H20/A80	2385 ± 113	43.7 ± 2.7	2.69 ± 0.14	0.67 ± 0.13
H80/A20-2SBR	4751 ± 247	69.2 ± 2.6	4.70 ± 0.54	2.78 ± 0.41
H80/A20-10SBR	3293 ± 334	46.3 ± 3.5	2.99 ± 0.32	1.02 ± 0.22
H80/A20-20SBR	899 ± 53	12.4 ± 5.3	2.07 ± 1.15	0.20 ± 0.18
H20/A80-2SBR	2217 ± 99	34.7 ± 1.1	1.65 ± 0.07	0.30 ± 0.02
H20/A80-10SBR	1502 ± 153	20.8 ± 1.6	1.50 ± 0.13	0.17 ± 0.02
H20/A80-20SBR	1020 ± 80	13.0 ± 2.1	1.75 ± 0.45	0.15 ± 0.06

coalescence during processing of initial AN domains of ABS. The other domains are small and seems to correspond to rubbery ones

that proceed from rubber recoil after fracture. Some fillers are also observed agreeing with the higher concentration of them in this

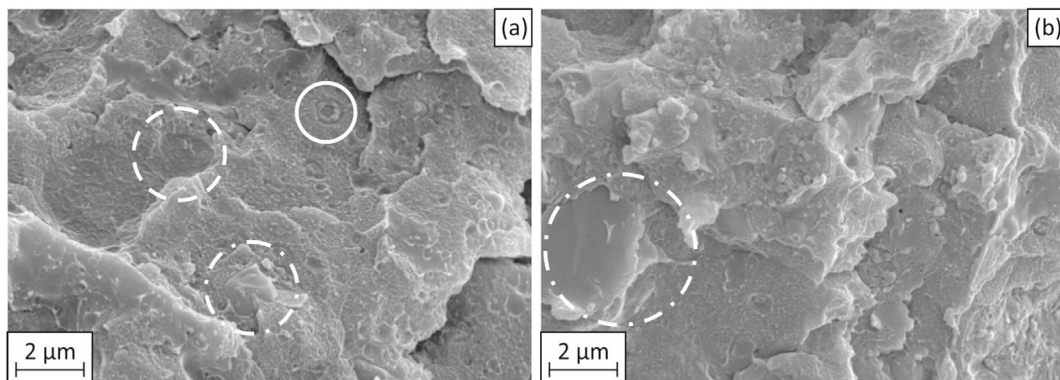


Fig. 3. Cryofractured surface SEM micrograph (20,000X) of: (a) H80/A20 and (b) H20/A80.

blend. The above morphology discussion is consistent with stiffness and strength improvement and, ductility decrease of H20/A80 blend.

In this work, the strategy of compatibilization includes the addition of SBR to HIPS/ABS physical blends in order to enhance their final properties. This copolymer was selected for its similar structure with HIPS and ABS. It is expected that blends with major content of HIPS will be better compatibilized by SBR due to the presence of the same components in both materials, St and Bu. SBR is a random copolymer which present a notable rubbery behavior as a consequence of its high rubber phase content (Bu up to 75 wt %). According to supplier's information, SBR contains 6 wt% of an organic acid, a byproduct from their polymerization process. In this sense, an analysis of the possible influence of this byproduct in compatibilization process was initially performed. Modrow et al. (2001) studied SBR thermal degradation and the influence of its additives and byproducts during processing, demonstrating that it is stable from 160 °C to 190 °C even when byproducts degrades. It was determined that the organic acid, which is present in the SBR used in this work, degrades at 160 °C then, it is expected the appearance of bubbles during blending.

Compatibilization efficiency is discussed in terms of glass transition variations, mechanical behavior improvement and blends morphology analysis of all compatibilized blends compared with their corresponding physical blend. Results are presented and discussed for each HIPS/ABS proportion following by the effect of compatibilizer concentration analysis.

### 3.1. HIPS as major component (H80/A20)

Glass transition temperatures of all blends prepared were obtained from reversible heat flow analysis. Thermograms of H80/A20 blend with 0, 2, 10 and 20 wt% of SBR are shown Fig. 4a, and the corresponding glass transition temperatures are listed in Table 2. For all H80/A20 compatibilized blends the  $T_g$  is very close to physical one. The biggest change observed is 1.3 °C when 20 wt% of SBR is added to H80/A20. Despite the small variation, this is an unexpected behavior because the SBR has a  $T_g$  of  $-40$  °C and  $T_g$  of H80/A20 is 94.2 °C. As it was explained above, in compatibilized blends it is expected that  $T_g$  value of each component tends to match each other. The observed change in H80/A20-20SBR blend could be attributed to interactions between SBR and fillers at molecular level. It was reported that, when SBR molecules are close fixed to nanoparticles the resulting structure is stiffer and then SBR presents a higher  $T_g$  (Arrighi et al., 2003; Freakley and Sirisinha, 1997).

The more conclusive compatibilization efficiency analysis was

performed through mechanical behavior study. Flexural stress-strain curves of all blend prepared are shown in Fig. 5 based on the physical blend involved. Mechanical behavior of H80/A20 blend with 0, 2, 10 y 20 wt% of SBR is presented in Fig. 5a while mechanical properties are summarized in Table 3. It is possible to observe that, when a low concentration of SBR is added (H80/A20-2SBR) stiffness and ultimate strength are notably improved (both around 200% respect to H80/A20) even more than initial WEEE materials properties. Meanwhile, ductility slightly decreases respect physical blend but, it is much higher than the ABS one. This mechanical behavior could be interpreted in terms of fillers "unmasking" by rubbery (Bu) phase. From the mechanical point of view this mechanism allows to explain the strength and stiffness improvement, as well as ductility reduction respect to physical blend.

This could only be possible if rubbery phase and mineral fillers are redistributed during blending. Jančář and Kučera (1990) explain that in ternary compounds could exists filler encapsulation or not, depending on fillers surface energy as well as the kind and size of rubbery phase. Similar results were obtained by other authors (Doan et al., 2013; Robertson et al., 2008). Particularly, in the system under study, the addition of 2 wt% of SBR seems to produce the coalescence of rubbery domains and, migration and redistribution of fillers along both, styrene and acrylic phases improving stiffness and ultimate strength with a slightly decrease in elongation. Please note that the decrement in ductility could proceed from both, bad filler/matrix adhesion as fillers change the matrix because of migration and, the presence of bubbles from SBR organic acid degradation. However, it is expected a small amount of bubbles in this blend as SBR concentration is low. Despite the slight decrease in ductility, the notable increase in stiffness and strength of H80/A20-SBR blend respect on H80/A20 one indicates that blend compatibilization is effective. It is important to note that, with the addition of just 2 wt% of a compatibilizer these properties are notably improved in comparison not only with physical blend but also with ABS. Particularly, ductility increases a 90% respect to ABS.

Blend with 10 wt% of SBR (H80/A20-10SBR) shows an increment in  $E$  and  $\sigma_u$ , about 70% and 24%, respectively but, a decrement in ductility of 50% respect to the physical blend. Consequently, toughness decreases 44%. Similar improvement is obtained respect to initial ABS. On the other hand, when 20 wt% of SBR is added (H80/A20-20SBR) all mechanical properties strongly decrease respect to H80/A20 physical blend and both initial materials (ABS and HIPS).

Mechanical behavior of blends with SBR is related to the relative contribution of fillers and, rubbery and acrylic phase by themselves, as well as, their interactions and bubbles influence. When 2 wt% of

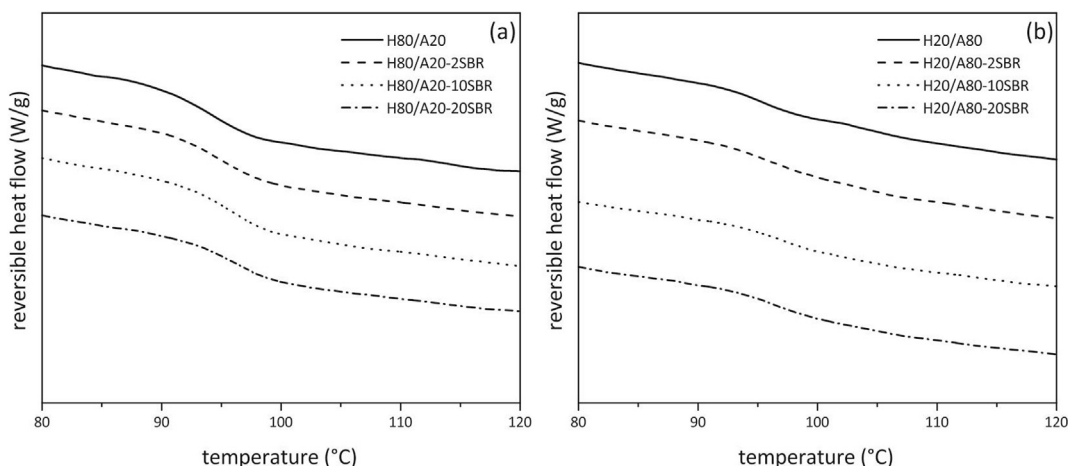


Fig. 4. Reversible Heat Flow (Exo-up) thermograms of: (a) H80/A20 blends with 0, 2, 10 and 20 wt% of SBR and (b) H20/A80 blends with 0, 2, 10 and 20 wt% of SBR.

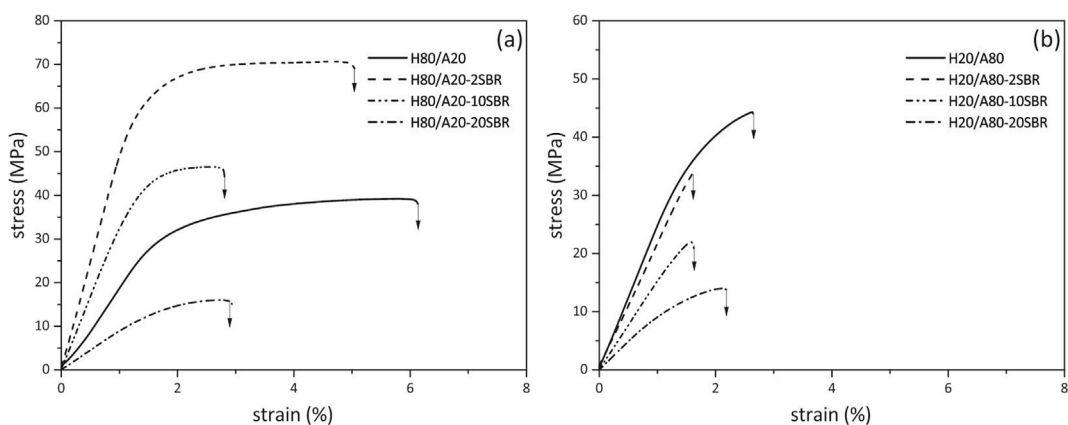


Fig. 5. Flexural Stress-Strain curves of: (a) H80/A20 blends with 0, 2, 10 and 20 wt% of SBR and (b) H20/A80 blends with 0, 2, 10 and 20 wt% of SBR.

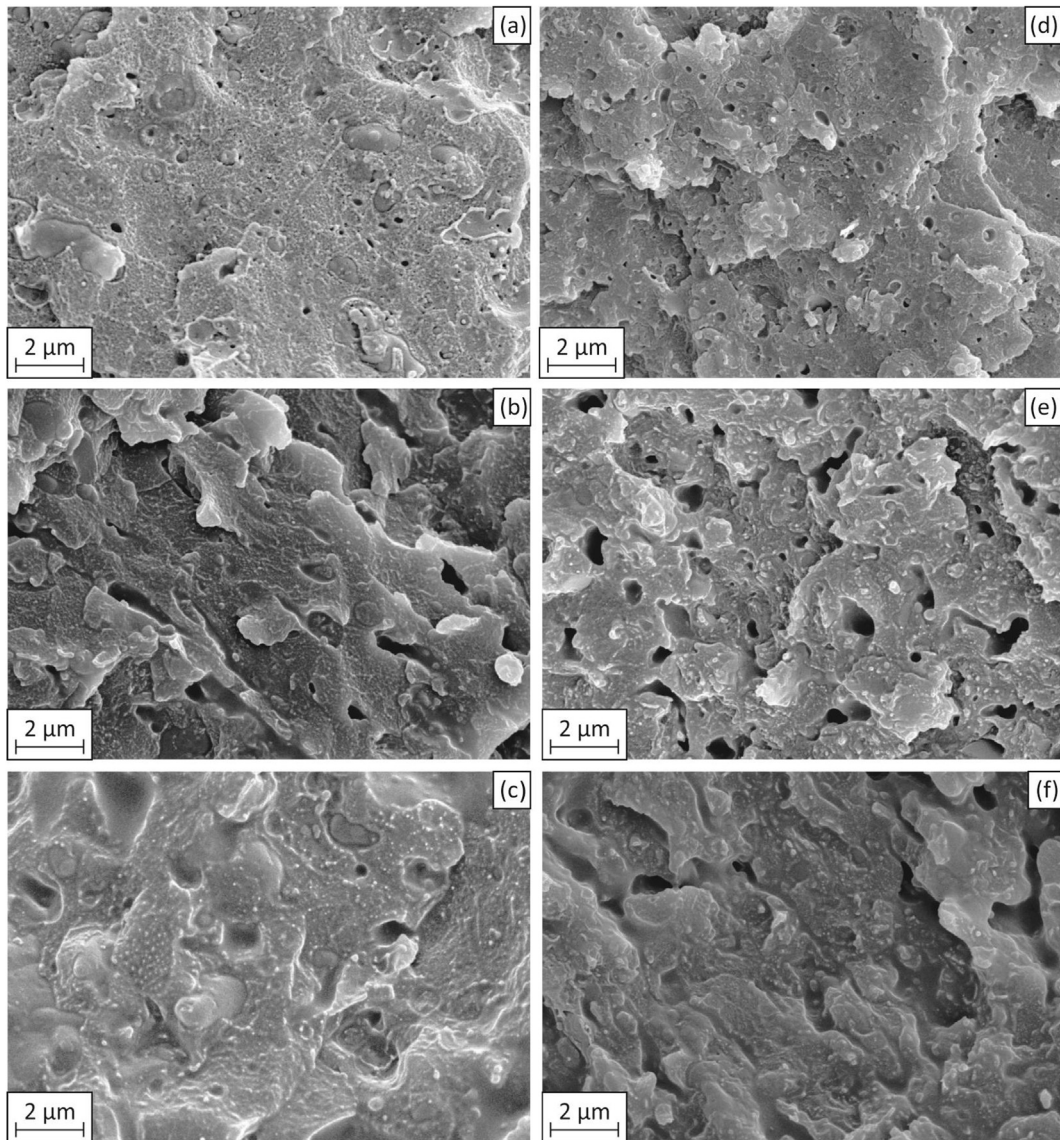
SBR is added to H80/A20 blend, SBR Bu rubbery phase contributes to fillers unmasking because they are more compatible with rubbery phase of initial blend and, as mentioned above, bubbles influence is small. However, when added amount of SBR increases, rubbery phase and bubbles increase, completely changing the blend morphology. In blends with 10 wt% and 20 wt% of SBR, Bu amount is much higher governing blend mechanical behavior at low-strain properties (strength) while bubbles dominate at high strain ones (ductility). Whereas both, bubbles and rubber phase contribute to the decrement of stiffness (zero-strain) (Nielsen and Landel, 1994). Results shows that ductility of blend with 10 wt% of SBR is very similar to blend with 20 wt% SBR one corroborating that bubbles presence domains mechanical behavior at high strain independently of their concentration. On the other hand, stiffness and strength strongly depend on SBR concentration as Bu phase and bubbles presence reduce them. This fact evidence that relative bubbles interaction with matrix and fillers is another aspect to consider when higher SBR concentrations are used as compatibilizer. Despite the use of such high amount of compatibilizers is neither practical nor sustainable for plastic recycling, clearly a typical rubber mastication process has to be done on SBR to avoid bubbles generation during blending (Noriman and Hanafi, 2012).

These results are very promissory since properties are notably improved respect to initial ABS from WEEE (Table 2) with the addition of only 2 wt% of SBR to a blend with 20 wt% of ABS. Then, direct replacement of ABS by this blend in Electrical and Electronic

Equipment (EEE) housing manufacturing industry could be possible. In order to assess actual causes of mechanical properties variation and to validate previous hypotheses, blend morphology was analyzed.

Cryofractured surface SEM micrographs of H80/A20 compatibilized blends with 2, 10 and 20 wt% of SBR are shown in Fig. 6–c, respectively. As it was expected, the higher SBR content the major amount and size of bubbles appear. In H80/A20-2SBR micrographs (Fig. 6a) matrix seems to be more “rubbery” than in physical blend, fact evidenced by rubber “coiling” after deformation. This claim is based on rubber domains coalescence during blending by the presence of SBR. Also, AN domains became more evident, bigger and unstuck from the matrix and some very small unmasked fillers are observed. This blend morphology completely agrees with thermal analysis and mechanical properties.

Regarding H80/A20-10SBR morphology (Fig. 6b), the size increment of both, rubber domains and bubbles is very noticeable. Also, it is possible to observe that matrix is less ductile (surface presents more brittle fracture) and domains present lower adhesion, agreeing mechanical performance. Several differences with previous images can be appreciated in H80/A20-20SBR SEM micrograph (Fig. 6c). The addition of 20 wt% of SBR generates a particular kind of matrix morphology with a few pull-out domains. Also, a great amount of big size bubbles can be appreciated. The final mechanical behavior results from the relative contribution of rubbery phase and bubbles amounts. It is important to note that



**Fig. 6.** Cryofractured surface SEM micrograph (20,000X) of: (a) H80/A20-2SBR, (b) H80/A20-10SBR, (c) H80/A20-20SBR, (d) H20/A80-2SBR, (e) H20/A80-10SBR and (f) H20/A80-20SBR.

there is no evidence of unmasked fillers in these blends morphology. It is expected because rubbery phase is such higher that fillers remains within these domains as they cannot migrate to the interphase.

### 3.2. Blends with ABS as major component (H20/A80)

Glass transition temperatures of H20/A80 blends with 0, 2, 10 y 20 wt% of SBR are listed in Table 2 and were obtained from thermograms presented in Fig. 4b. H20/A80 blend present two glass transitions. However, the same blend with the addition of 2 wt% of SBR evidence a single  $T_g$  around 95.4 °C with a slight increase respect to the first  $T_g$  of the H20/A80 blend. The second glass transition temperature does not appear, as it can be observed in Fig. 4b. This fact indicates an enhancement of initial materials interaction by action of the compatibilizer added. Also, the same situation can be appreciated with the addition of higher amounts of SBR. However, claims made from glass transition analysis are not conclusive and then, mechanical performance analysis was

performed.

Mechanical properties allow to better assess SBR compatibilization effectiveness onto H20/A80 blends. Representative stress-strain curves for H20/A80 blends with 0, 2, 10 and 20 wt% are presented in Fig. 5b, while mechanical properties are listed in Table 3. When 2 wt% of SBR is added (H20/A80-2SBR blend) it is possible to observe a notable decrease in strength and ductility respect to the physical blend. This behavior indicates that there is a decrease in phase adhesion with the addition of SBR, which can also be related to the presence of bubbles. On the other hand, stiffness unchanged evidencing that the relative contribution of fillers and rubbery phase has not been affected by the presence of a small amount of compatibilizer. Regarding blend with 10 wt% of SBR, strength and stiffness suffered a decrement respect not only to the physical blend but also to initial materials (ABS and HIPS). Also, ductility decrement respect to H20/A80 is the same when 2 wt% or 10 wt% of SBR is added. Similar behavior can be appreciated when 20 wt% of SBR is used as compatibilizer but, in this case, ductility is a little higher than in the other blends.



It is expected that, in this kind of blend (H20/A80), as the amount of SBR increases rubbery behavior is more notable. It would be evidenced by an increment in ductility and, strength and stiffness diminish. In blends under study, these two last properties variation agrees with this claim but, ductility shows an unexpected variation. This last fact can be attributed to bubbles presence. They proceed from organic acid contained in SBR that degrades during blending so, the greater amount of SBR the greater amount of bubbles and higher ductility deterioration. Also, the influence of bubbles in mechanical behavior is strengthened by the high content of ABS, which increase processing temperature by viscous heating (Soltani and Sourki, 2005). Please note that strength and stiffness decrease by the effect of both, rubber addition and bubbles presence (Nielsen and Landel, 1994; Ward and Sweeney, 2012). Then, mechanical behavior of these blends is the result of the combination of all these phenomena.

In order to verify claims made from mechanical results attributed to filler/rubbery phase/bubbles relative contribution a systematic and accurate morphological analysis through SEM was performed. Micrographs of blends with 2, 10 and 20 wt% of SBR are shown in Fig. 6d and f. It is possible to observe that the presence of bubbles is clear in all blends, increasing their size and amount with SBR concentration. Sharpen edges, typical of brittle fracture, are well defined in blend with 2 wt% of SBR. Also, there is a considerable amount of bubbles as inferred in mechanical behavior analysis. In the case of blend with 10 wt% of SBR (Fig. 6e), it is possible to observe a notable increase in size and amount of bubbles respect blend with 2 wt% of SBR. Also, its fracture surface corresponds to a more ductile behavior with distinguishable rubbery domains well distributed along the surface. On the other hand, a completely ductile fracture is observed in blend with 20 wt% of SBR (Fig. 6f). In this case, SBR amount is such high that its rubbery domains associated (during blending) with those from initial materials result in a compatibilized blend with a kind of “co-continuous” morphology. It means that there are less “rubbery domains” separated. This blend also contains several bubbles. The morphology of H20/A80-20SBR blend agrees with the notably decrease in stiffness and strength with a slight decrease of ductility respect physical blend. It is also consistent with the improvement in the ductility respect to blends with less SBR content. Please note that is not possible to identify mineral fillers by itself giving an evidence that rubber phase mask it. This fact also contributes to become blends less rigid as evidenced in mechanical behavior. Similar mechanical behavior tendencies were found by other authors working with filler ABS blends (Grellmann and Seidler, 2013; Grellmann et al., 2013).

#### 4. Conclusion

A systematic study of compatibilization of HIPS/ABS blends from WEEE to improve mechanical properties was performed in order to recycle them with added value. This methodology allows to recycle these plastic materials without sorting by type and consequently reduce labor costs as well as, increase recycling workers safety. Compatibilization of HIPS/ABS blends from WEEE is highly effective when 2 wt% of SBR is added to blends with HIPS as main component. Strength and stiffness were notably improved (244% and 186%, resp.) in comparison with its corresponding physical blend (H80/A20). Meanwhile, with the addition of 10 wt% and 20 wt% of SBR results were not as good as blend with 2 wt% of SBR and, the use of such high amount of compatibilizers is neither practical nor sustainable for plastic recycling.

For blends with ABS-major content, SBR is not an effective compatibilizer for any added concentration. In these blends the presence of bubbles, from SBR byproduct degradation, considerable affect final performance of all compatibilized blends. Clearly a

typical rubber mastication process has to be done on SBR in order to avoid bubbles generation during blending. This SBR mastication could improve mechanical performance of all final blends.

Additional remarkable conclusion is focused to direct replacement of ABS in Electrical and Electronic Equipment by HIPS-major content blends with the addition of a small amount of compatibilizer. The obtained properties in this kind of blends make them able to be used in housing manufacturing industry for Electrical and Electronic Equipment instead of ABS which leads to an easy and sustainable route to WEEE plastic recycling.

#### Acknowledgements

The authors are grateful to the following Argentinian institutions for their financial support: CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas), ANPCyT (Agencia Nacional de Promoción de Ciencia y Tecnología) and UNS (Universidad Nacional del Sur).

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