Waste Electrical and Electronic Equipment

Study regarding the plastic composition

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Waste electrical and electronic equipment (WEEE) generated in large amounts due to the development of IT and telecommunication industry is considered an important concern for environmental protection. The complex polymer composition of WEEE can be determined in order to consider a proper recycling process for polymeric materials. The aim of the study was to identify the constituent polymers by: density, burning test, solubility, Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), thermo-gravimetric analysis (ATG). The research led to a majority of polystyrenic polymers, together with polyesters, polycarbonates and polyamides.

Keywords: waste electrical and electrical equipment, polymer identification, polystyrene polymers

Waste electrical and electronic equipment (WEEE) is representing a major concern to the entire world, due to the fast growing of industrial development year after year. These waste materials present a complex material composition containing different types of plastics like polyethylene (PE - i.e. linear low-density polyethylene (LLDPE), l*ow-density polyethylene* (LDPE) and *high-density polyethylene* (HDPE)), acrylonitrile–butadiene–styrene (ABS), high-impact polystyrene (HIPS), polystyrene (PS), polyethylene terephthalate (PET), polycarbonate (PC), etc. [1-4]. Apart of this significant variety of polymeric materials, numerous additives are added to plastics, being capable of changing the material properties, like color, flammability, melting point, density, and cost. These additives are classified into pigments (e.g., TiO_2, ZnO, Fe_2O_3), flame retardants (e.g., brominated organics combined with Sb_2O_3 or polychlorinated biphenyls (PCBs)), and various stabilizers or plasticizers (e.g., compounds of Ba, Cd, Pb, Sn and Zn, or PCBs). However, these additives affect the identification process in different ways. For example, in the case of the waste material, the color does not allow a correct identification of the material if the piece has no international identification (codes) [1, 5-7].

In the literature, there were reported two ways of re-introducing the polymer components of these recovered materials into the economic circuit: the individual recycling of polymers and their composites, and the collective recycling of these polymeric materials [8-12].

After WEEE collection, there are several typical processes to which these materials are subjected for later reuse: dismantling, separation, and identification. The individual recycling of polymers requires separation from WEEE using different procedures: manual selection, density, flotation experiments, elasticity, etc. Polymers once separated present physical-mechanical properties with lower values of approximately 10-30%, comparing with virgin polymers, and this ratio depending on the aging degree of the material [13].

The polymers degradation is mainly due to the thermo-oxidative splitting of the chains by lowering their molecular weight. The recycling of these polymers is accomplished by their introducing into virgin polymers at a maximum of 20%; thus this proportion do not significantly reduces physical and mechanical standard indicators of the material. In the literature, there are also mentioned some methods of improving the physical-mechanical properties by increasing the molecular weight of the degraded polymers using coupling reactions, with different compounds (epoxy or anhydride functional groups). Mixed recycling of WEEE polymer components, after advanced dismantling, is used in the asphalt binders modification used especially in the construction of road arteries [6-8, 14, 15], the proportion not exceeding ~ 15%. The WEEE powder is also used to modify the bitumen used in road coatings, the modification degree varying with the initial viscosity of the bitumen in the proportion of 5-20%. The presence of WEEE powder in bitumen increases its melt viscosity, so its part is generally below 10%.

The proper recycling process, in order to obtain materials with performance properties, can be established after an advanced identification of the constituent polymers. The paper aims to use usual characterization techniques to determine the composition of WEEE samples.

Experimental part

The material composition was determined on dismantled WEEE components, i.e. monitor enclosures and central units, keyboards casing, mouse casings, parts of central units (DD-RAM, SD-RAM, PCI, ISA, FDD, IDE, AT, ATX etc.). The waste was initially washed and then sorted by material, color, shape, material codes, resulting in waste fractions which were subsequently cut into granules with dimensions between 1 and 10 mm, by using a laboratory cutting mill, and then were subjected to the identification process by density, burning test, solubility, Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC), thermo-gravimetric analysis (ATG).

FTIR analysis was performed on polymer samples using a Bruker Optik GMBH spectrometer, equipped with DRIFT accessory and ATR mode, in the wavelength range of 4000-400 cm^{-1}, 32 scans, 4 cm^{-1} resolution.

Differential scanning calorimetry (DSC) was carried out using a DSC Q2000 Calorimeter (TA Instruments). The method parameters were: Modulation ± 1.06 °C every 40s,

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Helium - purged gas with 50 mL/min., Ramp 10 °C/min to 300 °C, 100µL T_{zero} Aluminium pan.

Thermogravimetric analysis (TGA) was performed using a Q5000IR instrument (TA Instruments). Method: 1) Ramp 10°C/min to 700°C; 2) Select gas 2; 3) Isothermal for 5 min; purge gas 1: Nitrogen; purge gas 2: Air; sample pan: Platinium 100µL.

Results and discussions

The collected waste was sorted first by material, color, shape, material codes, resulting in waste fractions and the processes involved in the study are mentioned in figure 1.

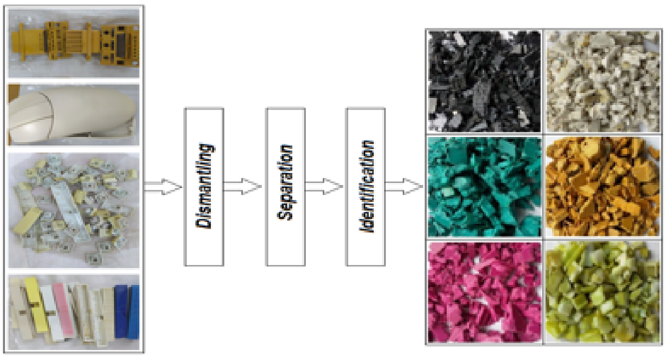


Fig. 1. The processes involved in the identification of WEEE

The sample density was determined by the pycnometer method. The density domains were determined for each category of material, this being particularly influenced by the amount of filler from each type of waste and by the proportion of each polymer in the copolymer.

From the burning test, results regarding the odor and flame color were obtained for each material. This method allows the identification of plastic materials based on the flame type (color) and odor. There are also some drawbacks regarding this test, such as the presence of additives, chemicals or polyoxymethylene (POM), which are characterized by an almost invisible flame.

The solubility test consisted of dissolution of the samples in different solvents. It has been found that polystyrene materials (PS, ABS, HIPS and mixtures of them) can be completely solubilized in tetrahydrofuran or chloroform. It was not possible to completely dissolve the polyamide and polyester materials. We believe that the solubilization in tetrahydrofuran is a suitable method for polystyrene compounds separation from other polymers present in waste (polyamide, polyester, polyolefins, etc.). The obtained results of the waste polymers are presented in table 1.

FTIR spectroscopy is an important spectroscopic technique that can be used as a very useful tool for plastic materials investigation, due to the fact that each polymer emits at a certain infrared wavelength and this makes possible the identification [16].

FTIR allows the study of transient effects in real-time and the main disadvantage of this technique is the equipment cost and the slow identification speed for commercial recycling of large quantities of WEEE [17]. Based on the FTIR spectra obtained, compared to the individual polymers (according to the literature), the composition of the studied WEEE mixture could be determined. In particular, polystyrene polymers (ABS, PS, HIPS and mixtures of them), polyamides (PA) and polyesters (e.g., PC and PET) have been identified according to figure 2.

The polystyrenic polymers (PS, ABS, HIPS) were identified based on the specific absorption bands, respectively: 3200-2800 cm^{-1} -aromatic and aliphatic C-H stretch; 1602 and 1494 cm^{-1} -aromatic ring; 1452 cm^{-1} -CH_2 scissoring; 900-966 cm^{-1} - unsaturated groups from polybutadiene phase; 700-770 cm^{-1} -aromatic ring or substituted phenyl ring [12].

For polycarbonate, the presence of the band from 1765 cm^{-1} related to carbonyl group and the peaks from 1225, 1190 and 1159 cm^{-1} associated to para aryloxy group led to PC identification [18].

The attribution of the absorption band for PET includes: 1706 cm^{-1} -C=O stretching; 1502 cm^{-1} -C=C stretching; 1452 and 1386 cm^{-1} -C-O stretching; 1242 cm^{-1} - terephthalate group; 1197 and 1014 cm^{-1} -methylene group; C-O vibration; 719 cm^{-1} - interaction of ester group with the aromatic ring [19].

For polyamide identification, the considered bands were: 3298 cm^{-1} characteristic for N-H stretching from amide; 1632 for carbonyl group, 1531 cm^{-1} for C-N stretching and CO-N-H bending, 1466 and 1140 cm^{-1} -CH_2 groups, 933 and 683 cm^{-1} characteristic for N-H bending vibration [20].

Thermal analysis is another method used to identify polymeric materials. DSC allows both the identification of phase transitions of polymers, and the identification of the miscibility degree between the components (for compatible materials, a single glass transition temperature - Tg different from that of the components will be recorded, and for the immiscible mixtures the specific temperatures will be recorded) [21]. Thus, for compatible polystyrene materials, the existence of a single Tg was noted, as shown in figure 3.

Tabel 1

PROPERTIES OF THE WASTE POLYMERS

Identified polymer	Density, g/cm^3	Burning test	Solubility tested in:
ABS	0.95-1.06	Orange-yellow flame, heavy, black, soot smoke, rubber smell	Tetrahydrofuran, chloroform, 1,2-dichlorethan
PS	0.94-0.97	Yellow flame, heavy, black, soot smoke, rubber smell	Toluene, cyclohexane, tetrahydrofuran
ABS-PS	0.94-0.97	Orange-yellow flame, heavy, black, soot smoke, rubber smell	Tetrahydrofuran, cyclohexane
ABS-HIPS	1.08-1.13	Orange-yellow flame with black smoke, rubber smell	Chloroform
ABS-PC	1.08-1.18	Orange-yellow flame with black smoke, rubber and phenolic smell	Chloroform
PA	1.20-1.45	Blue flame, white smoke, flows	Formic acid
PET	1.2-1.38	Yellow flame, plastic drips, light smoke	60:40 mixture of phenol / tetrachloroethane

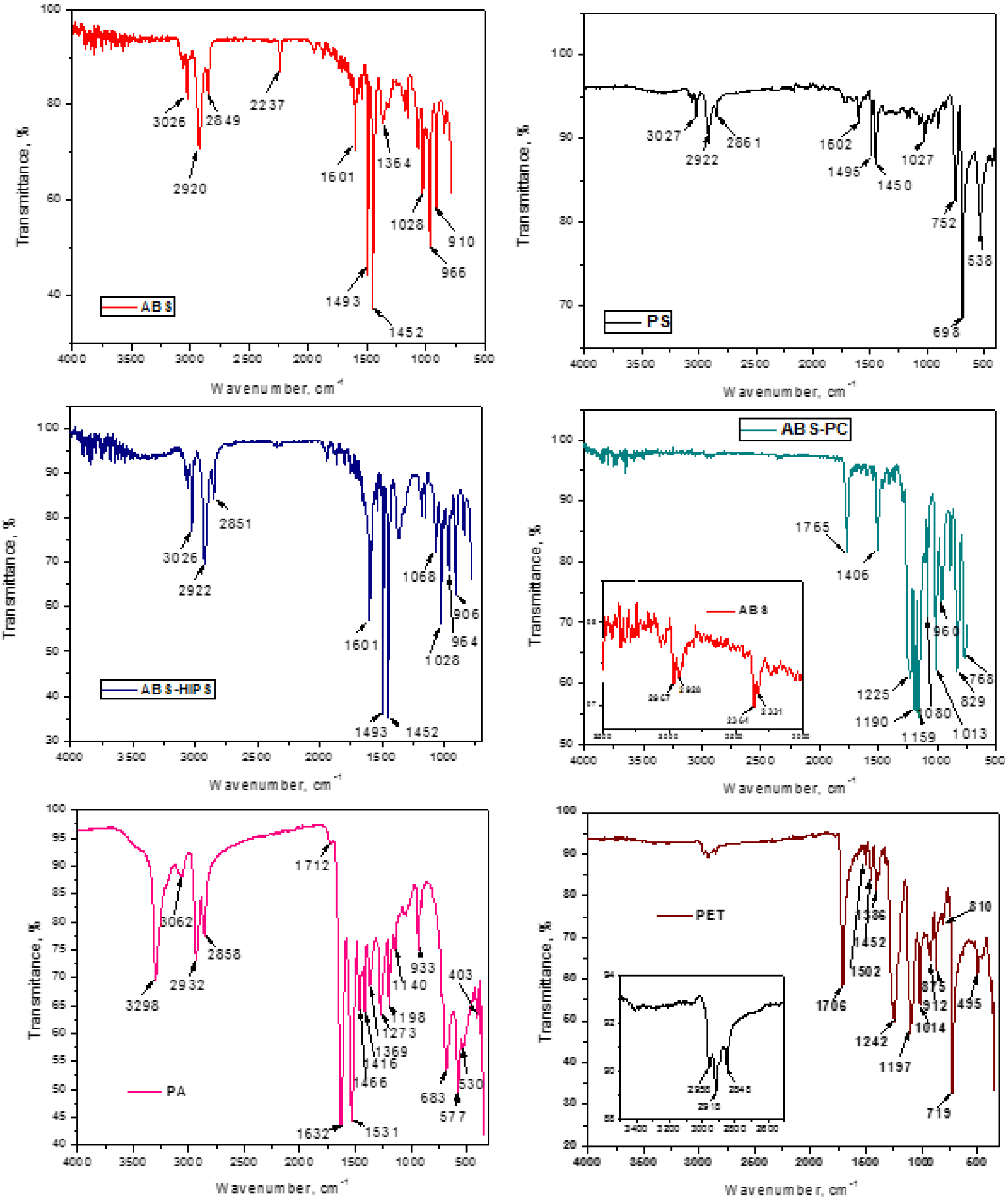
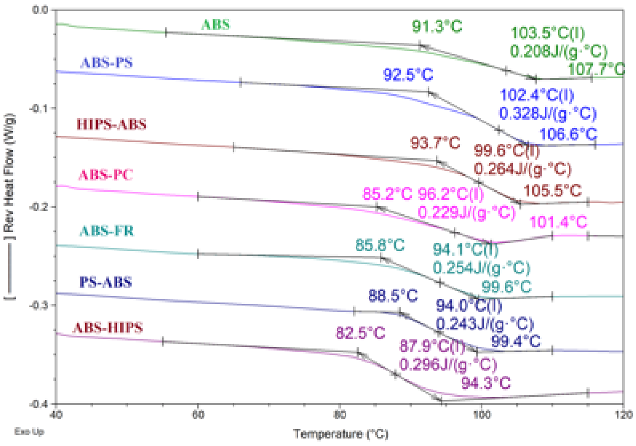


Fig. 2. FTIR spectra of the polymers identified in the WEEE mixture



Fig, 3. Glass transition temperature of polystyrene mixtures

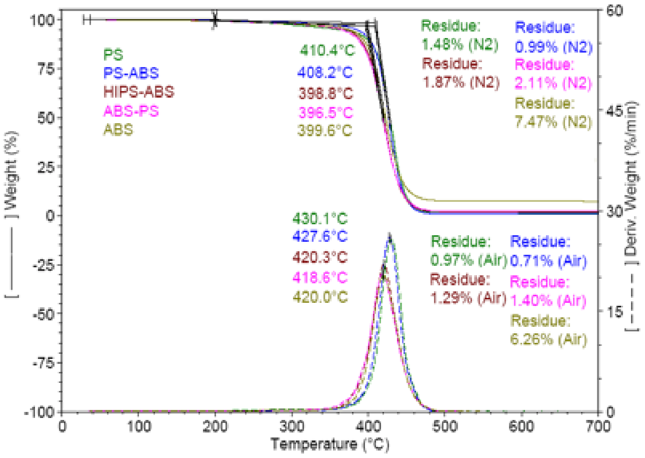


Fig. 4. TGA curves for polystyrene polymers

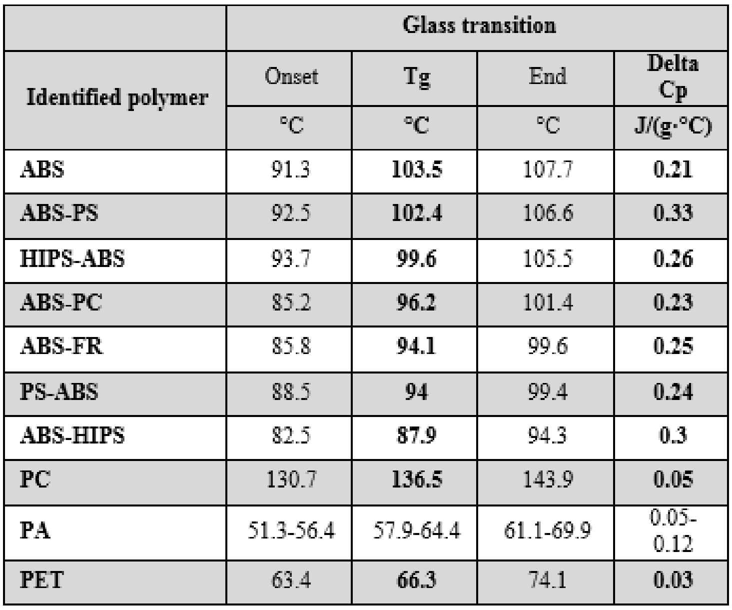
We consider that relatively small variations of the polystyrene-specific transitions in polymers identified in WEEE are both due to their different molecular masses and to polystyrene-compatible flame retardants.

Polyamide based materials exhibit a glass transition at about 60°C and a melting temperature (Tm) at about 220 °C, while polyesters (e.g., PET) exhibit Tg at about 66°C and a melting temperature of 255 °C. The results of the thermal analysis are presented in table 2 and table 3.

Thermogravimetric analysis (TGA) is an analytical technique used to determine the thermal stability of materials and the volatile component fraction by monitoring the differences of weight correlated with

Table 2

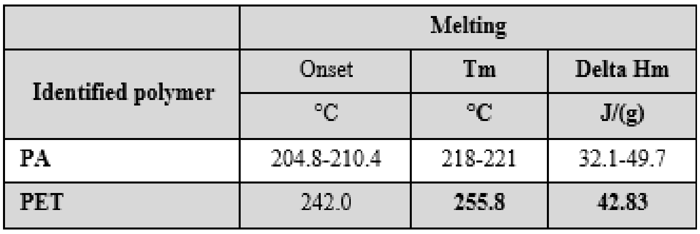
Tg FOR THE POLYMERS IDENTIFY IN WEEE



Identified polymer	Glass transition			
	Onset	Tg	End	Delta Cp
	°C	°C	°C	J/(g·°C)
ABS	91.3	**103.5**	107.7	**0.21**
ABS-PS	92.5	**102.4**	106.6	**0.33**
HIPS-ABS	93.7	**99.6**	105.5	**0.26**
ABS-PC	85.2	**96.2**	101.4	**0.23**
ABS-FR	85.8	**94.1**	99.6	**0.25**
PS-ABS	88.5	**94**	99.4	**0.24**
ABS-HIPS	82.5	**87.9**	94.3	**0.3**
PC	130.7	**136.5**	143.9	**0.05**
PA	51.3-56.4	57.9-64.4	61.1-69.9	0.05-0.12
PET	63.4	**66.3**	74.1	**0.03**

Table 3

T_m FOR THE POLYMERS IDENTIFY IN WEEE



Identified polymer	Melting		
	Onset	Tm	Delta Hm
	°C	°C	J/(g)
PA	204.8-210.4	218-221	32.1-49.7
PET	242.0	**255.8**	**42.83**

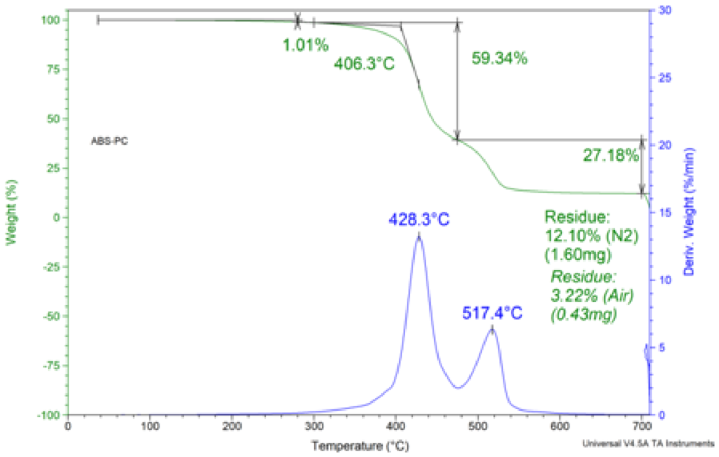


Fig. 5. ATG curve of ABS-PC waste

temperature and time. ABS, PS and HIPS have similar degradation curves starting at 400-410 °C. ABS degradation begins at a slightly lower temperature due to the -CN groups. The residue obtained after combustion in the air is up to 7%, attributed to the amount of inorganic filler contained by WEEE. The larger residue of up to 12% (combustion in nitrogen atmosphere) is due to the presence of organic filler (mainly flame retardant).

For ABS-PC, two stages of degradation are observed for both the constituent polymers. Besides the degradation of ABS that appears at approx. 420 °C, another stage of degradation, at approx. 517°C, is present, being attributed to PC, as can be seen in figure 5.

From the study on the composition of IT and telecommunications equipment waste, it was determined by the specific techniques that the blend consists of approximately 75% styrene polymers and copolymers, together with polyesters, polycarbonates and polyamides.

Conclusions

The study was achieved using plastic parts of waste electrical and electronic equipment, i.e. monitor enclosures and central units, keyboards casing, mouse casings, parts of central units (DD-RAM, SD-RAM, PCI, ISA, FDD, IDE, AT, ATX etc.). The identification of the various polymers highlighted a majority of polystyrenic polymers in WEEE composition. This procedure is an important step considered in the recycling process of WEEE both as individual polymers and blends.

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