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THERMAL AND SPECTRAL CHARACTERIZATION OF PP-TPE BLENDS

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Abstract

This paper presents the results of thermal analysis and spectral characterization of some polypropylene (PP) - thermoplastic elastomer (styrene-ethylene/propylene-styrene block copolymer) (TPE) blends. The thermal stabilities of different PP-TPE blends containing 0 - 20 % of TPE were assessed by isothermal differential scanning calorimetry **(***DSC). It was observed that particles reduced the degradation rate of the resulted material. Both the oxidation induction time (OIT) and the time to oxidation peak (t_m) values from isothermal measurements increase as increasing the TPE concentration. Similar conclusions were obtained from non-isothermal data. As the observed antioxidative effect is higher than that corresponding to the proportion of TPE, a synergistic behavior was concluded. The thermal effect of oxidation and melting peaks indicates that the blends are homogeneous in the investigated concentration range. The attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR) data are in agreement with those of thermal analysis. Some aspects about the optimum concentration of TPE on PP, were also evaluated from the experimental data.*

Key words: *PP - TPE blends, thermal analysis, spectral characterization, isothermal DSC, ATR-FTIR*

1. INTRODUCTION

Thermoplastic elastomers (TPEs), is an interesting category of polymers which combine rubber-like properties with the processing advantages of thermoplastics. Generally, TPEs are low modulus, flexible materials that can be stretched, similar to traditional thermo-set rubbers. TPE melt when the temperature exceeds a certain specific value. As compared to traditional elastomers, TPEs, present many advantages, such as design flexibility, lower fabrication costs, simpler processing time, little or no compounding required, completely recyclable scrap, lower consumption energy, total applicability of the forming processes specific for thermoplastics, better control of the product quality, more environmentally friendly, so on. [1].

Different types of TPE, presenting various chemical structures are known, most of TPE being block or graft copolymers [2]. Examples of TPE are polyurethanes (TPUs), co-polyesters (COPEs), polyamides (PEBAs), polyolefin based thermoplastics (e.g. Ziegler-Natta block copolymers, hydrogenated diene block-copolymers, polyolefin blends (TPOs), polyolefin alloys (TPVs) etc.) and styrene thermoplastic elastomers (S-TPEs, e.g. styrene-butadiene-styrene, styrene-ethylene/butylene-styrene, styrene-ethylene/propylene-styrene etc.) [2, 3]. They can be considered as more or less classic TPEs due to the fact that they are industrially produced for many years. However, new production processes and ameliorated polymer structures are continuously reported in this direction together other newer TPE categories, such as ionomers [2] or very low molecular weight - linear low density polyethylene (VLMW-LLDPE) [1].

Among TPE, styrene block copolymers are of wide importance. These co-polymers are synthesized by anionic polymerization in a non-polar solvent, in presence of organometallic catalysts (e.g. butyl lithium). By both accurate control of the polymerization temperature and reagents purity, the resulting polymer presents typical molecular weights from 100,000 to 300,000 g/mole, and narrow molecular weight dispersion (with a typical polydispersity index of 1.04 - 1.05). Such characteristics are essential to enable phase separation that is responsible for the elastomeric properties [4]. In some cases, special techniques, such as continuous polymer fractionation (CPF) [5] and continuous spin fractionation (CSF) [6] methods are applied for block copolymers preparative fractionation [7].

There are different structures in this category of the styrene TPEs:

- styrene-diene block copolymers, such as styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS) or styrene-(butadiene-isoprene)-styrene (S-(B/I)-S) block copolymers;

- styrene-olefins block copolymers, such as styrene-ethylene-propylene-styrene (SEPS) or styrene-ethylene-butylenes-styrene (SEBS).

The styrene block copolymers present interesting and useful properties due to their structure which consists in polystyrene domains dispersed in a rubber (e.g. poly-diene, ethylene-propylene or ethylene-butylene) matrix, hence they are applied in a wide range of applications, such as lithography techniques for micro and nanotechnologies [8], nanocomposite materials [9]. TPEs replace now the traditional rubbers in many applications. They can be readily mixed with other polymers, oil, and fillers, allowing versatile tuning of product properties [4]. Blends of TPEs with different polymers are widely used, as for example, to improve the impact strength of rigid thermoplastics [1], to increase the water treeing resistance of both XLPE and EVA insulation materials [10] or to increase the radiation strength of PP based polymeric materials [11] as well as to prepare various nanocomposite materials [9]. The applications range from radiation-sterilization of medical items [11], automotive, electronics, and sport products, to civil-engineering processes [12].

In this paper, the properties of several TPE-PP blends, containing a SEPS block copolymer of styrene and ethylene-propylene were studied. This work is a preliminary step, aiming the characterization and the optimization of the properties of several mixtures, TPE-thermoplastic polymer, in order to prepare materials with improved properties to be used as polymer matrix in further technical applications.

Polypropylene (PP) was chosen as thermoplastic polymer in this work because it one of the widespread and versatile polymers known, being used in different forms, in a wide range of applications.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1. Materials

Styrene-ethylene-propylene-styrene (S-EP-S) TPE in the form of black pellets was kindly supplied by an Europe-based company.

Iso-tactic polypropylene (J 700) pellets used in this study was of injection molding grade, with a MFI value of 14.0 g/10 min at 230 °C. Pellets containing 0, 5, 10, 15, 20 and 100 % TPE were prepared using a double-screw extruder with L/D = 25 and D = 90 mm according to specific procedure.

The resulted blend samples were denominated as PP/TPE *a*, where *a* is TPE content (percent).

2.2. Instruments and method

Both isothermal and non-isothermal (temperature ramp at constant heating rate) Differential Scanning Calorimetry (DSC) measurements were performed on a Setaram 131 evo (Setaram Instrumentation, Fr) instrument using the Calisto Data Acquisition application.

The calculations of different DSC parameters (e.g. thermal effects, oxidation induction time (OIT), oxidation onset temperature (OOT), glass transition temperature (T_g) and so on, were performed by Calsito Data Processing application of Setaram/AKTS.

For the isothermal measurements, the following procedure and conditions were applied: the sample was heated under inert atmosphere (nitrogen, 50 mL/min) from room temperature up to the testing temperature (190 °C), and then the air (50 mL/min.) was admitted in the analysis chamber of DSC instrument. The non-isothermal sequence of heating in nitrogen atmosphere was separately recorded.

In the case of non-isothermal measurements in air (temperature ramp, constant heating rate), the sample was heated form 30 °C to 350 °C in air atmosphere (50 mL/min.) at a heating rate of 10 K/min. Similar procedure was applied for the measurements in inert atmosphere, using nitrogen in the gas flow.

In all cases, 1 - 2 mg samples, sliced from pellets, were placed in 30 μL aluminum pans. A similar empty pan was taken as reference.

Attenuated Total Reflectance – Fourier Transform Infrared spectroscopy (ATR-FTIR) spectra were measured on a Jasco 4200 spectrometer. The ATR accessory Jasco ATR PRO 470-H with diamond crystal was mounted to enable the measurement of ATR-FTIR spectra. The following measurement conditions were used: wave number range: 4000 – 400 cm^{-1}; sample scan time: 48 scans; resolution: 4 cm^{-1}.

SEM micrographs was carried under field emission crossbeam workstation (FESEM-FIB) model Auriga made by Carl Zeiss SMT. Low accelerating voltages were applied (in the range of 1 kV) to ensure the images accuracy. An Everhart Thornley type detector (in chamber) was used for secondary electrons topography. The magnifications of SEM images were in the range of 500 X - 10.000X.

3. RESULTS AND DISCUSSION

Non-isothermal DSC scans in nitrogen atmosphere presented the following effects (see table 1):

a) A *glass transition* of polystyrene domains (figure 1), at around 90 °C, which is quite close to those usually reported for polystyrene domains in styrene TPE (see for example reference [3]). This behavior suggests that PS domains are not modified or they are less modified by interactions with PP matrix in the blends. In the case of PP/ TPE 100 sample, the T_g value is lower suggesting a certain

modification of PS domains possibly by interaction with PP and PE segments. Note also the lower value of the melting point of PP in PP/TPE 100 sample, which suggests different crystalline form of PP segments as compared to the homopolymer.

The ΔC_p values tend to slightly increase from PP/ TPE 5 to pure TPE (PP/TPE 100 sample) as the styrene content increases. An explanation of the fact that the T_g values are somewhat scattered could be the low content in polystyrene of the analyzed materials that make difficult the determination of T_g by DSC [13].

A relaxation process, occurring both in polypropylene and in TPE containing blends near to the glass transition can be another explanation for the mentioned dispersion of T_g and ΔC_p values. Similar relaxation process was considered to be responsible for the difficulties in determination of glass transition of PS domains in the case of styrene-butadiene block copolymers [3].

b) An *endothermic peak at ca. 120 °C* assigned to the melting of the polyethylene segments. The thermal effect increases with the TPE content in the blend, while the melting temperature tends to decrease in the same direction.

c) An *endothermic peak at ca. 164 °C* assigned to melting of the polypropylene (PP), including the blocks existing in TPE, which are probably in dissolved state in the PP matrix. The thermal effect decreases as increasing the TPE content (PP concentration decreases), while the melting temperature tends to decrease slowly in the same direction. In the case of the pure TPE, the melting temperature is considerably lower indicating a different crystalline form of PP segments, due to possible interaction with ethylene segments and styrene blocks.

Similar shifting in the melting temperature of PP in blends with other polyolefins were reported, as for example in paper [14] for polypropylene - polybuthylene blends and were explained by either a decrease in crystallite size or a change in crystalline order. Such an explanation holds also for the above mentioned decrease in melting temperatures of the polyethylene segments.

Because no shoulders on the melting peak of the polypropylene were observed for all the studied blends, a homogeneous dispersion of the EP segments of SEPS in the polyethylene matrix can be concluded. The polypropylene domains of SEPS are probably dissolved in the polypropylene matrix, as mentioned above, enabling uniform dispersion of SEPS.

Table 1: Characteristics of glass transition and melting processes in the studied PP/TPE blends

Sample	Glass transition		PE domains melting		PP domains melting	
	T_g (°C)	ΔC_p (mW)	T_m (°C)	ΔH (J/g)	T_m (°C)	ΔH (J/g)
PP/TPE 0	-	-	-	-	164.7	68
PP/TPE 5	90	0.13	122.0	0.8	165.0	61
PP/TPE 10	83	0.18	121.6	0.74	164.3	55
PP/TPE 15	90	0.19	121.9	1.0	163.5	48
PP/TPE 20	94	0.18	120.9	2.51	163.2	47
PP/TPE 100	84	0.25	118.7	3.32	151.3	7.7

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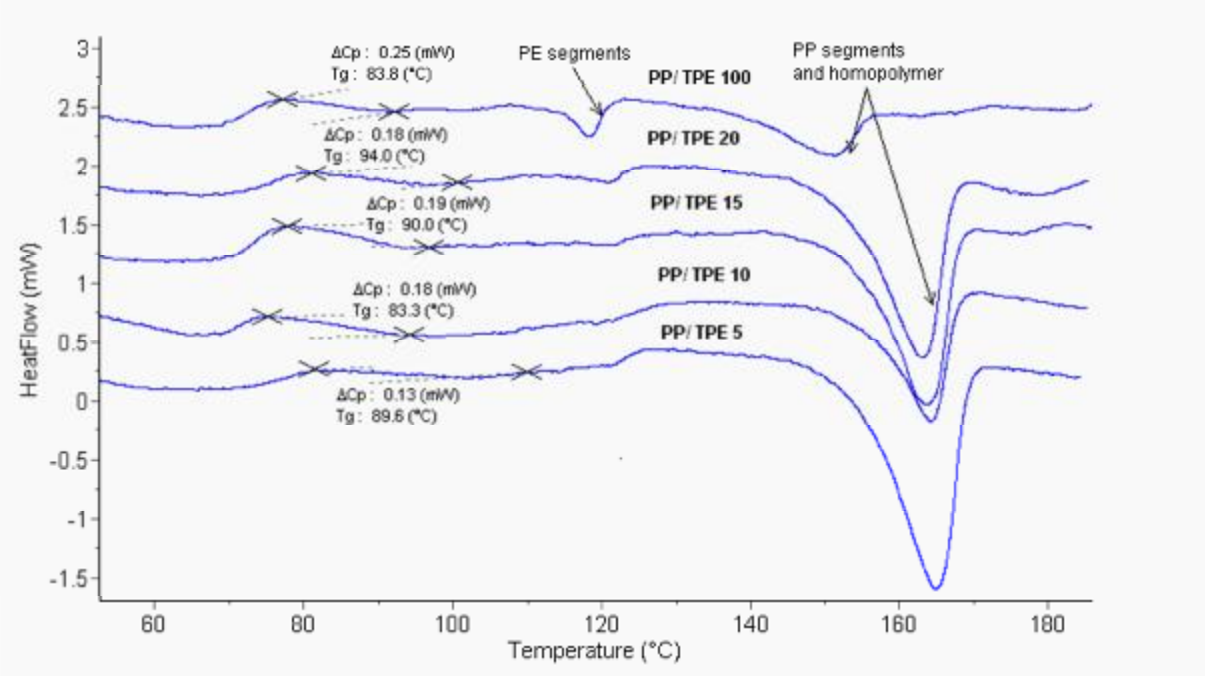

Fig. 1: Non-isothermal DSC curves of different PP/ TPE blends in nitrogen atmosphere (10 K/min.)

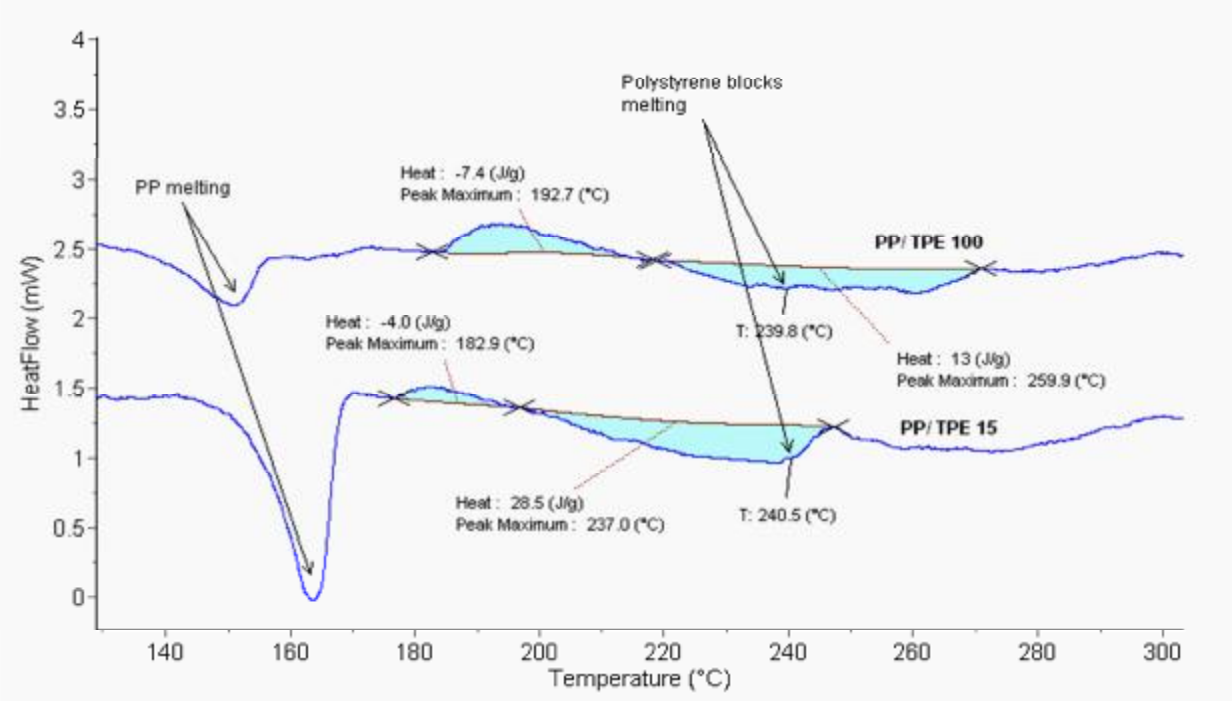

Fig. 4: Non-isothermal DSC curves in the high temperature region, in nitrogen atmosphere (heating rate 10 K/ min.) of PP/ TPE 15 and PP/ TPE 100 samples

SEM micrographs (figures 2 and 3) lead to similar conclusions as DSC concerning the uniformity of PP/TPE blends: in the studied composition range no distinct phases or domains were observed in the case of the blends as compared to PP and generally, the morphologies of both PP and blends appear to be similar.

d) The *endothermic peak at 240 °C* corresponding to the polystyrene domains melting is masked by a larger and broader decomposition peak with several shoulders. However, a shoulder at 239 - 240 °C (figure 4) is still visible and it can be assigned to styrene blocks melting process.

ATR-FTIR spectra (figure 5) confirmed the conclusions of DSC analysis. The characteristic bands of C-H bonds [3] were clearly observed (table 2) and indicate PP as a major component of the blends. The presence of PP, PE and PS in the TPE structure is also confirmed.

The bands observed at 1415 cm^{-1} (CH_2=CH- deformation [15]) and 727 cm^{-1} (CH wagging [3]) suggest the presence of an unsaturated compound, possibly a crosslinking agent. The occurrence of a crosslinking process is indicated by the exotherm peak observed in DSC at ca. 190 °C in TPE and, at lower temperatures, in PP/TPE blends (see figure 4).

Several small peaks were found in the region of 1700 cm^{-1} of both PP/TPE 100 and blends, indicating the possible presence of the carbon black as filler in these materials.

In non/isothermal measurements, the oxidation process starts at more than 200 °C for all the samples. The oxidation onset temperature (OOT) is considerably higher for the blends as compared to polypropylene (figure 6) indicating a higher thermal stability of the blends. Similar behavior was observed in the case of iso-thermal measurements, i.e. OIT values sharply increased when TPE was present: the sample containing 5 % TPE presented an OIT value comparable to that of 20 % TPE or 100 % TPE (figure 7 and table 3).

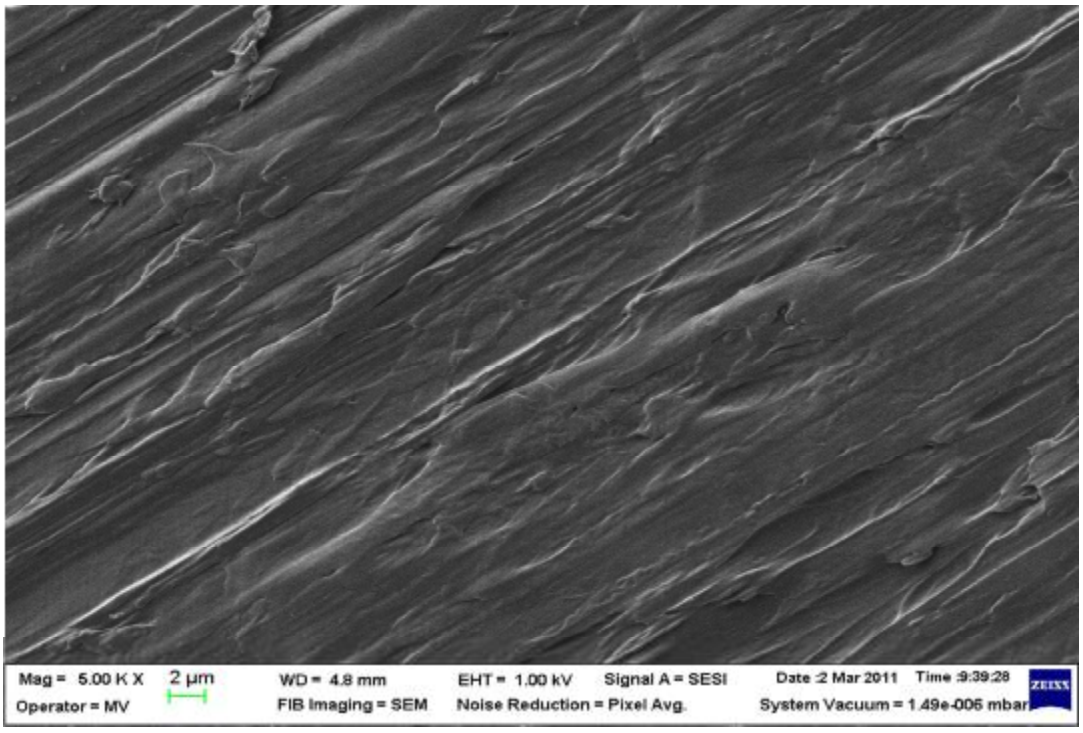

Fig. 2: SEM micrograph of PP/TPE 0

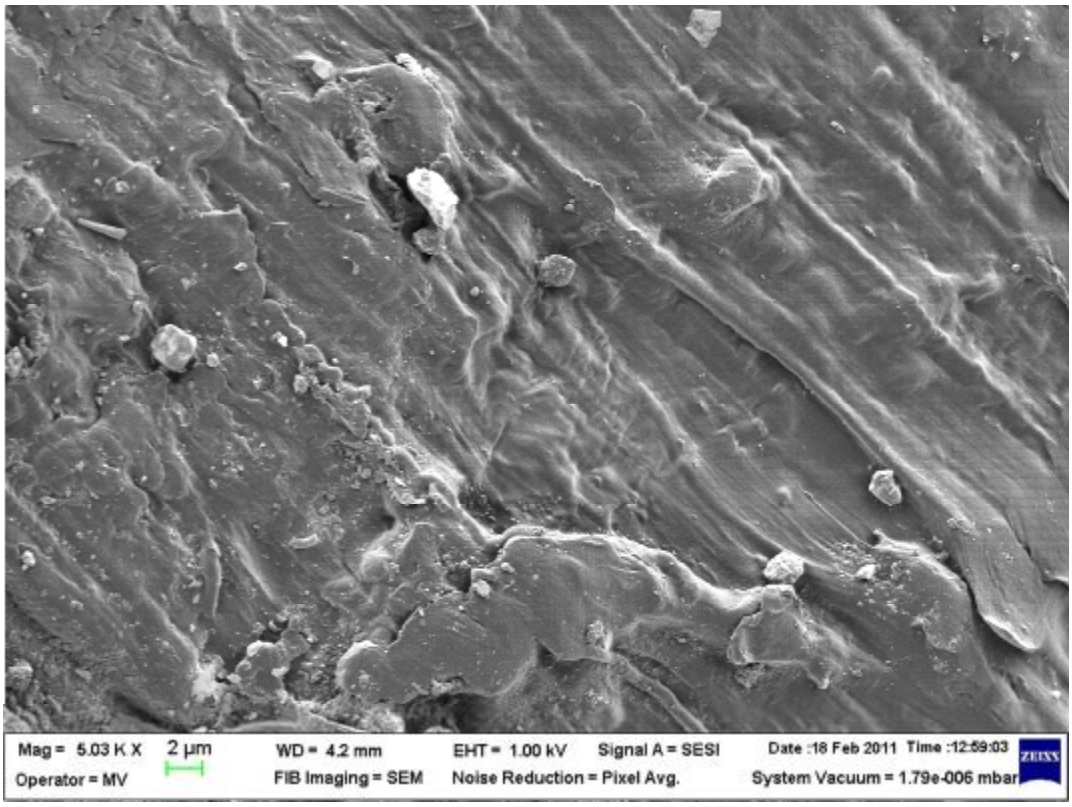

Fig. 3**: SEM micrograph of PP/TPE 10**

Table 2: Structural assignment of the observed frequency peaks in the studied PP, TPE and their blends

Sample code/ peak wavenumber (cm^{-1})				Peak assignment
PP/TPE0	PP/TPE5	PP/TPE15	PP/TPE100	
2950	2952	2951	2951	$\nu_{asim}(CH_3)$ in PP [16]
2915	2916	2918	2919	ν(CH) in PP and ν(CH) (crystalline), $\nu(CH_2)$ (amorphous) in PE [16] $\nu_{sim}CH_3$ in PS [16]
2870	2871	2870	-	ν_{sim} CH_3 in PP [16]
-	-	-	2850	ν_{sim} CH_2 in PS and PE [16]
2836	2838	2838	-	ν_{sim} CH_2 in PP [16]
2722	2718	2723	2727	ν_{sim} CH_3
-	-	1608	-	νC-C of aromatic rings [3, 16, 17]
1455	1456	1456	1455	symmetric deformation of CH_3 in PP and PP [16]
	1414	1415	1415	δCH_2 in vinyl units [15]
1375	1377	1375	1378	symmetric deformation of CH_3 in PP and PE [16] CH_2 deformation in PE (amorphous) [16]

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Sample code/ peak wavenumber (cm^{-1})				Peak assignment
PP/TPE0	PP/TPE5	PP/TPE15	PP/TPE100	
1360	1360	1360	-	combined CH equatorial bending and CH_2 twisting (hybrid vibration mode) [16]
1295	1301*	1301*	1307	combined wagging CH_2 and twisting in PP (hybrid vibration mode) [16] CH_2 twisting in PE, at 1303 cm^{-1} [16] (*in blends, these bands are masked by the PS ring vibration at ca. 1312 cm^{-1})
1254	1254	1255	1260	combined twisting CH_2 and axial bending CH_2 in PP [16]
-	-	1187	1185	ring vibration in PS [3, 16]
1167	1166	1166	-	combined axial rocking of CC and CH_3 in PP (hybrid vibration mode) [16]
1106	1108	1106	-	combined axial rocking of CH_3 and CC in PP (hybrid vibration mode) [16]
-	-	-	1078	ring vibration in PS [3, 16]
1034	1037	1037	1041	stretching C-CH_3 bond in PP
-	-	-	1018	possible ring vibration in PS [16] and/or in additives
999	997	997	-	combined CH_3 rocking and CH bending (hybrid vibration mode) in PP [16]
973	974	972	970	CH_3 rocking in PP and PE [16]
			910	CH vibration in styrene blocks [16]
901	899	900	-	CH_3 and CH_2 rocking [16] in polypropylene matrix
		876	873	possibly ring vibration in styrene blocks
840	841	840	845	CH_2 rocking in polypropylene [16]
810	808	807	809	This band appears in all materials. It can be related to deformation vibrations of 2 C-H bonds in the aromatic ring of a substituted phenol antioxidant [16]
-	764	759	760	γCH in polystyrene [16]
-	-	-	728	CH bending (wagging)
-	-	715	714	CH_2 rocking in PE [16]
-	700	699	700	CH bending in aromatic rings. Typical for monosubstituted aromatic rings [3, 16, 17, 18]
-	540	538	538	Polystyrene units [3]

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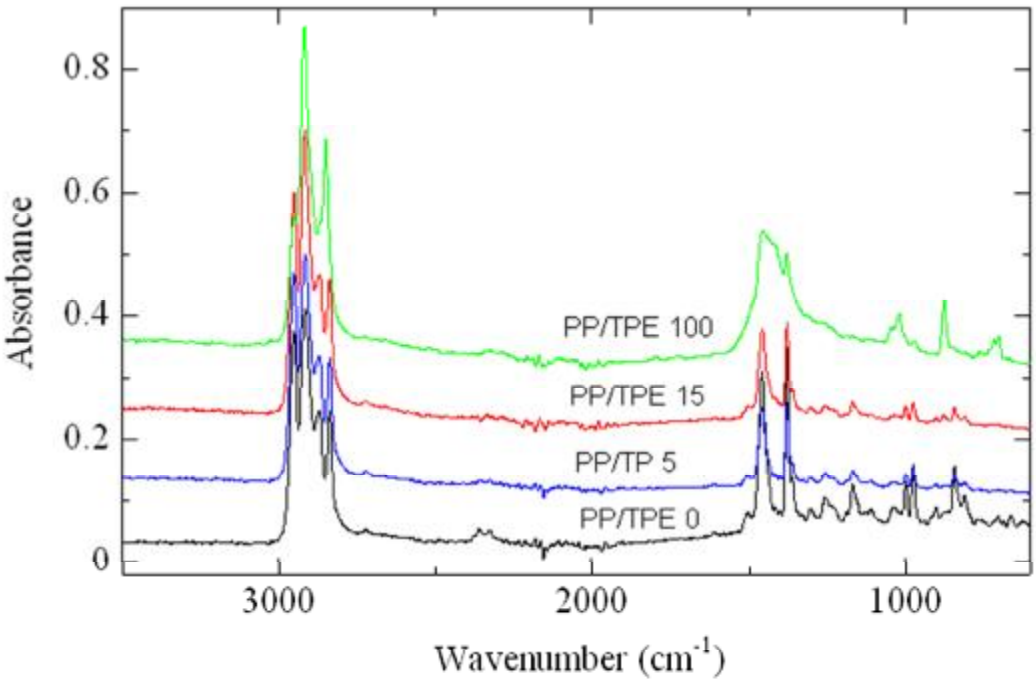

Fig. 5**:** FTIR spectra of various PP/TPE blends

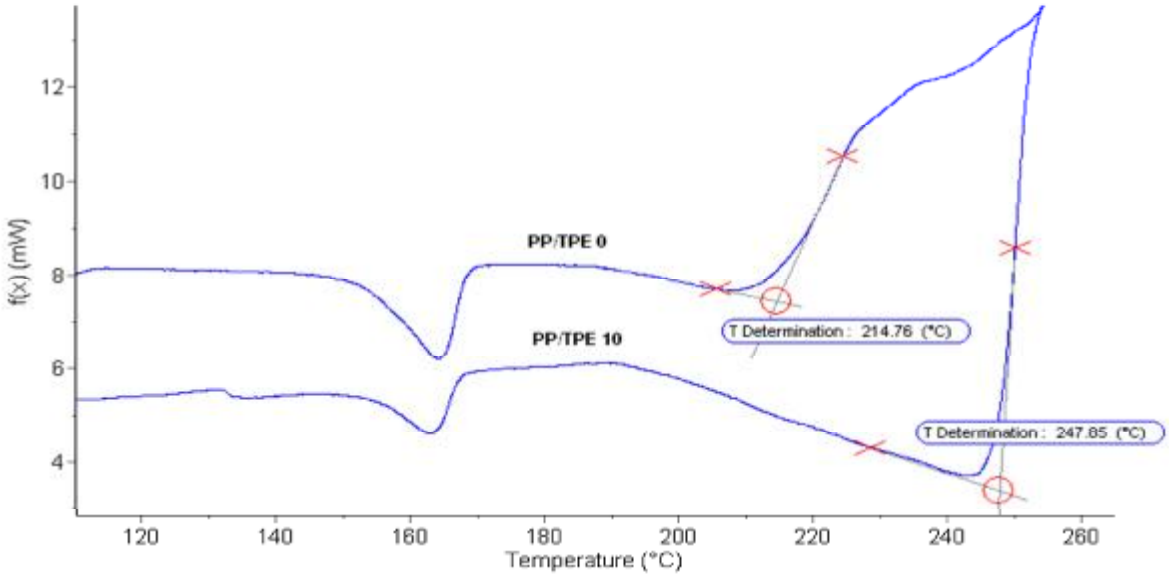

Fig. 6: DSC non-isothermal curves in air atmosphere of PP and of a PE/TPE blend containing 10 % TPE (air flow: 50 mL/min.; heating rate 10 K/min.)

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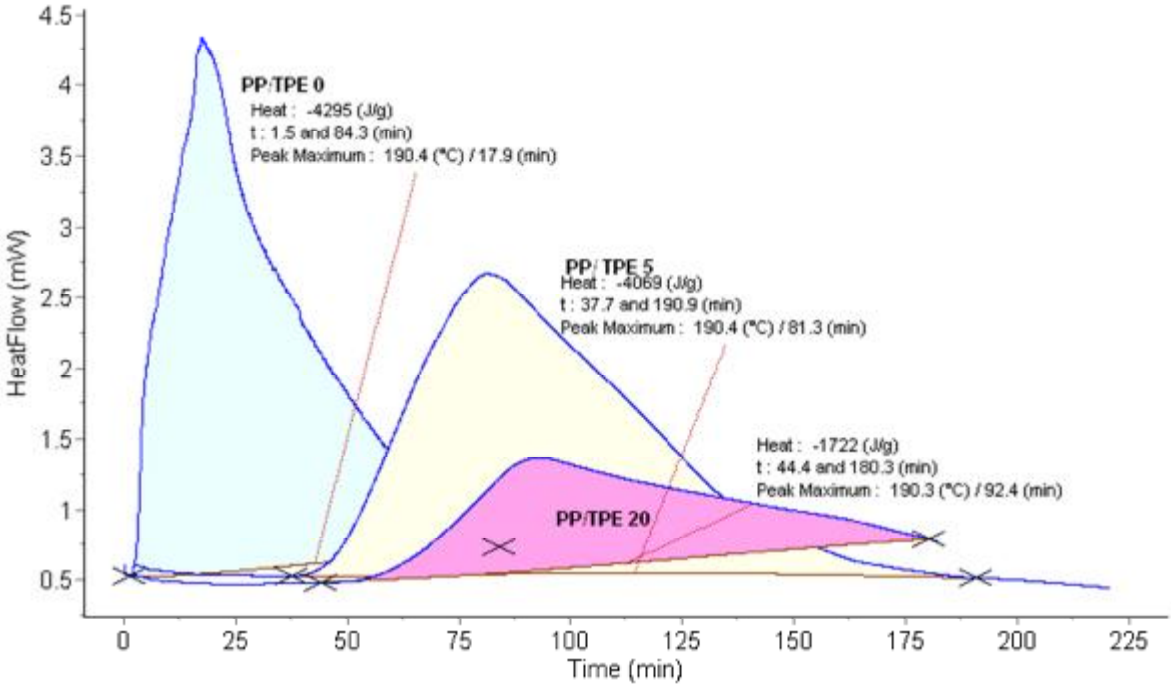

Fig. 7 **:** DSC isothermal curves in air atmosphere of different PE/TPE blends (T_{iso} = 190 °C; air flow 50 mL/min.)

Table 3**: Kinetic parameters of PP/TPE blends oxidation in non-isothermal and isothermal conditions**

Sample	OOT (°C)	$OIT_{190\,°C}$ (min.)	t_{max} (min.)	v_{ox} (%/min.)	ΔH_{ox} (J/g)
PP/TPE 0	200.9	3	18	20.5	-4295
PP/TPE 5	221.3	47	83	3.4	-4069
PP/TPE 10	247.4	65	87	3.1	-3567
PP/TPE 15	255.1	-	-	-	-
PP/TPE 20	-	57	91	3.2	-1722
PP/TPE 100	-	71	94	6.23	-626

As the stabilization effect appears to be not cumulative, it can be assumed the occurrence of a synergistic effect of the stabilizers present in the components. However, as no significant variation of the stability with the composition, a supplementary stabilization effect produced by TPE macromolecules can be also considered. Thus, is possible that the styrene domains act by different simultaneous mechanisms in stabilization of the PP/TPE blends: de-activation of the high energy states formed in PP matrix oxidation (energy scavenging mechanism [19, 20], and termination of radicals at the border of the interface polystyrene-polypropylene [21]. Moreover, PP de-activating of

PS macro radicals through intermolecular reactions is also possible [22]. The occurrence of these supplementary stabilization effects is in agreement to the decrease of the oxidation heat (ΔH_{ox}) as the TPE content increases (table 3).

4. CONCLUSIONS

The thermal stabilities of different PP-TPE blends containing 0 - 20 % of TPE were assessed by isothermal differential scanning calorimetry **(**DSC). It was observed that TPE component are reducing the degradation rate of the resulted material. Styrene domains may act by different simultaneous mechanisms in stabilization of the PP/TPE blends, e.g. de-activation of the high energy states formed in PP matrix oxidation (energy scavenging mechanism or termination of radicals at the border of the interface polystyrene-polypropylene).

DSC behavior at the PP melting point suggests that the polypropylene domains of SEPS are dissolved in the polypropylene matrix enabling the uniform dispersion of SEPS. SEM and ATR-FTIR data confirm this conclusion.

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