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THERMAL ANALYSIS OF SEBS BLENDS WITH PHASE CHANGE MATERIAL FOR INJECTION MOLDING

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***Abstract*—** Thermal analysis: Differential Scanning Calorimetry and Thermogravimetric Analysis (DSC and TGA) of SEBS blends with phase change materials (PCMs) have been studied in this paper. SEBS blends were made using two transparent SEBS commercial grades with extreme hardness values. The first thermal property determined in SEBS blends was the evaluation of the thermal degradation at high temperatures DSC. Another thermal property of the SEBS blends consists in knowing the degradation process of the blend TGA. It should be emphasized the good resistance to degradation for both, the two commercial grades of virgin SEBS with extreme hardness, and blends obtained with these materials, showing a remarkable effect on thermal regulation close to the melting point of the PCM, 37 ºC.

***Keywords*—** thermal analysis, DSC, TGA, SEBS, blends, injection molding.

I. INTRODUCTION

STYRENE-ethylene/butylene-styrene (SEBS) is useful in applications in which the use of SBS is restricted due to its sensitiveness to degradation [1]-[2]. SEBS polymers are obtained by hydrogenation of styrene-butadiene-styrene (SBS) polymers; this process allows to remove the unsaturation, typical of the butadiene components (carbon-carbon double bonds are saturated with hydrogen) and this has a positive effect on environmental, thermal and UV radiation resistance maintaining, thermoplastic behavior. The excellent aging resistance of SEBS polymers is due to the absence of carbon-carbon double bonds. By varying the relative ratio of the components (styrene, ethylene and butylene) on SEBS formulations, it is possible to obtain a wide range of elastic modulus and hardness values, which allow increasing its use in the industry. Also, SEBS polymers successfully combine elastomeric properties with low processing costs typical of commodity plastics and they are available in white color or even in transparency grades. In addition, SEBS polymers can be processed at relatively low temperatures and shows excellent resistance to high temperatures.

This study focuses on SEBS blends from the provider's SEBS extreme hardness (Shore-A 5 and Shore-A 90), additived with microencapsulated phase change materials (PCMs) with melting point at 37 ºC.

The objective of this present work is to study the Thermal analysis: Differential Scanning Calorimetry and Thermogravimetric Analysis (DSC and TGA) of SEBS blends.

II. EXPERIMENTAL

A. Materials

SEBS blends were made using two transparent SEBS commercial grades with extreme hardness values: Megol TA-5 and Megol TA-90 with Shore A hardness of 5 and 90 respectively, supplied by Applicazioni Plastiche Industriali (API). Generic properties of all SEBS Megol TA provided by the manufacturer are shown in Table I.

TABLE I
MECHANICAL CHARACTERIZATION VALUES OF THE VIRGIN ABS, VIRGIN HIPS AND VIRGIN SEBS

Property	Values
Shore hardness range	5-90 A
Compatibility	PP-PE-EVA
Ageing resistance Ozone (72h - 40(°C) - 200ppcm)	Excellent
Weathering	Excellent
Density (g/cm3)	0.88-0.89
Tear strength w.n. (KN/m)	22-44
Tensile modulus 100% elongation (MPa)	1.1-4.2
Tensile modulus 300% elongation (MPa)	1.9-5
Tensile strength (MPa)	6-7.2
Elongation at break (%)	700-550

PCMs show a remarkable effect on thermal regulation in the temperature range close to the melting point,

37(ºC).

B. Preparation of blends

The blends were carried out using an injection molding machine Meteor 270/75 by Mateu & Sole (Mateu & Sole, Barcelona, Spain) with 95% of a SEBS blend (70% Megol TA-5 and 30% of Megol TA-90) and different % of PCM37D. Blends proposed for the analysis of miscibility and mechanical properties characterization, are shown in Table II.

TABLE II
BLENDS COMPOSITION USED FOR ANALYSIS OF MISCIBILITY AND MECHANICAL CHARACTERIZATION.

Blend ID	SEBS 70% TA-5 + 30% TA 90 wt%	PCM37D wt%
M04:70-30	100	0
PCM05	99	1
PCM06	98	2
PCM07	95	5
PCM08	90	10

C. Differential Scanning Calorimetry (DSC)

Thermal degradation at high temperatures (DSC tests) was carried out using a measuring cell Mettler-Toledo 821 (Schwerzenbach, Switzerland) [3].

This experimental technique is very useful for evaluating the thermal processes [4] that may be experienced by materials when are subjected to isothermal cycles or a constant rate of heating. Similarly, supports the identification of plastics.

It is used to determine thermophysical parameters as heat capacities of materials as a function of temperature, enthalpies of certain reactions, state transitions or phase changes (especially fusion), transitions that occur in the same state (eg, order-disorder in the solid state, liquid crystals, etc.) with corresponding transition temperatures, evaluation of kinetic parameters, control and purity determination of substances (solids) and solids polymorphism study.

TABLE III
MAIN FEATURES OF THE DSC EQUIPMENT.

Feature	Value
Temperature Range	Room temperature to 700 (ºC)
Accuracy in temperature	± 0,2 (ºC)
Temperature reproducibility	± 0,1 (ºC)
Heating rate	0 (isothermal cond.) to 100 (ºC/min)
Cooling rate (air)	Max. T to 100 (ºC) in 8-9 (min)
Cooling speed (N2 liq.)	100 oC to -100 (ºC) in 15 (min)
Accurately measures enthalpy	± 2 %
Sensor type	Ceramic
Signal time constant	2,3 s
Measuring range 100 oC	± 350 (mW)

DSC records were made with a measuring cell Mettler-Toledo 821 (Schwerzenbach, Switzerland), belonging to the set of thermal analysis-integrated series and STAR-2000, in accordance with ISO 11357-4:2005 [ISO 11357-4, 2005]. The main characteristics are shown in Table III.

The temperature program used for the different materials is shown in Table IV:

TABLE IV
DSC TEMPERATURE PROGRAM FOR SEBS BLENDS.

Phase	Temperature Program
Heating phase	-30 ºC to 100 ºC at 10 ºC · (min^{-1})
Cooling phase	100 ºC to -30 ºC t at o -10 ºC · (min^{-1})
Heating phase	-30 ºC to 350 ºC at 10 ºC · (min^{-1})

D. Thermo Gravimetric analysis (TGA)

The thermal degradation process using Thermo Gravimetric Analysis (TGA) determines the change of the mass of the blend as a function of temperature [5]. It was done using a measurement cell Mettler-Toledo TGA / SDTA 851 (Mettler-Toledo Inc., Schwerzenbach, Switzerland) [6]-[8]. The thermal program used for SEBS tests was as follows: from 30 (°C) to 700 (°C) at a 20 C • min^{-1} [9]-[11].

III. RESULTS AND DISCUSSION

A. Differential Scanning Calorimetry (DSC)

Accordance with the conditions described in paragraph III.3.2.1 have been determined the thermal properties of SEBS blends evaluating thermal degradation at high temperatures. The phase change point is determined as the minimum peak, and the melting heat was calculated by integrating the peak and normalizing the size of the sample.

The following shows the curves generated by the DSC for M04:70-30 SEBS blend: 100-0 (Fig. 1) PCM05 blend (Fig. 2), PCM06 blend (Fig. 3), PCM07 blend (Fig. 4) and PCM08 blend (Fig. 5).

All curves show at 100 (°C) the melting state step (energy absorption) which corresponds with the temperature as a parameter included in Moldflow ® for an amorphous, partially crystalline. This parameter is equal to 100 (°C) in the database for all Moldflow ® amorphous materials, thereby demonstrating the same justification. In the same way, show the melting state of the PCM at 37 (ºC).

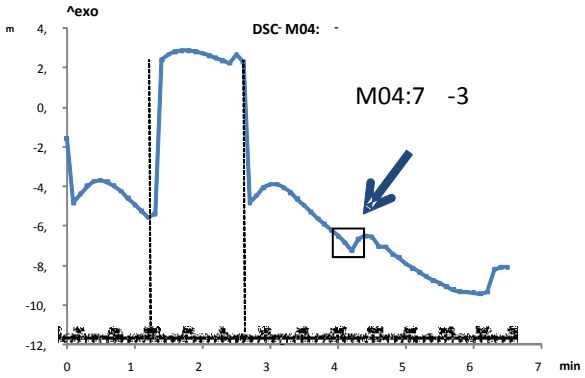

Fig. 1. DSC calorimetric curve generated by the mixture of SEBS M04:70-30, subjected to a heating-cooling cycle overheating.

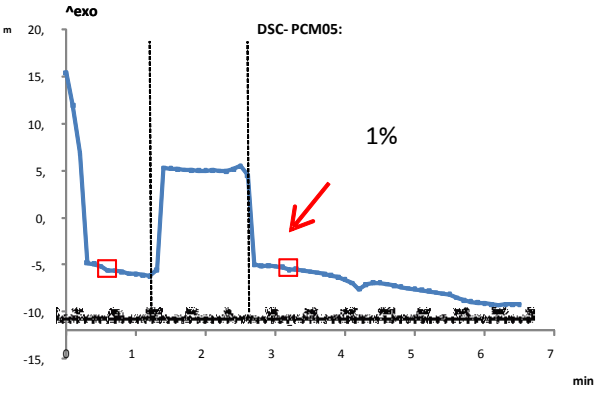

Fig. 2. DSC calorimetric curve generated by the mixture of SEBS PCM05, subjected to a heating-cooling cycle overheating.

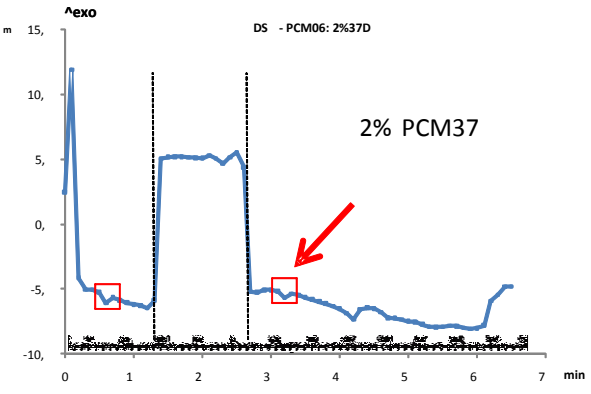

Fig. 3. DSC calorimetric curve generated by the mixture of SEBS PCM06, subjected to a heating-cooling cycle overheating.

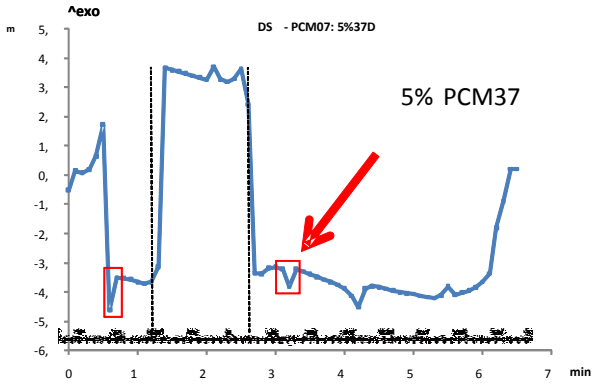

Fig. 4. DSC calorimetric curve generated by the mixture of SEBS PCM07, subjected to a heating-cooling cycle overheating.

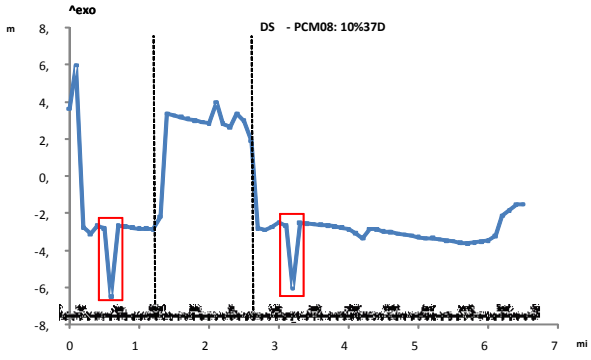

Fig. 5. DSC calorimetric curve generated by the mixture of SEBS PCM08, subjected to a heating-cooling cycle overheating.

B. Thermo Gravimetric analysis (TGA)

Another thermal property of the SEBS blends consists of knowing the degradation of the mixture.

TGA tests were made with a measuring cell Mettler-Toledo TGA / SDTA 851 (Mettler-Toledo Inc., Schwerzenbach, Switzerland), belonging to the set of modules integrated thermal analysis of the STAR e-2000 series.

This technique is particularly suited to study the course of the degradation processes of polymeric materials through the identification of the different processes and the estimation of the main kinetic parameters.

The results show similar behavior between the two extreme hardness virgin materials and blends held between them, generating a set of encompassed curves between the two curves corresponding to the materials M04:70-30 and PCM08.

Any peak does not appear, so that the blend is homogeneous, not degrading any material separately.

Similarly, shows the TGA results for the blends M04:70-30, PCM05, PCM06, PCM07 and PCM08 (Fig. 6), representing material weight% versus temperature.

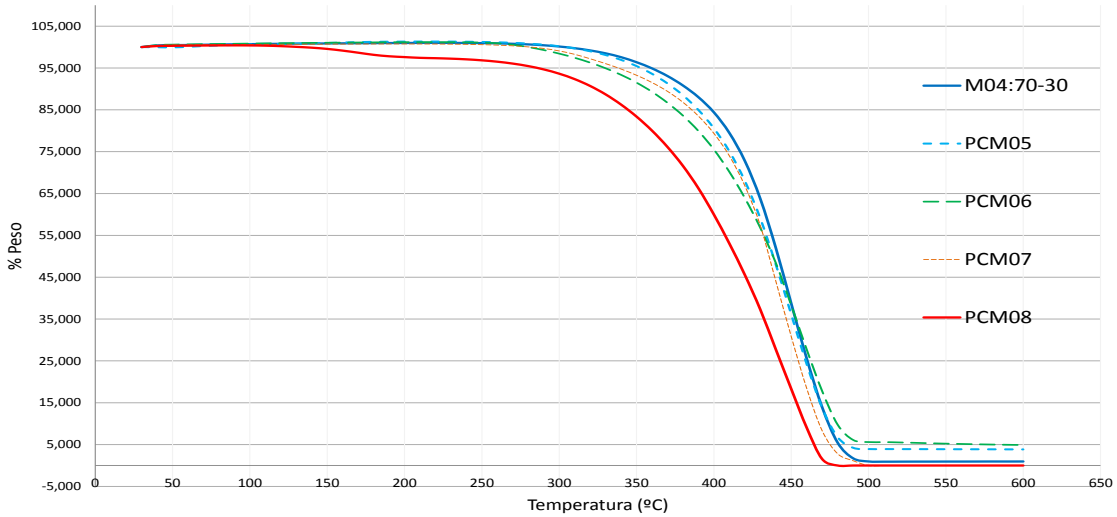

Fig. 6. Thermogravimetric comparative curves of SEBS blends (%weight vs temperature).

The following shows the results obtained for the parameters of thermogravimetry of each material (Table V).

TABLE V
THERMAL DEGRADATION PARAMETERS AT HIGH TEMPERATURES FOR SEBS BLENDS, OBTAINED BY THERMOGRAVIMETRY (TGA).

Blend	Onset (ºC)	Endset (ºC)	Inflect. Pt. (ºC)	Step (%)
M04:70-30	401,87	475,66	447,04	-100,05
PCM05	396,77	476,64	448,44	-97,3
PCM06	393,07	481,33	454,34	-95,58
PCM07	399,40	470,75	435,32	-99,68
PCM08	372,97	471,43	433,56	-102,74

If taken as a reference the inflection point of the thermogravimetric curve as the point of degradation, it is seen that almost all the mixtures have points of degradation between 430 and 460 (°C), not being observed significant changes or a clear trend in the evolution of this parameter. Furthermore it is seen that all the curves are in the same range. In this regard, it is worth noting the good performance against degradation both of the two commercial grades of SEBS virgins with extreme hardness as well as the blends obtained with these materials.

IV. CONCLUSIONS

We studied the Thermal analysis: DSC and TGA of SEBS blends. Thermal degradation at high temperatures curves DSC show at 100 (°C) the transition to molten state (energy absorption), which coincides with the temperature parameter included in Moldflow® for an amorphous, partially crystalline material. This parameter is equal to 100 (°C) in the Moldflow® database for all amorphous materials, thereby demonstrating the justification for it. Figures show the melting point at 37 ºC for the PCM. The thermal degradation process using TGA shows similar behavior between the two extreme hardness virgin materials and blends carried out between them. Curves show no peak, so that the blends are homogeneous, non-degrading any material separately.

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