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## ORIGINAL ARTICLE

# Effect of PET functionalization in composites of rubber–PET–HDPE type

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## KEYWORDS

PET functionalization;  
Plastic wastes;  
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**Abstract** The functionalization of polyethylene terephthalate (PET) from tire rubber–PET–high density polyethylene (HDPE) composites represents a key strategy for improving the composite properties. This is a practical and effective method to improve the interface between matrix (waste tire rubber) and fillers (waste PET and HDPE). By PET functionalization, adherence and surface properties of composite materials can be controlled. PET functionalization was performed with polyethylene glycol (PEG 400, 1%) and sodium dodecyl sulphate (SDS 1%). The characterization of the components and composite are discussed in terms of surface energy values (evaluated from water contact angle measurements) and surface morphology by using scanning electron microscopy (SEM). The structural and conformational changes were investigated by Fourier Transform Infrared (FTIR) Spectroscopy while the crystalline structure was studied by X-ray diffraction (XRD). The improved interfacial adhesion, thermal stability and mechanical properties (stress–strain, compression and impact resistance) of the composites are correlated with the PET functionalization, with non-ionic (PEG) and an anionic surfactant (SDS). The results proved that the interface properties are improved by functionalization of PET. The best mechanical properties were recorded at 30 min moulding. The samples with 45% PET–SDS showed the best combination of mechanical properties: tensile strength ( $1.56 \text{ N/mm}^2$ ), impact strength ( $43.72 \text{ kJ/m}^2$ ) and compression ( $158.78 \text{ N/mm}^2$ ).

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## 1. Introduction

Nowadays, rubber and plastic wastes disposal raises significant problems as they often are trashed to landfills, although this is no longer an acceptable way from both ecological and economical point of view. A sustainable alternative is the use of rubber and polyethylene terephthalate (PET) as second raw materials, for developing new products.

Huge amounts of rubber wastes result from car tyres and many papers report the use of scrap tire rubber in cement mortar and concrete (Siddique and Naik, 2004) and in asphaltic

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concrete mixes (Oner and Sengoz, 2015; Karacasu et al., 2015) as a filling material in road construction (Eldin and Senouci, 1993), as a conductive filler to obtain composite materials for electric components (Ahverdov et al., 2006; Zubko et al., 2009), and as composite matrix or filler along with plastics for construction applications.

Poly(ethylene terephthalate) (PET) is used for various applications due to its excellent mechanical strength, inertness to many chemical reactions, and thermal resistance (Awasthi et al., 2010); however, although largely investigated, PET recycling does not represent a solved problem when considering its use as second raw material.

The main problems with composites based on rubber and PET are the weak adhesion interfaces and phase separation because these components are immiscible. This leads to large interfacial tensions and, in general, to poor physical-chemical properties. Therefore, a compatibility agent should be added; in an attempt to develop composites fully based on wastes, previous studies showed that waste high density polyethylene (HDPE) supports the development of strong interfaces among rubber and PET (Cosnita et al., 2013). Besides the compatibility effect, the use of HDPE can decrease the processing temperature, support interfacial adhesion, and allow cost reductions.

The composites have weak intermolecular forces between the non- or slightly polar components. Therefore, the PET percentage reported in previous composites was limited (35%) (Cosnita et al., 2013; Cazan et al., 2013). However, the tensile strength of PET (47 N/mm<sup>2</sup>) is almost double compared to rubber (22 N/mm<sup>2</sup>); thus, PET inclusion in a higher ratio might be of interest in obtaining composites with higher mechanical performances and low cost, through an inexpensive and lower energy intensive process.

To increase the PET content, interfaces with increased strength should be developed and one path is to increase the surface polarity of the components by functionalization. Basically, polymers functionalization aims at improving the compatibility with other polymers or as reactive treatment, using agents in various mixtures, to obtain composite materials with controlled morphology and good mechanical properties. Increased compatibility can also be obtained by tailoring the morphology of the blends, by decreasing the size of the dispersed phase or by improving the interfacial adhesion between the two phases, and by minimizing the interfacial tension (Yousfi et al., 2013; Vladuta et al., 2009, 2010).

There is an increased interest in developing new methods to functionalize the surfaces for changing the properties according to given applications. Functionalization of polymers surface can be obtained by using different methods: physical deposition/adsorption, wet chemical and plasma techniques. The method selection mainly depends on cost, materials specifications and requirements and possible implementation in an industrial production process. Other criteria such as safety, toxicity and environmental effects should also be considered.

Literature mentions that the PET surfaces can be functionalized by hydrolysis (López-Fonseca et al., 2009; Kao et al., 1998), reduction (Bu'I et al., 1993), glycolysis (Viana et al., 2011; Zhu et al., 2012), aminolysis (Ellison et al., 1982; Fukatsu, 1992), amination (Nissen et al., 2008) and carboxylation (Yang et al., 2000). These processes were performed to introduce/attach to the PET surface reactive groups (hydroxyl, ether, amino, amine, carboxyl, etc.), that can adjust the surface

free energy, to increase the hydrogen bonding and to facilitate chemical bonding between the material components.

Plasma treatment is probably one of the most used techniques for polymer surface treatment (Kogelschatz, 2003) that can lead to better adhesion strength. It is an ecologically method and is gradually replacing traditional wet chemical techniques, which usually involve application of ecologically unfriendly chemicals. The surface incorporation of polar groups, such as carbonyl, carboxyl and hydroxyl, during the plasma treatment, increases the surface energy of the polymers, respectively the wettability (Nastuta et al., 2008). A drawback of plasma treatment for polymers activation is ageing. Functional groups formed on the plasma treated surface are not stable in time (the surface is at a non-equilibrium state and frequently recovers to its untreated state). Thus, the surface is spontaneously losing its hydrophilic character.

The polymers functionalization with surfactants could solve the above limitations and lead to improved surface properties and mechanical strength, in a technological simple and effective process. Particle size, crystallinity, process kinetics and morphology of the composite materials can be easily controlled by using surfactants. In mixed surfactant-polymer systems complexation is expected and the ionic surfactants better interact with neutral polymers than with non-ionic surfactants (Kwak, 1998; Hassan et al., 2013).

In this paper, to investigate the control of the surfactant-polymer system, a non-ionic surfactant (polyethylene glycol, PEG 400) and an anionic surfactant (sodium dodecyl sulphate, SDS) were selected. Studies on SDS interaction with polyolefin were reported to increase the compatibility of carbon nanotubes with the polymer matrix (Cheng et al., 2012; Lu et al., 2007) but, to the best of our knowledge, there are no reports on PET functionalization with PEG 400 or SDS, to develop composite materials.

The paper reports on novel composite materials obtained using wastes (tire rubber, PET, HDPE) and investigates the effect of PET component functionalization on the structure, morphology and mechanical properties of the resulted composites. The physical and chemical interface properties in the rubber-PET-HDPE composites and their influence on the mechanical response were correlated with the crystalline structure (XRD), composition (FTIR), morphology (SEM), and with the surface energy values (contact angle). According to their properties, these composite materials can be used as construction materials, reducing thus large amounts of wastes.

## 2. Experimental

### 2.1. Materials

Rubber tire waste was obtained from the Radburg company (Romania). Rubber from truck tires was used to obtain the composites; this contains natural rubber (43%w) and synthetic rubber (styrene butadiene rubber and butadiene rubber < 22.8%w). The tire rubber contains vulcanizing agent (sulphur < 0.8%w), accelerators (MBT/TMT < 0.8%w), inorganic activators (calcium/zinc oxide < 3.3%w), other ingredients (carbon black < 27%w), plasticizers (mineral oil), antioxidants and antiozonants (< 1.3%w) and other components (< 1%w). The rubber tire density is 0.87 g/cm<sup>3</sup> and the tensile strength is 34.67 N/mm<sup>2</sup>.

The tires are processed by the company on specially designed machines and rubber mills. The procedure is essentially mechanical and runs four phases of grinding: cutting beads, shredding (pieces of about 100 mm), granulation (granules from 0 to 15 mm) followed by blades grinding to obtain granules and rubber powder in pieces ranging from 0.2 to 6 mm.

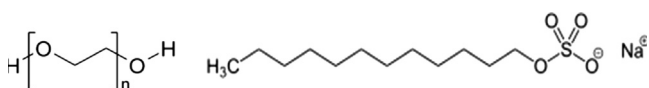
The plastic wastes, PET and HDPE, were purchased as small pellets with an average diameter of 1 cm from the Eco Green company (Romania), that processes plastic household wastes. The plastic wastes were further milled (centrifugal mill ZM 200, Retsch) to obtain grains with the average size of 1 mm with the following densities: for PET is 1.22 g/cm<sup>3</sup> and for HDPE is 0.89 g/cm<sup>3</sup>.

In the composite development the tire rubber was used as matrix, PET as dispersed phase in the polymer–polymer composite and HDPE as additive to strengthen the PET/rubber interface.

## 2.2. PET functionalization

To increase the interfacial adhesion in the composite material, the component with the highest hydrophilicity (PET) was functionalized with 1% solutions of SDS (Alfa Aesar, 99%) and PEG 400 (Alfa Aesar, 99%), prepared using distilled water. Both surfactants are hydrophilic and have low toxicity; PEG 400 is a low-molecular-weight grade polyethylene glycol, Fig. 1a, and SDS is an anionic surfactant with the formula H<sub>3</sub>-(CH<sub>2</sub>)<sub>11</sub>OSO<sub>3</sub>Na, Fig. 1b.

For functionalization, the milled PET grains were inserted into the 1% surfactant solution (SDS, respectively PEG 400), for 1 h. Then, they were dried (200–300 ECV type thermostat) at 80 °C for 60 min, before using them to obtain the composites.



**Figure 1** (a and b) Structural formula for PEG 400 and SDS surfactant.

## 2.3. Composites synthesis

Blends of rubber–PET–HDPE at various compositions were prepared by compression moulding (thermostatic oven type ECV 200–300), in two series of experiments: at 220 °C (samples *Type a*) and 240 °C (samples *Type b*). Two moulding durations were investigated: samples *Type 1*: 60 min and samples *Type 2*: 30 min, respectively. Samples of 15 g were obtained as composites with mass ratio rubber:PET:HDPE = (60 – x):x:5, where x = 35; 40; 45; a volume of 20 mL surfactant solution 1% was used to functionalize the corresponding amount of PET. The following compositions were studied in: composite *Type a*: rubber: PET:HDPE = 60:35:5; composite *Type b*: rubber:PET:HDPE = 55:40:5, and rubber:PET:HDPE = 50:45:5 – composite *Type C*.

The ratio functionalized PET:solution was 5.25–6.75 g:20 mL for obtained samples (depending on the composite composition). The effect of the functionalizing additives was comparatively investigated with samples using PET that was not functionalized; thus, three series of rubber:PET:HDPE composites were obtained, using

- PET functionalized in SDS solution 1%, samples *Type S*;
- PET functionalized in PEG 400 solution 1%, samples *Type P*;
- Un-functionalized PET, samples *Type N*.

The sample preparation data and their codes are given in Table 1.

## 2.4. Characterization

### 2.4.1. Composition and structure properties

The chemical structure of the composites and the interface bonds were investigated using Fourier Transform Infrared (FTIR Spectroscopy, Spectrum BX Perkin Elmer) in reflectance mode, in the range from 600 to 4500 cm<sup>-1</sup> and a scan resolution of 4 cm<sup>-1</sup>.

The crystalline structure and structural changes induced by the PET functionalization in the composite materials were

**Table 1** Sample codes and preparation parameters.

Sample composition (weight ratio)	Moulding duration (min)	$T_{\text{moulding}}$ (°C)	Type of samples with		
			PET	PET–SDS	PET–PEG
Rubber:PET:HDPE 60:35:5	60	220	1a-AN	1a-AS	1a-AP
		240	1b-AN	1b-AS	1b-AP
Rubber:PET:HDPE 55:40:5	60	220	1a-BN	1a-BS	1a-BP
		240	1b-BN	1b-BS	1b-BP
Rubber:PET:HDPE 50:45:5	60	220	1a-CN	1a-CS	1a-CP
		240	1b-CN	1b-CS	1b-CP
Rubber:PET:HDPE 60:35:5	30	220	2a-AN	2a-AS	2a-AP
		240	2b-AN	2b-AS	2b-AP
Rubber:PET:HDPE 55:40:5	30	220	2a-BN	2a-BS	2a-BP
		240	2b-BN	2b-BS	2b-BP
Rubber:PET:HDPE 50:45:5	30	220	2a-CN	2a-CS	2a-CP
		240	2b-CN	2b-CS	2b-CP

studied using X-ray diffraction (XRD, Bruker, D8 Discover, with a  $\text{CuK}_\alpha$  radiation source).

#### 2.4.2. Thermal properties

Differential scanning calorimetry (DSC, PerkinElmer, DSC-2) was used for the thermal characterization of the composites. The melting temperature ( $T_m$ ), and melting enthalpy ( $\Delta H_m$ ) of the un-functionalized and functionalized PET, were estimated based on the experimental data collected in inert atmosphere ( $\text{N}_2$ ), from 100 to 300 °C, at a heating rate of 10 °C/min.

#### 2.4.3. Surface properties

Static contact angle measurements based on the sessile drop method were performed and analysed using an OCA-20 contact angle meter (DataPhysics Instruments). The liquids used for measurements were distilled water ( $\sigma = 72.10$  mN/m,  $\sigma^p = 52.20$  mN/m,  $\sigma^d = 19.90$  mN/m) and NaCl 3.5% solution ( $\sigma = 73.76$  mN/m,  $\sigma^p = 23.02$  mN/m,  $\sigma^d = 50.26$  mN/m). Drops of 3  $\mu\text{L}$  were deposited on the surface of the polymer composite, and the measurements were made after 30 s, time considered sufficient for the drop to reach thermodynamic equilibrium at the surface; thus, Eqs. (1) and (2) could be applied. Based on the experimental contact angle data, the work of adhesion ( $W_a$ ), the surface energy ( $\sigma_{LV}$ ), and its polar and dispersive components were obtained ( $\sigma_{LV}^p$ ,  $\sigma_{LV}^d$ ), along with the polarity ( $P$ ) using the Owens, Wendt, Rabel and Kaelble (OWRK) method (Fowkes, 1967; Busscher, 1984), according to Eqs. (1)–(4):

$$W_a = \sigma_{LV}(1 + \cos \theta) \quad (1)$$

$$W_a = 2\sqrt{\sigma_{LV}^p \sigma_{SV}^p} + 2\sqrt{\sigma_{LV}^d \sigma_{SV}^d} \quad (2)$$

$$\sigma_{LV} = \sigma_{LV}^p + \sigma_{LV}^d \quad (3)$$

$$P = \frac{\sigma_{LV}^p}{\sigma_{LV}^p + \sigma_{LV}^d} \quad (4)$$

The morphology of the composite surface was investigated using a scanning electron microscope (SEM, Hitachi, S3400N, type II); quantitative elemental analysis of the samples surface was performed using EDX (Thermo, Ultra Dry, Noran System 7, NSS Model, 2,000,000 counts/s), with the sensitivity down to a few atomic percentages.

#### 2.4.4. Mechanical properties

Stress–strain and elasticity modulus were experimentally evaluated for each of the prepared formulations. The Zwick/Roell Z20 universal testing machine was used for tensile tests, at a crosshead speed of 100 mm/min, according to SR EN ISO 527-4:2000.

Compression resistance was tested on the same mechanical testing equipment, according to SR EN ISO 527-4:2000.

The tensile and compression tests were carried out for at least five samples of each prepared formulation and the mean value of the results is reported.

Impact strength: the standard Izod impact test was applied using Impact (Galdabini, Italy) as per SR EN ISO 180:2001. Experiments were done at room temperature for five specimens and the mean value is reported.

### 3. Results and discussion

#### 3.1. Functionalization of PET

The polymer chains interact with both the polar/ionic parts and the hydrocarbon chain of the surfactants; thus, PET–surfactant interactions can be of electrostatic and/or dispersive types. During functionalization with SDS (at a concentration higher than the critical micelle concentration,  $\text{CMC} = 2307$  ppm = 0.23%), the polymer chains support the formation of SDS micelles/aggregates bounded on the PET chains, Fig. 2.

Therefore, the PET macromolecular chains will be the subject of rearrangements and stretching, with opening of the SDS micelles and orientation in hydrophobic–hydrophobic PET–SDS interactions, that leave the hydrophilic part outwards, pushing hydrophilic areas at the surface of the system.

When using the PEG 400 surfactant, the similarities between the surfactant and the polymer may led to extensive dispersive or slightly polar interactions surfactant–polymer, in certain position on the PET chains.

Following functionalization, the PET surface state will change, the interfaces in the composite might contain different bonds and the transition temperatures will be modified; the functionalization process requires re-optimizing the composition and the technical parameters: the PET percentage in the composite, the processing temperature and its duration.

#### 3.2. Composition and structural properties

The chemical structure/interface bonds of the PET component (un-functionalized and functionalized) and of the composites were investigated using Fourier Transform Infrared Spectroscopy analysis. The FTIR spectra of the composites contain several bands belonging to the basic components, but new bands appear as a result of mechanical adhesion during moulding, along with physical or chemical bonds formed between components because of their affinity or due to the oxidative processes, with development of new interfaces.

The FTIR spectra of un-functionalized PET and functionalized PET are shown in Fig. 3a–c. The variations in the spectra measured within the wave number range of 600–1000  $\text{cm}^{-1}$ , are associated with the vibrations of unsaturated structures, mainly the bending vibrations of the C–H groups at the C=C bonds, corresponding to the aromatic nuclei.

The FTIR spectra of un-functionalized PET show bands at 1018  $\text{cm}^{-1}$  (C–O stretching), and 873  $\text{cm}^{-1}$  ( $\text{CH}_2$  rocking), which are attributed to the gauche/amorphous conformation.

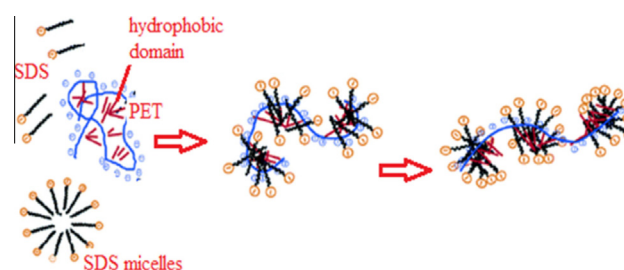
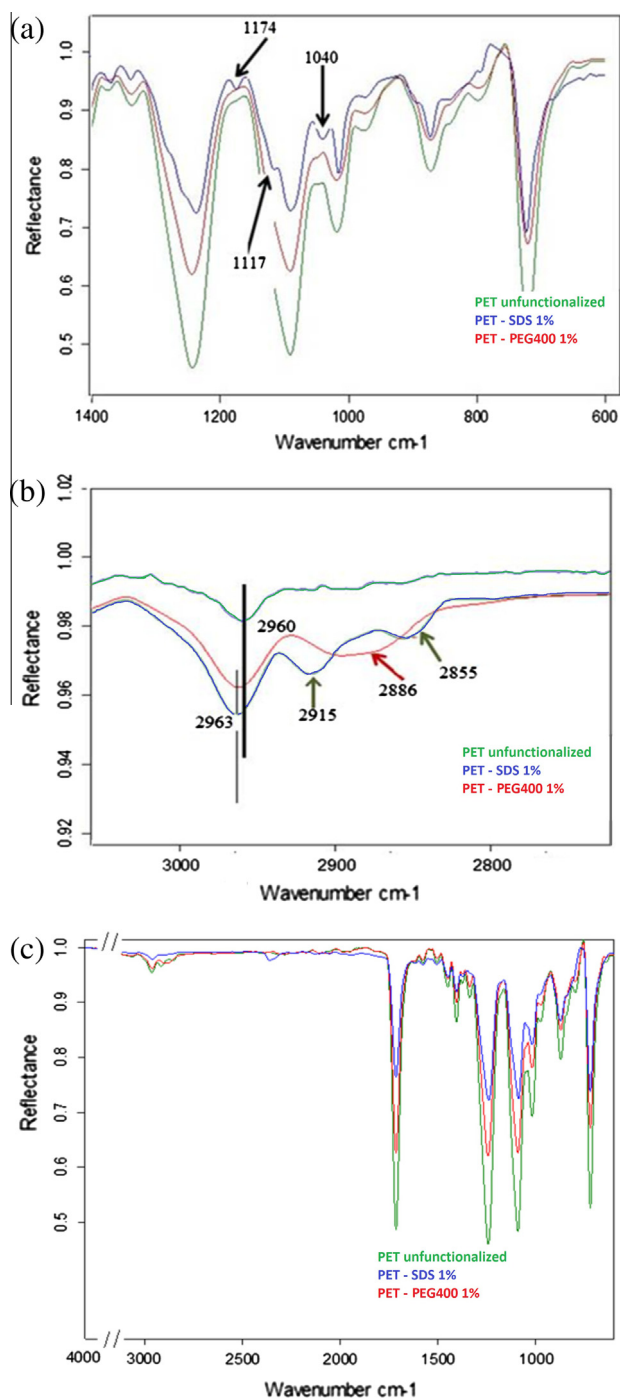


Figure 2 Formation of SDS micelles on PET chain.



**Figure 3** (a-c) FTIR spectra for un-functionalized PET, PET-SDS and PET-PEG.

Other spectral features confirm the PET crystallinity, such as the strong band corresponding to the carbonyl stretching band at  $1715\text{ cm}^{-1}$ . This spectral pattern is determined by the ordered structure in crystalline PET where the carbonyl groups are coplanar with the benzene rings.

There are displacements of the characteristic bands, as those at  $944\text{ cm}^{-1}$ , corresponding to the ethylene glycol moiety in the *trans* conformation which also indicates crystallinity in PET. This band is shifted to lower wavelengths for functionalized PET ( $914\text{ cm}^{-1}$  for PET-SDS and  $923\text{ cm}^{-1}$  for PET-

PEG), outlining a crystallinity decrease in the functionalized PET. Displacement can be observed in the reflectance maxima of some bands for PET-PEG, such as those at  $1448\text{ cm}^{-1}$  displaced to  $1456\text{ cm}^{-1}$  corresponding to C=C vibrations and  $-\text{CH}_2$  of ethylene unit planar vibrations, or those at  $1088\text{ cm}^{-1}$  moved to  $1092\text{ cm}^{-1}$ , corresponding to the aromatic nuclei and vibrations of the *gauche* conformation. This means that some of the dipoles existing in the polymers undergo vibration alterations due to the change in their close vicinity, following the functionalization effect.

After the functionalization of PET with SDS structural and conformational changes occur. Characteristic bands of the group  $-\text{SO}_3\text{H}$  are between  $1245\text{--}1155\text{ cm}^{-1}$  and  $1080\text{--}1040\text{ cm}^{-1}$ . In the PET-SDS spectra, the  $-\text{SO}_3\text{H}$  band appears at  $1174\text{--}1117\text{ cm}^{-1}$  and  $1040\text{ cm}^{-1}$  (these bands overlap with the specific aromatic nuclei and *gauche* conformers' vibration). These results are consistent with contact angle analysis; thus, the SDS molecules bind to PET with the hydrophobic part, leading to smaller contact angle values.

In the composites spectra with PET-SDS and PET-PEG there are missing bands at  $2916\text{ cm}^{-1}$  ( $-\text{CH}_2-$ ),  $2839\text{ cm}^{-1}$  ( $\text{CH}_2=\text{CH}-$ ),  $2128\text{ cm}^{-1}$  (intramolecular OH gr. C=O),  $1715\text{ cm}^{-1}$  (C=O)O- terephthalate units), and  $1267\text{ cm}^{-1}$  ( $-\text{CO}-$ ). The absence of these bands indicates the formation of new physical-chemical interfaces between the components in the composites. There are interactions at the molecular level between PET and SDS thus increasing the ability of PET to form the polymer-matrix interfaces. Oxidative degradation (absence of band  $2839\text{ cm}^{-1}$ ) also takes place, obtaining a new radical that initiates chemical reactions in composite, involving the C=O or the intramolecular  $-\text{OH}$  groups (band  $2128\text{ cm}^{-1}$ ), and depolarizing the surface. The new bands in the spectra of functionalized PET ( $2915\text{ cm}^{-1}$  and  $2855\text{ cm}^{-1}$  for PET/SDS;  $2886\text{ cm}^{-1}$  for PET/PEG corresponding to  $\text{CH}_2=\text{CH}-$ ) confirm the surface changes in the PET structure.

The FTIR spectra of the samples obtained at 30 min moulding have similar bands as samples obtained in 60 min moulding but with higher intensity.

A comparative analysis of the FTIR bands for (un)functionalized PET and for the three composite samples is presented in Table 2.

As a result of oxidative degradations on macromolecular chains from the rubber-PET-HDPE composites, new bands appear at  $3150\text{ cm}^{-1}$  ( $-\text{OH}$ ),  $1867\text{ cm}^{-1}$  (C=O, acid) and  $1162\text{ cm}^{-1}$  (*gauche* conformers). Another important spectral range significantly influenced by the amorphous/crystalline state of the composites includes the bands at  $1162\text{ cm}^{-1}$  (C-O stretching),  $924\text{ cm}^{-1}$  and  $813\text{ cm}^{-1}$  corresponding to *trans* and *gauche* conformers. These bands are responsible for the crystallinity in the composites.

The PET crystallization and high stereoregularity in the macromolecules are due to nuclei position of phenylene and coplanar ester groups, Fig. 4a. PET characteristic peaks were identified at  $2\theta = 16.8^\circ$  and  $25.2^\circ$ , with an overall crystallinity degree of 56.8%. In PET functionalized with SDS and PEG, this band moved to lower wave numbers (at  $1713\text{ cm}^{-1}$  and  $1712\text{ cm}^{-1}$  respectively). The crystallinity percentage in the composite type I-S and type I-P, decreases with 8.9% respectively 4.4% (Fig. 4b), as a result of structural changes affecting the *trans* conformers during functionalization (the band at  $944\text{ cm}^{-1}$ ).

**Table 2** The main bands ( $\text{cm}^{-1}$ ) in the FTIR spectra of the PET components and rubber–PET–HDPE composites.

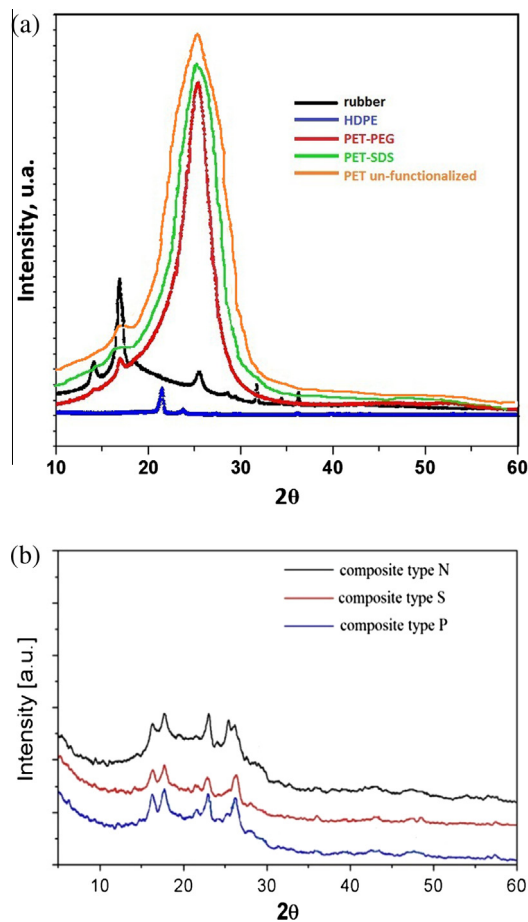
Observation	Materials					
	PET	PET SDS	PET PEG	1b-BN	1a-CS	1a-CP
Valence vibration —CH	—	3620	—	3686	—	—
—OH primary alcohol	—	—	—	—	3150	3163
—CH $\delta$ —CH <sub>2</sub>	2960	2963 2915	—	2916	—	—
—CH=CH <sub>2</sub>	—	2855	2886	2839	—	—
—OH intramolecular; C=O aliphatic	2359	—	—	2128	—	—
—C—H aromatic; C=O acid	—	—	—	—	1867	1866
Stretching vibration of C=O terephthalate units	1715	1715	1715	1715	—	—
C=C from aromatic nuclei	1576	—	—	1575	1598	1597
	1506	1525	—	—	1528	1529
C=C vibration in the plan; CH <sub>2</sub> of ethylene units	1448	1401	1456	1447	1483	1484
	1405	—	—	—	1430	1430
Stretching vibration of —C—C— from —C—CH <sub>3</sub>	—	—	1349	—	1360	1361
Valence vibration C—C	—	—	1295	1267	—	—
	1240	1240	1248	—	—	—
Aromatic rings; gauche conformers vibration; symmetric stretching vibrations of the group —SO <sub>3</sub> H	1170	1174	—	—	—	—
(1245–1155; 1080–1040 $\text{cm}^{-1}$ ) and SO <sub>2</sub> <sup>-</sup> in sulphone	—	1117	—	—	1162	1163
(1360–1335 $\text{cm}^{-1}$ ; 1170–1140 $\text{cm}^{-1}$ ) (Lambert et al., 1987)	1088	1088	1092	—	—	—
	1018	—	—	1027	—	—
	—	1040	—	—	1040	—
Vibration transconformers ethylene glycol	944	914	923	—	924	922
Aromatic rings; gauche conformers vibration	873	873	884	—	813	813
Deformation vibration of styrene nuclei; leg. C—H terephthalate units	721	756	723	—	756	756

**Table 3** The per cent values of crystallinity in rubber–PET–HDPE composites.

PET	$\chi_c$ (%)	PET–SDS	$\chi_c$ (%)	PET–PEG	$\chi_c$ (%)
<i>The per cent of crystallinity in samples obtained at 60 min</i>					
1a-AN	28.8	1a-AS	30.3	1a-AP	34.7
1b-AN	27.5	1b-AS	27.0	1b-AP	27.1
1a-BN	27.2	1a-BS	32.0	1a-BP	29.1
1b-BN	29.2	1b-BS	34.1	1b-BP	33.4
1a-CN	25.6	1a-CS	28.2	1a-CP	25.7
1b-CN	23.4	1b-CS	31.1	1b-CP	28.4
<i>The per cent of crystallinity in samples obtained at 30 min</i>					
2a-AN	31.5	2a-AS	32.7	2a-AP	29.8
2b-AN	23.6	2b-AS	26.6	2b-AP	27.9
2a-BN	27.6	2a-BS	30.5	2a-BP	31.5
2b-BN	28.2	2b-BS	33.7	2b-BP	33.6
2a-CN	25.4	2a-CS	24.7	2a-CP	28.8
2b-CN	26.9	2b-CS	28.4	2b-CP	30.4

In the Type 1 composites series, the samples 1b-BS and 1a-AP recorded the highest crystallinity degrees (34.1% and 34.7%), as presented in Table 3, while for the Type 2 samples the values slightly decrease by 1–1.5%.

The data in Table 3 outline that SDS effect can be well observed at the higher processing temperature (240 °C) and at a high PET percentage (40% and 45%), acting as a possible plasticizer and yielding ordered structures with increased crystallinity. The SDS molecules will change orientation: with the ionic group towards the PET polar zone and the hydrocarbon chain at the surface of the hydrophobic components in the system, particularly those who impose crystallinity to the

**Figure 4** XRD diffraction for: (a) rubber, HDPE and (un)functionalized PET; (b) composites with (un)functionalized PET.

composite (HDPE). PEG functionalization allows a similar trend but with lower overall effect, as a possible result of a lower ordering effect (consequence of weaker interactions with PET).

According to the experimental results, the composites crystallization was suggested to be due to PET functionalization (with SDS and PEG 400) and the nuclei migration across the interface or altered chain mobility at the interface. This modification provides nucleation sites for crystallites formation with a consequent increase in the tensile modulus and in the mechanical strength of the compounds. The increase in the PET content slightly lowers the crystallinity degree and a similar effect is observed at longer processing duration. For both processing durations (60 and 30 min) the highest crystallinity degrees correspond to the samples containing 40% of PET obtained at 240 °C, functionalized with SDS (sample 1b-BS, 2b-BS) and with PEG (1b-BP and 2b-BP).

### 3.3. Thermal properties

The thermal characterization (DSC analysis) is in good agreement with the FTIR measurements, indicating the modification in the thermal behaviour of PET due to its functionalization. Differential scanning calorimetry results showed that the PET-SDS sample recorded the lowest melting temperature ( $T_m = 200.39$  °C), Table 4 and Fig. 5. The decreased transition temperatures and the melting enthalpies of functionalized PET allowed the assumption that rubber-PET-HDPE composites may be obtained at lower temperatures than 240 °C (temperature previously optimized for these types of composites with lower PET content (Cazan et al., 2014)).

### 3.4. Surface properties

By adding the functionalized PET in composites, the control of the interfacial tension is aimed at, to promote adhesion between the blended components, resulting denser structures in the composites. However, PET functionalization will also influence the composites surface; therefore, contact angle measurements were done to evidence the nature of changes and the surface energy of the composites.

In a first step, the polar and dispersive contributions of the surface energies were calculated for the PET component, based on the initial contact angle values, and the data are given in Table 5.

The functionalization of PET (with SDS and PEG 400) increases the surface energy, due to the development of an area dominated by polar components, with a significant increase of  $\sigma_{SV}^p$ . This represents over 69.36% of the total surface energy for PET-SDS and 62.97% for PET-PEG. Thus, the PET sample functionalized with SDS shows the best hydrophilic

properties, and can be best wetted by NaCl solutions, confirming the uniformly distributed polar groups at the surface. The opposite effect, represented by low surface energies (with the majority dispersive component) is recorded for sample with un-functionalized PET. For the PET-PEG component, the highest value of the contact angle was recorded; however, the highest surface energy was found for this sample (with predominant polar component, 37.23 mN/m, given the amount of oxygen present in PEG), confirming the PEG effect that promotes a higher homogeneity of the surface charge.

These results are consistent with FTIR analysis, and indicate that functionalization can be a tool to control the hydrophilicity/hydrophobicity of the composites surface.

Further on, surface energy experiments for the composite sample Type 1 (moulding duration of 60 min) were done and the results are presented in Table 6.

In the N type composite series (un-functionalized PET), the contact angle values decrease with increasing the PET percentage, supporting a hydrophilic character of the surface. A similar effect is observed for composites with PET-SDS (composite type S) proving an increased wettability, thus a higher surface contribution of PET (more polar than the rubber matrix). By comparing the N and S sample types, the SDS effect is obvious, as the un-functionalized samples are more hydrophilic; this could be a result of the surface composition or of the surface morphology. In the P-type composites (PET-PEG series) an opposite trend is observed, with increased hydrophobicity, thus a predominant hydrocarbon-rich surface or a less density of highly polar groups, as result of a possible increased stability to side oxidation effects during processing.

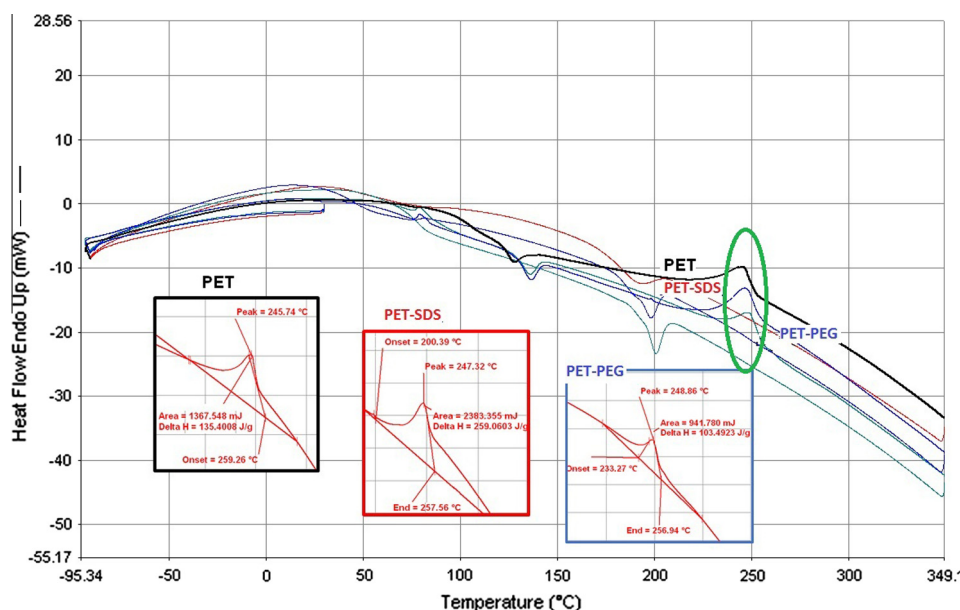
The moulding temperature also influences the surface energy. Basically, higher processing temperatures are responsible for two main effects with opposite consequences: (1) a better interface adhesion and (2) a higher oxidation likelihood, supporting the development of polar groups (carbonyl, carboxyl) or reactive polar bonds as -OH (confirmed by FTIR). The results show that the PET composition and functionalization have a significant influence in balancing these two effects: higher functionalized PET content supports a lower surface energy, with a more evident effect in the P-type composites, confirming the higher oxidation stability.

To investigate the effect of the moulding duration, similar investigations were done for the samples of Type 2 (processing duration: 30 min) and the results are given in Table 7.

The values corresponding to the samples moulded for a shorter duration show a more significant effect of the processing temperature that leads to higher surface energy for all the samples (except one, 2b\_AN); this may be the result of faster oxidations that, at longer processing durations (60 min) can further promote interfacial bonds and a surface redistribution of the components. This assumption is also supported by the reversed variation of the surface energy with

**Table 4** Thermophysical parameters for PET, PET-SDS, PET-PEG.

Materials	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_{\text{cris}}$ (°C)	$\Delta H_m$ (J/g)	$T_g$ (°C)	$\Delta C_p$ (J/g °C)
PET	259.26	135.40	117.71	-65.15	55.20	1.83
PET-SDS	200.39	259.06	147.97	-33.66	44.72	3.31
PET-PEG	233.27	103.49	206.50	-29.94	46.48	3.55



**Figure 5** Differential scanning calorimetry for un-functionalized PET, PET-SDS, and PET-PEG.

**Table 5** The value of contact angle and surface tension for the PET component.

Materials	$\theta_{\text{water}}$ (°)	$\theta_{\text{salt}}$ (°)	$\sigma_{SV}$ (mN/m)	$\sigma_{SV}^p$ (mN/m)	$\sigma_{SV}^d$ (mN/m)	Polarity (%)
PET	79	85	33.21	11.05	22.16	33.27
PET/SDS	72	68	45.41	31.50	13.19	69.36
PET/PEG	81	87	59.12	37.23	21.89	62.97

the PET composition, registered for both functionalized PET series of samples (Type S and Type P).

The surface energy data outline the sensitivity of the surface composition and morphology to the processing parameters; therefore, further investigations were done on SEM images (morphology) and EDX analysis (surface composition) and the results are presented in Fig. 6. Analyses were collected from four or five different zones, to outline the specifics of the composite components; the components below 0.5%w were not mentioned as their contribution proved to be quite randomly distributed at the surface. Three representative samples were discussed but similar results were registered for all the samples of types N, S and P.

The data allow to distinguish the phases and interfaces in the composite and between the components. As expected, the composite is a mix of large aggregates (where chemical strong interfaces could be developed) and aggregates composed of smaller grains among which mechanical interfaces are observed.

According to the surface composition, zones 1 and 2 are rich in rubber (also confirmed by S from vulcanizing and by Ca and Si used as oxides in fillers) and HDPE. The presence of oxygen in these areas shows improved oxidation stability (zone 1, with % O < 14%) or higher oxidation sensitivity (zone 2 with % O > 21%). These aggregates may also be responsible for the crystalline part of the composite, due to the HDPE content.

By marking zone 3, the mechanical interfaces were highlighted, involving rubber (with traces of Si, Zn, S) and HDPE; the data, confirmed also by the FTIR results, show a slight/null involvement of PET, as this zone is oxygen poor.

Zone 4 indicates the PET scrap, as recording a high per cent of oxygen and the amounts of Na (sample 2a-CS) following PET functionalization with SDS. The elemental analysis on zone 5 shows that the PET functionalized composite also includes large voids, particularly larger for the Type P composite; this confirms that SDS promotes a better attraction among PET and the hydrocarbon components, thus denser composites.

Corroborating these observations with the surface energy data, it may be concluded that the surface energy mainly depends on the morphology and less on the surface composition; however, the surface oxygen content, thus the oxidation stability of rubber and HDPE during moulding is significantly influenced by functionalization and increased stability is attained on smaller aggregates when using functionalized PET-PEG (zone 2), confirming the improved homogeneity of the surface charge.

### 3.5. Mechanical properties

The mechanical properties are of interest, allowing to identify the best suited application for the tailored composites. The



**Table 6** Contact angle values and surface energies of the samples moulded for 60 min.

Code	Samples	$T_{\text{processing}}$ (°C)	$\Theta_{\text{water}}$ (°)	$\Theta_{\text{salt}}$ (°)	$\sigma_{SV}$ (mN/m)	$\sigma_{SV}^d$ (mN/m)	$\sigma_{SV}^p$ (mN/m)
<b>Samples with PET un-functionalization</b>							
1a-AN	Rubber:PET:HDPE	220	78.42	72.45	31.07	21.14	9.94
1b-AN	60:35:5	240	95.12	89.26	18.84	13.76	5.08
1a-BN	Rubber:PET:HDPE	220	63.24	59.47	42.10	24.75	17.34
1b-BN	55:40:5	240	59.45	58.37	43.79	22.89	20.90
<b>Samples with PET functionalization in SDS</b>							
1a-AS	Rubber:PET:HDPE	220	92.43	90.30	18.33	10.72	7.61
1b-AS	60:35:5	240	83.15	104.20	29.82	0.04	29.77
1a-BS	Rubber:PET:HDPE	220	80.63	85.40	24.46	8.09	16.37
1b-BS	55:40:5	240	97.90	88.10	20.37	2.99	17.38
1a-CS	Rubber:PET:HDPE	220	88.48	76.70	28.89	24.66	4.23
1b-CS	50:45:5	240	104.6	85.88	27.09	26.80	0.29
<b>Samples with PET functionalization in PEG 400</b>							
1a-AP	Rubber:PET:HDPE	220	92.43	81.10	39.50	3.68	35.83
1b-AP	60:35:5	240	64.10	88.00	47.85	0.48	47.37
1a-BP	Rubber:PET:HDPE	220	74.20	73.20	31.25	16.52	14.74
1b-BP	55:40:5	240	69.80	84.40	34.17	3.77	30.41
1a-CP	Rubber:PET:HDPE	220	93.52	87.41	20.07	14.71	5.36
1b-CP	50:45:5	240	92.43	98.22	16.54	12.32	4.22

results of the mechanical testing of the composites obtained at 60 min of moulding (Type 1) are shown in Table 8.

Literature data show that PET functionalization improves the mechanical properties of composites. The highest value of tensile strength was 2.01 N/mm<sup>2</sup> for the 1a-CP composite, but lower than CNT/PMMA composite (4.1 N/mm<sup>2</sup> for the 12 wt% CNT/PMMA composite) (Weng et al., 2014) and graphene/LDPE composite (12.5 N/mm<sup>2</sup>) (Han et al., 2014). However, functionalization does not always improve the mechanical properties, as for nanocomposites of waterborne polyurethane (WPU) reinforced with functionalized graphene

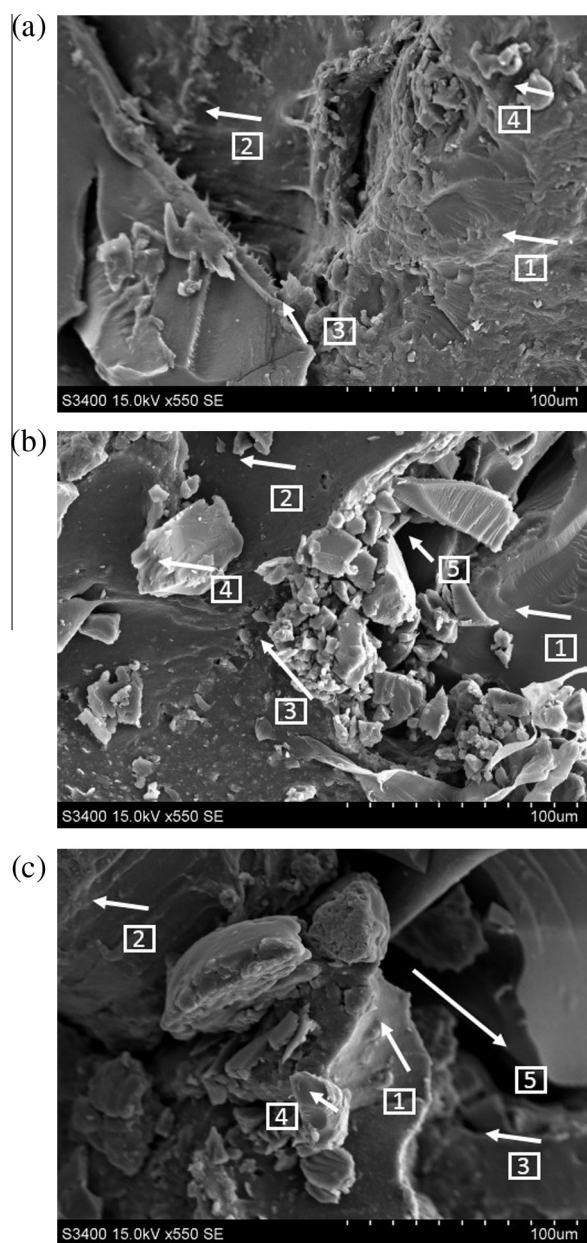
sheets (FGSs) (Choi et al., 2012), where the tensile strength and elongation at break, measured at high deformation, decreased with increasing FGS in the nanocomposite.

The results in this paper show that for a composite that only contains wastes, surfactant functionalization of PET represents an effective and low-cost path to improve the interfaces and thus the mechanical properties.

For the un-functionalized (type N) samples, the best mechanical properties (tensile strength and compression) are obtained for the 1b-AN composite; by increasing the PET percentage, the samples become increasingly brittle, and the mix-

**Table 7** Contact angle values and surface energies of the samples moulded for 30 min.

Code	Samples	$T_{\text{obtaining}}$ (°C)	$\Theta_{\text{apa}}$	$\Theta_{\text{sare}}$	$\sigma_{SV}$ (mN/m)	$\sigma_{SV}^d$ (mN/m)	$\sigma_{SV}^p$ (mN/m)
<b>Samples with PET un-functionalization</b>							
2a-AN	Rubber:PET:HDPE	220	81.29	78.23	29.18	19.09	10.09
2b-AN	60:35:5	240	83.41	85.14	23.41	11.40	12.01
2a-BN	Rubber:PET:HDPE	220	70.23	69.74	37.23	23.13	14.10
2b-BN	55:40:5	240	69.18	60.19	40.12	12.05	28.07
<b>Samples with PET functionalization in SDS</b>							
2a-AS	Rubber:PET:HDPE	220	91.36	75.19	32.28	30.08	2.21
2b-AS	60:35:5	240	65.19	87.99	44.84	0.73	44.11
2a-BS	Rubber:PET:HDPE	220	71.15	73.24	31.25	16.43	14.82
2b-BS	55:40:5	240	69.76	84.37	34.22	3.75	30.47
2a-CS	Rubber:PET:HDPE	220	86.52	88.97	20.65	8.32	12.33
2b-CS	50:45:5	240	82.59	81.11	24.91	13.70	11.21
<b>Samples with PET functionalization in PEG 400</b>							
2a-AP	Rubber:PET:HDPE	220	81.22	80.79	25.45	12.39	13.05
2b-AP	60:35:5	240	88.14	78.28	27.61	4.09	23.52
2a-BP	Rubber:PET:HDPE	220	89.35	92.31	18.65	11.61	7.04
2b-BP	55:40:5	240	87.48	78.08	27.48	5.55	21.93
2a-CP	Rubber:PET:HDPE	220	75.03	85.26	30.10	25.29	4.80
2b-CP	50:45:5	240	78.23	77.81	27.74	13.57	14.17



**Figure 6** SEM images of: (a) sample 2b-AN; (b) sample 2a-CS; (c) sample 2a-BP.

ture containing 45% of PET did not actually lead to an aggregated composite structure.

After PET functionalization, a larger PET amount ( $\geq 45\%$ ) could be incorporated in the composite and the mechanical strength is significantly modified, for both samples type S and P (PET-SDS and PET-PEG).

The S-Type samples (containing PEG-SDS) obtained at 220 °C have improved mechanical properties in terms of compression and impact compared with those obtained at 240 °C in good agreement with crystallinity degree. Sample 1a-CS shows remarkable compression resistance as due to the higher amount of PET-SDS incorporated in the matrix, stronger interfaces are developed (as confirmed by FTIR analysis). The PET functionalization improves the composites'

processing by decreasing curing temperature, as the thermal analysis shows.

The results show that PET functionalization with SDS has a stronger effect than with PEG, by possible electron conjugations as  $e^-$  (p- $\pi$ ) and  $e^-$  (p-p), and by changes of *trans-gauche* conformers, making it more reactive. In this case, new physical-chemical interfaces PET-rubber, PET-HDPE and rubber-HDPE were developed, mainly based on stronger electrostatic interactions promoted by the anionic SDS as compared to the polar PEG. These results are also supporting the assumptions made based on the SEM and EDX data which show denser structures for the S-type composites.

It is important to outline that the sample with the highest PET content in the P-type composites series also shows the highest mechanical/tensile strength, due to new mechano-physical interfaces between the hydrocarbonated part of functionalized PET and unsaturated part of rubber/HDPE.

These results show that PET can be incorporated in a larger amount if functionalized and the final application (requiring tensile strength and/or compression and/or impact resistance) will indicate the type of functionalizing agent to be selected.

To obtain these types of composite in a lower energy intensive process, the processing duration was reduced at 30 min and the results of mechanical testing are shown in Table 9.

The samples obtained at 30 min with un-functionalized PET have recorded poorer strength compared to the samples obtained during 60 min of moulding, outlining that, without functionalization, 30 min of processing is not enough to develop suitable interfaces.

The PET-functionalized composites show significant increase in the compression strength and impact resistance, while also preserving good tensile strength. The interface plays an important role in the mechanical properties of these composite materials, as here the load transfer from the matrix to the dispersed phase occurs. The blends with functionalized PET showed considerable improvement in mechanical properties over the blends with un-functionalized PET, as a result of a better adhesion when using functionalized PET. Additionally, this can be the result of lower degradation/oxidative side-processes that can affect both the components and the interfaces. These samples also have higher values of the elasticity modulus, because the functionalized PET has a higher modulus that provides less means of absorbing or dissipating energy.

The sample 2a-CS from type S has impressive compressive strength and good tensile and impact strengths, being the best in the S-Type series (and the best among all in terms of compression strength), because rubber is better maintaining its elastomeric properties during the shorter processing duration.

In type P samples the mechanical strength is lower compared to the Type S composites; however, in this series an amount of 45% PET allowed obtaining the higher mechanical resistance and the sample 2b-CP also has a high value of the Young's modulus.

The significant influence of the functionalized component supports the assumption that SDS or PEG is inserted between macromolecular chains, modifying not only the surface charge but also promoting interface relaxing. This assumption is confirmed by the high compressive strength compared with the reference specimens (with un-functionalized PET). The composite with the highest dimensional stability (2a-CS) was analysed on the fractured surface after the tensile test, using SEM, and the result is presented in Fig. 7.

**Table 8** Mechanical properties for samples obtained at 60 min.

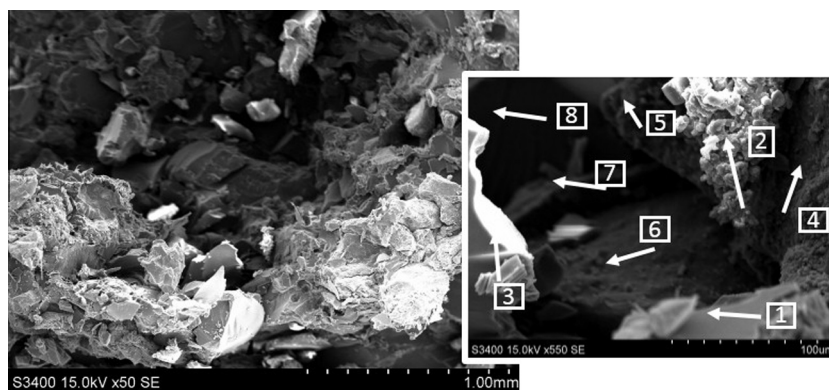
Type	Samples	$T_{\text{obtaining}}$ (°C)	$\sigma_{ir}$ (N/mm <sup>2</sup> )	$E$ (N/mm <sup>2</sup> )	$F_C$ (N)	$R_c$ (N/mm <sup>2</sup> )	Impact (kJ/m <sup>2</sup> )
<b>Samples with PET un-functionalization obtained at 60 min</b>							
1a-AN	Rubber:PET:HDPE	220	1.21	0.89	3541	25.41	9.36
1b-AN	60:35:5	240	1.57	2.56	6966	69.66	12.12
1a-BN	Rubber:PET:HDPE	220	1.35	1.09	2540	25.40	12.05
1b-BN	55:40:5	240	0.85	1.31	3120	31.20	10.56
<b>Samples with PET functionalization in SDS obtained at 60 min</b>							
1a-AS	Rubber:PET:HDPE	220	1.38	4.06	5534	55.34	32.85
1b-AS	60:35:5	240	1.09	1.06	3938	39.38	32.50
1a-BS	Rubber:PET:HDPE	220	1.15	2.05	5281	52.81	31.80
1b-BS	55:40:5	240	1.13	1.75	4526	45.26	26.96
1a-CS	Rubber:PET:HDPE	220	0.97	1.92	6123	61.23	21.32
1b-CS	50:45:5	240	1.21	2.15	5708	57.08	25.18
<b>Samples with PET functionalization in PEG obtained at 60 min</b>							
1a-AP	Rubber:PET:HDPE	220	1.02	0.27	4006	40.06	25.94
1b-AP	60:35:5	240	1.15	0.38	4679	46.79	23.59
1a-BP	Rubber:PET:HDPE	220	1.08	0.52	3896	38.96	14.83
1b-BP	55:40:5	240	1.06	0.46	4484	44.84	18.01
1a-CP	Rubber:PET:HDPE	220	2.01	1.20	5141	51.41	20.58
	50:45:5	240	1.87	0.84	4384	43.84	18.06

**Table 9** Mechanical properties for samples obtained at 30 min.

Type	Samples	$T_{\text{obtaining}}$ (°C)	$\sigma_{ir}$ (N/mm <sup>2</sup> )	$E$ (N/mm <sup>2</sup> )	$F_C$ (N)	$R_c$ (N/mm <sup>2</sup> )	Impact (kJ/m <sup>2</sup> )
<b>Samples with PET un-functionalization obtained at 30 min</b>							
2a-AN	Rubber:PET:HDPE	220	0.89	0.89	2145	21.45	10.52
2b-AN	60:35:5	240	0.93	1.56	3156	31.56	12.56
2a-BN	Rubber:PET:HDPE	220	0.72	1.09	3568	35.68	11.45
2b-BN	55:40:5	240	1.01	0.85	3522	35.22	9.36
<b>Samples with PET functionalization in SDS obtained at 30 min</b>							
2a-AS	Rubber:PET:HDPE	220	1.32	4.165	9448	94.48	39.66
2b-AS	60:35:5	240	0.98	0.351	9097	90.97	29.36
2a-BS	Rubber:PET:HDPE	220	1.25	1.956	7649	76.49	18.66
2b-BS	55:40:5	240	1.25	1.956	9587	95.87	41.50
2a-CS	Rubber:PET:HDPE	220	1.56	3.647	15,878	158.78	43.72
2b-CS	50:45:5	240	1.11	0.421	10,958	109.58	31.80
<b>Samples with PET functionalization in PEG 400 obtained at 30 min</b>							
2a-AP	Rubber:PET:HDPE	220	1.20	2.41	8921	89.21	30.12
2b-AP	60:35:5	240	0.92	1.79	7436	74.36	31.79
2a-BP	Rubber:PET:HDPE	220	1.07	1.21	7027	70.27	21.39
2b-1BP	55:40:5	240	1.31	2.55	8431	84.31	35.71
2a-CP	Rubber:PET:HDPE	220	1.47	2.24	9425	94.25	28.36
2b-CP	50:45:5	240	1.12	2.41	9178	91.78	32.84

The scanning electron microscopy images of the fractured surface show that the large aggregates of zone 1 are preserved; thus, stress failure occurs on the interfaces dividing the smaller aggregates. As stress-strain fractures lead to a variety of structures, eight zones were investigated by EDX. All the phases (except zone 4) have similar elemental content, thus derived from the same components (rubber, PET, HDPE), but in different per cent. Zone 4 only contains C and Si elements from rubber and HDPE. Based on the oxygen content, the PET

occurrence in the fractured surface can be approximated and can be corroborated with the shape of the ruptured zones to make an assumption on the stress failure order; thus, it is possible that during the tensile test, the zones rich in PET (mainly 2 and 6 but also 3) are firstly affected, followed by 1, 5 and 7 (containing PET and oxidation compounds), where the tensile force promotes sliding among the components, before fracture; the least affected zones are 6 and 7. Zone 8, containing only carbon could be allocated to the black carbon aggregates from



**Figure 7** SEM images of the fracture surface after tensile failure (1a-CS).

rubber. These results outline the need for focusing on PET as being the component mostly responsible for the mechanical strength in the composites.

#### 4. Conclusions

A path for increasing the PET content in composites with rubber matrix and HDPE compatibility agent was investigated. As PET and rubber compatibility is limited, the increased PET content can only be reached by surface/interface modifications and the paper presents a low-cost, technological simple path, based on wet-functionalization of PET using surfactant solutions, prior to the composite moulding. An anionic (SDS) and a non-ionic (PEG 400) surfactant was comparatively investigated and it was outlined that the different surface charges obtained on PET after functionalization significantly influence the interfaces and the open surface, and consequently the wettability and mechanical properties.

Functionalization has also the advantage of allowing lower processing temperatures that limit the side-oxidative processes and lower the production costs.

The results show that there is a need for jointly optimizing the composites composition, PET functionalization and the processing parameters, to tailor the mechanical and wettability properties, as the result of the control over interfaces and overall crystallinity, morphology, surface charge and macro-homogeneity.

According to the applications, these rubber-functionalized PET-HDPE composites can be obtained for indoor or outdoor applications, e.g. as construction materials. The best composite in terms of dimensional stability and mechanical performance was found to be the composite rubber-PET/SDS-HDPE obtained at 220 °C for 30 min of compression moulding. If very high compression strength is not a prerequisite in the application, the PET-PEG functionalized composites obtained in similar conditions, also represent good candidates for developing various plates, panels or other construction items.

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