

STUDY OF THE THERMAL PROPERTIES OF ACRYLONITRILE BUTADIENE STYRENE – HIGH IMPACT POLYSTYRENE BLENDS WITH STYRENE ETHYLENE BUTYLENE STYRENE

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Abstract— A binary blend Acrylonitrile Butadiene Styrene – High Impact Polystyrene (ABS-HIPS 50% wt) was prepared on a twin-screw extruder at 190-210 °C. The different properties were then analyzed using melt flow index (MFI), thermogravimetric analysis (TGA), and Fourier Transform Infrared spectroscopy (FTIR). FTIR analysis indicated heterogeneous distribution of the blend in injected pieces and SEM micrographs show heterogeneous distribution of both phase (ABS and HIPS). On the other hand, we have prepared ternary blends of ABS-HIPS-Styrene Ethylene Butylene Styrene (SEBS), varying the percentage of SEBS from 10 to 30 %wt using a twin screw extruder at 190-210°C. The addition of SEBS to the binary system (ABS-HIPS) allowed us to increase the ductile properties as well as reducing the viscosity.

Keywords— Additive, blend, compatibility, extrusion, thermoplastic.

I. INTRODUCTION

Plastic blends have been widely studied from years as evidence remarkable works of Meireles, Dawson, Olabisi, and Weber et al. [1]-[2]-[3]-[4]. Even there are a lot of studies about polymers, there are lots of problems to be solved. In order to reduce manufacturing costs to increase their competitiveness, the companies are optimizing their manufacturing processes. Reducing the material depletion is one way of optimization.

Polimeric recovery companies take their main input source from municipal solid [5]. The consumption drop has reduced dramatically their raw material inputs. As the quantity of material to be recovered has been

reduced, they must change the processing line more often, as they don't have individual lines for each material. This way, the processing line is used to recover different polymers. This process set up produces a certain amount of blend material that cannot be sold. This is one of the most recent problems in polymer recovery, where ABS and HIPS are the most representative materials [5]-[7]. During the recovery process of these materials, an ABS-HIPS blend is produced, which cannot be sold as HIPS nor ABS, but it must be commercialized as a blend with certain characteristics.

From this point, the main aim of this work is to carry out the characterization of the ABS – HIPS blend and their later revaluation through a SEBS addition. Jiang [9], Cataño [10], Equiza [11], and Rek et al. [12], works, show the use of additives to improve the properties of the polymer blend.

II. EXPERIMENTAL

A. Material

The HIPS, ABS, and SEBS used in the experiment are commercial products HIPS (PS Impact 6541; Total petrochemical, Belgium), ABS (Terluran® GP22, BASF, Germany), and SEBS (Megol® TA, Applicazioni Plastiche Industriali, Italy).

B. Sample preparations

A binary blend (50%ABS – 50%HIPS wt) was conducted on a conventional twin-screw extrusion

machine, at 190 – 195 – 200 – 210 °C extrusion temperatures. Finally, ternary blends were prepared by varying the SEBS content, from 0% to 30 % (wt %), at the same conditions of ABS-HIPS blends.

C. Thermal analysis (MFI – DSC – TGA)

Melt flow index measurements were obtained with an extrusion plastometer (Ats Faar S.p.A, Vignate, Italy) equipped with a heating chamber set at 200 °C and 220 °C where the blended granules were introduced. After a previously established melting time, the material was forced through a capillary by means of the application of a 5 and 10 kg weight.

The calorimetric analysis was carried out using DSC Mettler-Toledo 821 equipment (Mettler-Toledo Inc., Schwerzenbach, Switzerland). Samples ranging between 6 and 7 mg in weight were used. A first heating (30 °C – 120 °C at 5 °C min⁻¹) was completed, followed by a cooling process (120 °C – 75 °C at 5 °C min⁻¹) to eliminate the thermal history, and was finished with a second heating (75 °C – 120 °C at 5 °C min⁻¹). The T_g values have been determined from the second heating process. Tests were performed in a nitrogen environment (flow rate 30 ml/min).

Thermogravimetry Analysis (TGA) was carried out using a Mettler-Toledo TGA/SDTA 851 (Mettler-Toledo Inc, Schwerzenbach, Switzerland) with initial temperature 30° C and final temperature 600 °C using a 10 °C min⁻¹ heating rate. The samples used weighed 7 mg approximately. Tests were performed in a nitrogen environment (flow rate 50 ml/min).

D. FTIR analysis

Fourier transformed infrared spectroscopy (FTIR) measurements were carried out using Perkin–Elmer Spectrum BX infrared spectrometer (Perkin–Elmer España, S.L., Madrid Spain). For completion of this, films with sufficient transparency were obtained through dissolution with toluene and subsequently dried to remove all solvent traces. One hundred scans at a resolution of 4 cm⁻¹ were carried out for each sample.

III. RESULTS AND DISCUSSION

A. ABS-HIPS System.

Mechanical characterization takes on a greater importance when we consider the actual application of the polymer material, but it is important not to forget that there are other properties to consider, such as viscosity, which is also important in the transformation of the materials. We can obtain the melt flow index values quickly and simply using an extrusion plastometer.

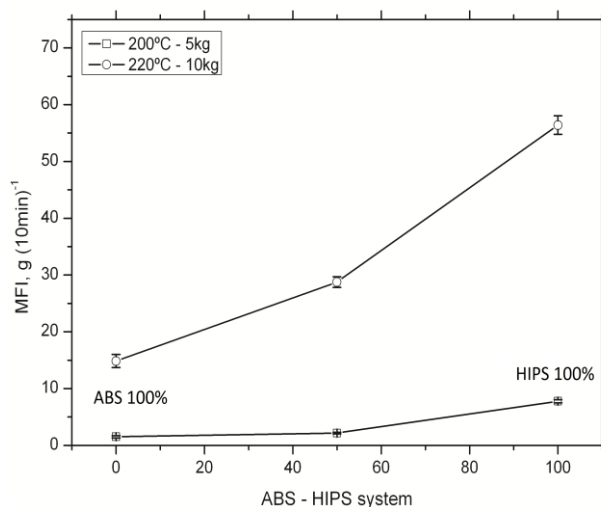


Fig. 1. Melt flow index for the virgin (ABS and HIPS) and the 50% blend.

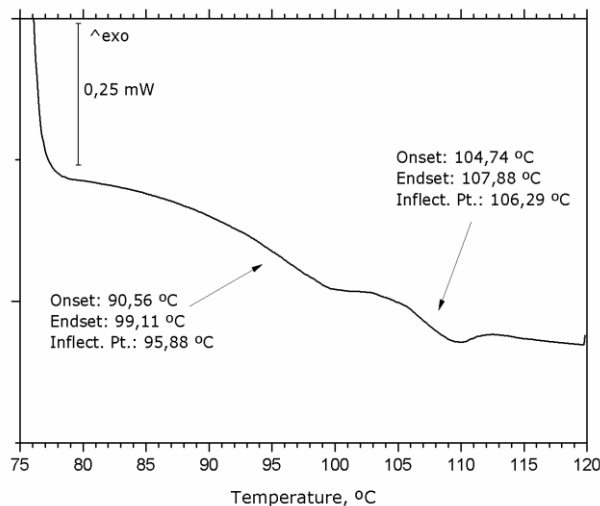


Fig. 2. DSC measurements for the ABS and HIPS blend.

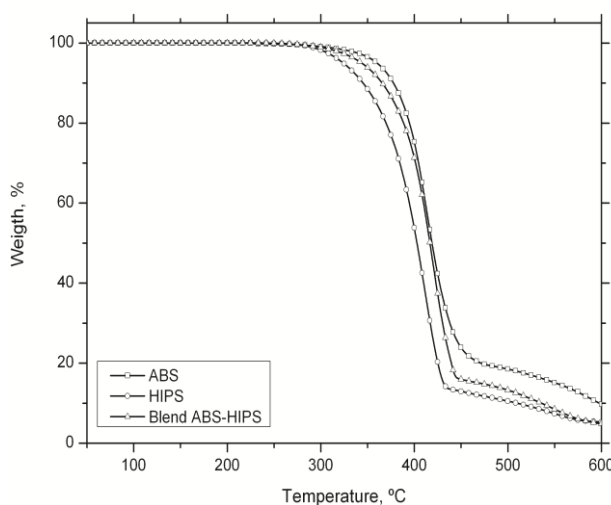


Fig. 3. TGA measurements for the virgin (ABS and HIPS) and the 50% blend.

Fig. 1 shows the melt flow index values of the ABS –

HIPS system. The test conditions for virgin material are different; in the case of HIPS, standard procedure is to use a temperature of 200 °C and 5 kg of weight, while ABS requires 220 °C and 10 kg. We carried out tests on both virgin materials and the blend under study using both test conditions. The melt flow index values for the blended material are between the values of virgin HIPS and ABS, both in the HIPS test conditions and the ABS test conditions. Thus, we can conclude that the effective processing conditions for the blend fall between those of the two virgin materials.

The study of the compatibility of polymer blends, are based on DSC measurements using the study of the changes in the glass transition temperature (Tg). ABS and HIPS display Tg values of 106.00°C and 91.96°C respectively, the usual values for this type of polymer. But ABS – HIPS blend (50 wt%) show two clearly differentiated transitions, the first of these corresponds to the Tg of HIPS phase and the second corresponds to the Tg of de ABS phase. This behavior leads to the conclusion that both polymers are not compatible (Fig. 2).

Thermogravimetry allows us, among other things, to determine thermal stability. In this case, decomposition process is very similar between all materials, (Fig. 3).

Finally, infrared spectroscopy is an extremely sensitive technique which allows us to identify any polymers through their infrared absorption wavelengths. Fig. 4 shows IR spectrums of ABS, HIPS and ABS-HIPS blend. ABS and HIPS have a very similar structure and we cannot observe significant differences between IR spectrums, except for the presence of the peak corresponding to the CN bond (around 2238 cm⁻¹), according to Bai and Karahaliou et al. this peak is indicative of the amount of AN present in ABS [13]-[14].

From the relationship between the areas of the characteristic peaks, 966 cm⁻¹ (trans-2-butene-1,4-diyl moieties), 1603 cm⁻¹ (styrene moieties) and 2238 cm⁻¹ (nitrile moieties), we can find out the distribution of the mixture throughout the surface. We can see how the relationship between these areas is different for the external faces and internal part of the samples analyzed. This result shows a heterogeneous distribution throughout the break surface of the blend which causes a loss of ductile properties in the material.

B. ABS – HIPS – SEBS System.

Having obtained the results from the ABS – HIPS blend, we analyzed the addition of Styrene-Ethylene-Buthylene-Styrene (SEBS) to the blend, with the aim of improving the blend's ductile properties.

According to Jiang, Rek, Jazani, Jelcic and Jazani et al. SEBS has been used as an element to achieve compatibility between polymers [8]-[9]-[12]-[15]-[16]-

[17], often with excellent results, thus the option of using SEBS with the HIPS – ABS system has real promise.

The incorporation of a new element in the blend could have two effects: the new polymer could act as an interface between the HIPS and the ABS and thus improve the overall properties of the initial mixture, or, it could have the complete opposite effect, causing a general loss of properties due to a lack of interaction between the components of the original system.

Before carrying out any mixing processes, we proposed the following hypothesis:

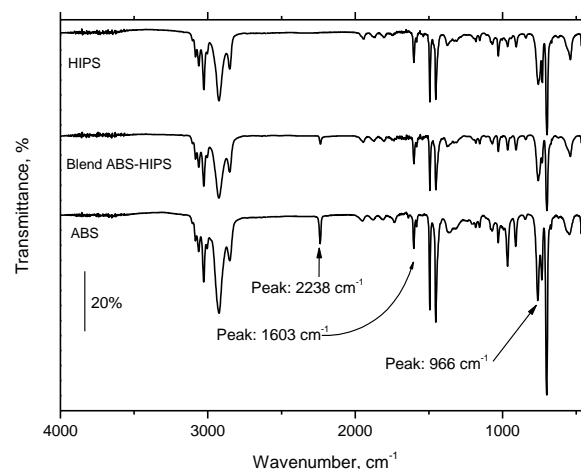


Fig. 4. FTIR spectrum of ABS, HIPS and Blend ABS-HIPS (50% wt).

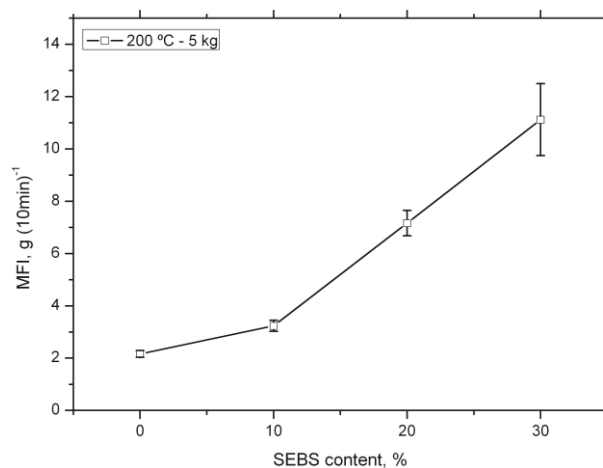


Fig. 5. Melt flow index for ABS – HIPS – SEBS blends.

According to Agari et al., HIPS is compatible with SEBS [18], and ABS is compatible with SEBS, then there are the strong probability that SEBS acts as an agent of compatibility between ABS and HIPS.

In order to complete the characterization of the ternary blends, the MFI of all blends was measured, because MFI data is important for industrial

applications, especially during processing. The high fluidity of SEBS ($194.88 \pm 13 \text{ g } 10\text{min}^{-1} 200 \text{ }^\circ\text{C} - 5 \text{ kg}$) produces an increase in fluidity in any mixture to which it is added. This increase in fluidity values are very interesting because it greatly reduces the energy consumed during the transformation processes of these mixtures (Fig. 5).

Finally, the degradation process carried out in a single stage indicates good interaction between the elements making up the ternary blend. We saw that the parameters for the degradation process for the ternary blend falls between those of the 50% binary blend and those of virgin SEBS. On the other hand, the DTG curves do not show significant differences, and even the degradation rate is very similar between all samples, in spite of using high percentages of SEBS (Fig. 6).

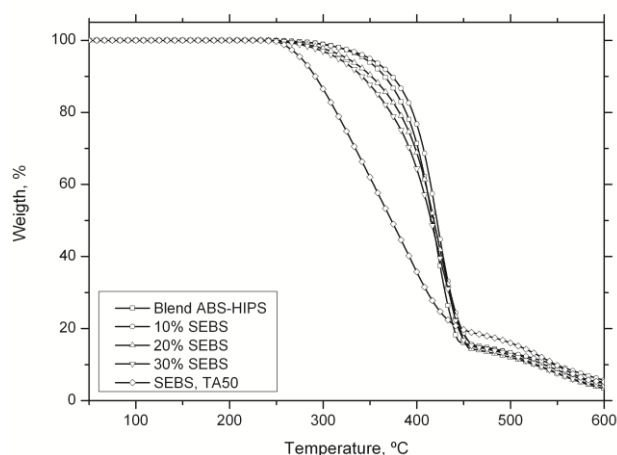


Fig. 6. TGA measurements for the virgin SEBS, ABS – HIPS blend and ABS – HIPS – SEBS blends.

IV. CONCLUSIONS

Our results suggest that the compatibility between ABS and HIPS is only partial. The use of extremely sensitive techniques, such as infrared spectroscopy, has allowed us to observe differences between the external faces and the internal part of the injected sample pieces. Concerning fluidity, the addition of SEBS has one major advantage; that it increases fluidity in the blend which means we can lower the processing conditions and thus save energy.

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