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Additional Information

**Styrene-Ethylene-Butylene-Styrene (SEBS) influence on the properties of
Acrylonitrile Butadiene Styrene (ABS) – High Impact PolyStyrene (HIPS)
blends.**

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Abstract

A binary blend (ABS-HIPS 50% wt) was prepared on a twin-screw extruder at 190-210 °C. The different properties were then analyzed using tensile strength and impact tests, melt flow index (MFI), thermogravimetric analysis (TGA), and Fourier Transform Infrared spectroscopy (FTIR). The analysis of mechanical properties showed a decrease in elongation at break and impact strength. 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-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 (elongation at break and impact strength), as well as reducing the viscosity.

Keywords:

additive, blend, compatibility, thermoplastic, extrusion

1 INTRODUCTION.

According to Meireles, Dawson, Olabisi, and Weber et al. the study of mixtures of polymer materials has been the subject of a great deal of intense research in the last few decades [1-4]. However, in spite of this study, there are still many problems associated with production of these materials which need to be studied and analyzed in order to find a solution. The current economic crisis has meant that, more than ever, companies need to optimize their production processes and make the maximum possible reductions in their costs in order to become more competitive. Cost reduction includes minimizing the losses due to waste in production processes or alternately creating new value from this waste at low cost.

According to Rejewski, one of the principal sources of materials for companies that operate in the polymer recycling area is the waste generated by public consumption [5]. As the economic crisis has seen a reduction in consumption, recycling companies are facing a huge reduction in their supply of raw material. All of this has meant that, in order to prevent stoppages in production, the material used in the production line has to be changed more frequently. This has been one of the problems in recovery processes of materials such as styrene waste, where HIPS and ABS are the most common materials according to Brennan and Hosseini et al. [6-8].

The economic viability of polymer waste recovery processes rests on recovery of a large quantity of waste material, and given the great variety of polymers in existence it is not possible to have separate production lines for each type of material, so each line must be used for a range of polymers. This recovery process configuration produces a significant quantity of mixed material that has

no commercial value. During styrene waste recovery processes, a mixture of ABS - HIPS is often produced which cannot be sold or used as either HIPS or ABS, but which must be commercialized as a blend with particular characteristics.

Following on from this, the objective of this study is to characterize ABS – HIPS blends and then to use SEBS to add value to these blends, according to Jiang, Cataño, Equiza, and Rek et al., it is a frequently used compatibilization strategy between polymers [9-12]. Optimization of the production process requires that the recycling production line does not stop for a moment, and for this reason, when there is a change of material (from HIPS to ABS or vice versa) a certain quantity of each is lost.

2 EXPERIMENTAL.

2.1 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)

2.1.1 Sample preparation

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. Figure 1 presents a flow-diagram of process used at blends fabrication.

2.1.2 Mechanical properties measurement

The mechanical properties of the samples were evaluated using an ELIB 30 electro-mechanical universal testing machine made by Ibertest (S.A.E. Ibertest, Madrid, Spain), with a load cell of 5 kN. All tests were carried out following the UNE-EN ISO 527 standard, at a speed of 50 mm min⁻¹.

Impact strength was determined by using the Charpy impact machine (S.A.E. Ibertest, Madrid, Spain) according to ISO-179.

The values of all the mechanical parameters were calculated as averages over 5 specimens for each composition.

The flat specimens, used for mechanical characterization, were produced using a conventional injection machine Meteor 270/75 made by Mateu & Solé® (Barcelona, Spain) working at 230 °C. Prior to the injection process, the virgin ABS was dried at 80 °C for four hours using a MDEU1/10 drier made by Industrial y Comercial Marse S.L.® (Barcelona, Spain). Figure 2 shows the shape and dimensions of flat specimens.

2.1.3 Thermal analyses (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).

2.1.4 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.

2.1.5 Microscopy Electronic (SEM)

Morphology analysis of fractured surfaces of blends was carried out by using a scanning electron microscope JEOL JSM-6300 (Jeol USA, Peabody) operated at an acceleration voltage of 15 kV. Prior to observation, samples were covered with a 5–7 nm Au layer in vacuum conditions.

3 RESULTS AND DISCUSSION

3.1 ABS – HIPS – System

The mechanical properties of any material are fundamental for its use in any particular application. Traction and impact tests are extremely important because they allow us to understand properties such as tensile strength, elongation at break and impact strength.

In the study carried out on the ABS-HIPS system, the graph showing tensile strength for the virgin (ABS and HIPS) and the 50% blend show a linear evolution of the values, where the 50% by weight blend has values that fall between those of virgin ABS and HIPS. This result indicates the compatibility between the elements that form the blend (Figure 3).

However, the values for elongation at break and impact strength of the 50% blend are very low; even lower than those of virgin material. While the elongation at break values indicate a clear compatibility of the compounds, the properties related to ductility show they are not completely compatible (Figure 4).

According to Brennan et al., this behaviour has been observed when they are analyzing the properties of the blend obtained from recovery of waste materials from the electrical and electronic sectors [6].

The superficial characteristics after the breaking process allow us to more easily understand the mechanical behaviour of the material under test. This breaking process includes both the beginning of the crack and its evolution.

When we observe the break sections of virgin material (ABS and HIPS) and the 50% blend, we can see some differences in the way the break occurs and develops. Firstly, both virgin materials show a break section that is completely

perpendicular to the stresses applied, while on the other hand, the break section of the ABS - HIPS blend occurs initially as a fan shaped crack before developing perpendicular to the stresses applied (Figure 5).

Similarly, the break section of the ABS – HIPS blend after the impact test shows a wave shaped progression of the crack, and there was no plastic deformation in the fracture surface. On the other hand, both the virgin HIPS and the virgin ABS showed a linear advance of the crack (Figure 6).

The reason for the loss of ductile mechanical properties could be due to a heterogeneous distribution of the two materials in the blend in the injected piece (Figure 7).

Infrared spectroscopy is an extremely sensitive technique which allows us to identify any polymers through their infrared absorption wavelengths. Figure 8 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 moities), we can find out the distribution of the mixture throughout the surface. Table I shows the relationship between the areas of different absorption bands. 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.

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.

Figure 9 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 (T_g). ABS and HIPS display T_g 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 T_g of HIPS phase and the second corresponds to the T_g of de ABS phase. This behavior leads to the conclusion that both polymers are not compatible (Figure 10).

Finally, thermogravimetry allows us, among other things, to determine thermal stability. In this case, decomposition process is very similar between all

materials, but DTG data in table II show the maximum decomposition rate for ABS-HIPS blend (420.59 °C).

Although the tensile strength values are fairly intermediate, the rest of the mechanical properties (elongation at break and impact strength) are lower, which reduces the range of applications for the blend.

3.2 ABS – HIPS – SEBS System

Having obtained the results from the ABS – HIPS blend, we analyzed the addition of Styrene-Ethylene-Butylene-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, 15-17], 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:

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.

The elastic character of SEBS must bring improved ductile properties to the ABS – HIPS system. One of the first effects that can be observed in the

mechanical properties is a decrease in tensile strength as the percentage of SEBS increases. This decrease is lighter for a SEBS content of 10%, and after this the tensile strength declines more rapidly reaching a loss of 60% for a 30% SEBS content.

Although there is a loss in tensile strength, the recovery of high elongation at break and impact strength values more than compensate for this loss (Table III). On analyzing the results from the addition of SEBS to the ABS – HIPS blend, we conclude that the ideal percentage of SEBS is 10%, which causes a 10% decrease in tensile strength but a 50% increase in both elongation at break and impact strength values.

We found the reason for this recovery of ductile properties in the break sections of the samples, where the incorporation of SEBS to the ABS – HIPS blend causes a radical change in the break surface. Where previously we saw a fairly rough area, the addition of SEBS causes a peak which increases in size with the addition of more SEBS. The presence of this peak indicates the capacity of plastic deformation which is recovered with the presence of SEBS in the blend (Figure 11).

In order to complete the mechanical 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 ($194.88 \pm 13 \text{ g } 10\text{min}^{-1} \text{ } 200 \text{ } ^\circ\text{C} - 5 \text{ kg}$) 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 (Figure 12).

4 CONCLUSIONS

Our results, obtained from the ABS-HIPS / ABS-HIPS-SEBS mixture of flat specimens, suggest that the compatibility between ABS and HIPS is only partial and that a significant loss of ductile properties is produced in the 50% by weight blend of the two materials. Our study of the surfaces of the breaks, both in the tensile test and the impact test, shows that the crack advances in a different way to the cracks in virgin materials, indicating a heterogeneous distribution of the materials in the surfaces of the break. 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, which corroborate the phenomenon observed in the break surfaces.

The addition of SEBS allows us to recover the ductile properties of the ABS – HIPS blend, with some loss of tensile strength. Analyzing the break surfaces allowed us to understand more easily the results obtained in the mechanical characterization as we saw an increase in plastic deformation when the percentage of SEBS is higher. 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.

5 ACKNOWLEDGEMENTS

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Figures Caption

Figure 1. Flow-diagram of process used at blends fabrication.

Figure 2. The shape and dimensions of flat specimens.

Figure 3. Graph showing the tensile strength of the ABS-HIPS system.

Figure 4. Variations in elongation at break and impact strength of ABS-HIPS system.

Figure 5. Micrographs of the break sections obtained from the tensile strength test on the various samples.

Figure 6. Micrographs of the sections obtained after the impact tests.

Figure 7. SEM micrographs of the sections obtained from the tensile strength test of ABS, HIPS, and ABS-HIPS blends (5000x).

Figure 8. FTIR spectrum of ABS, HIPS and Blend ABS-HIPS (50 %wt).

Figure 9. Melt flow index values of the ABS – HIPS system.

Figure 10. DSC calorimetric curve of ABS-HIPS blend, glass transition zone.

Figure 11. Micrographs of the break surfaces after the traction tests as a function of SEBS content.

Figure 12. Melt flow Index of the (ABS – HIPS) blend in function of SEBS content.

Table Caption

Table I. Relationship between absorption bands.

Table II. DTGA results of ABS, HIPS and ABS-HIPS blend.

Table III. Mechanical properties of ABS-HIPS blend in function of SEBS content.

Table I. Relationship between absorption bands.

Material	966/1603		2238/1603	
	Mean	Standard deviation	Mean	Standard deviation
ABS	3,54	0,12	2,01	0,09
HIPS	0,57	0,01	0,00	0,00
Blend (ABS-HIPS)	2,02	0,03	0,92	0,04
Blend (ABS-HIPS) external	1.87	0,05	0,74	0,01
Blend (ABS-HIPS) internal	2,10	0,04	1,15	0,00

Table II. DTGA results of ABS, HIPS and ABS-HIPS blend.

Material	Onset, °C	Endset, °C	Peak, °C
ABS	386.59	441.85	415.59
HIPS	369.90	430.44	413.01
Blend (ABS-HIPS)	386.05	439.86	420.59

Table III. Mechanical properties of ABS-HIPS blend in function of SEBS content.

SEBS content, wt%	Tensile Strength, MPa	Elongation at Break, %	Impact Strength,
0	27.05±2.20	8,65±3,01	2.25±0.13
10	24.04±0.70	12,41±1,15	8.51±0.32
20	18.10±1.78	22,98±1,90	11.37±1.18
30	11.13±0.87	27,71±3,42	13.18±0.89

Figure 1.

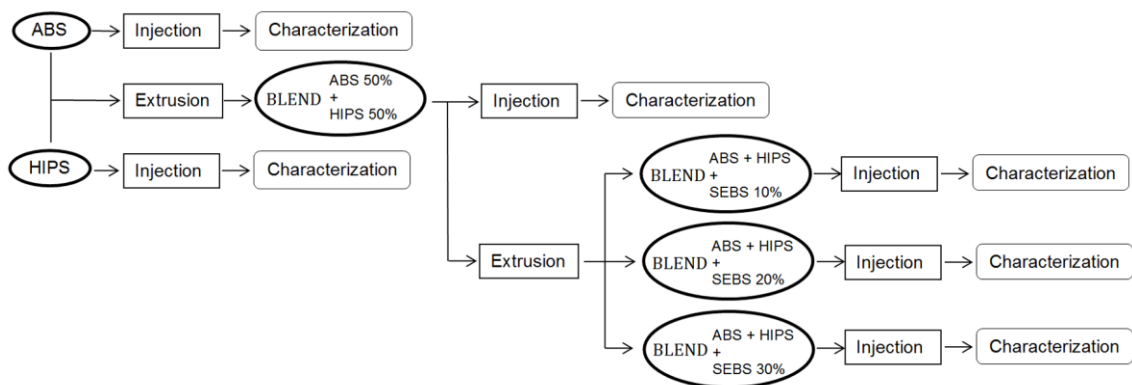


Figure 2.

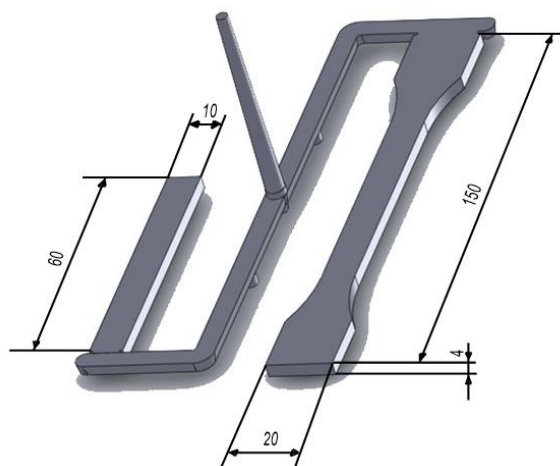


Figure 3.

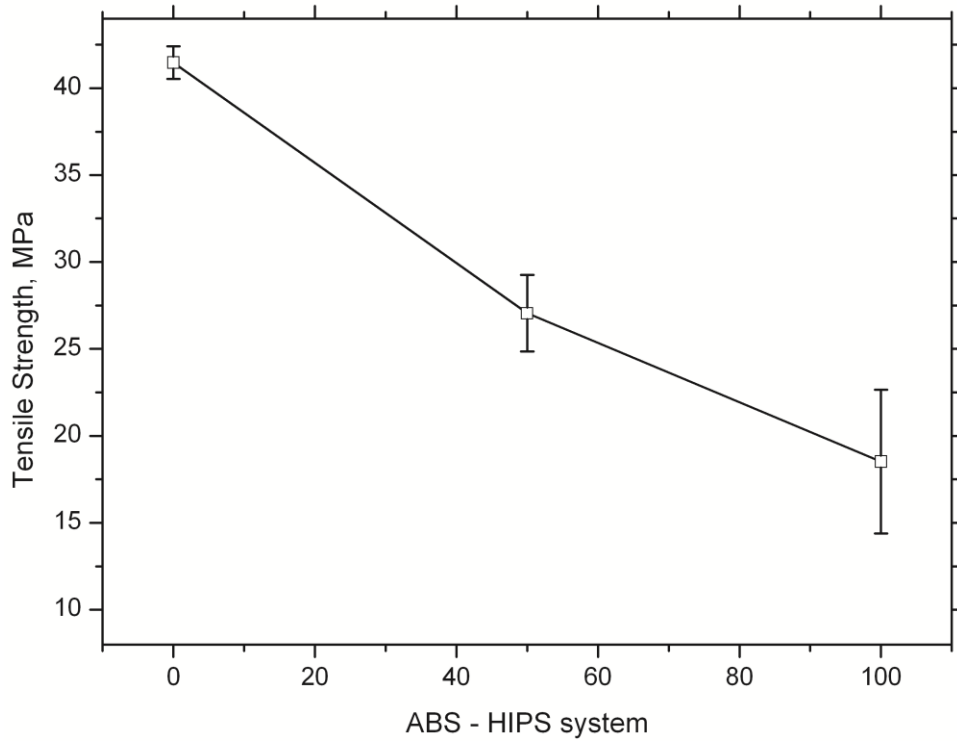


Figure 4.

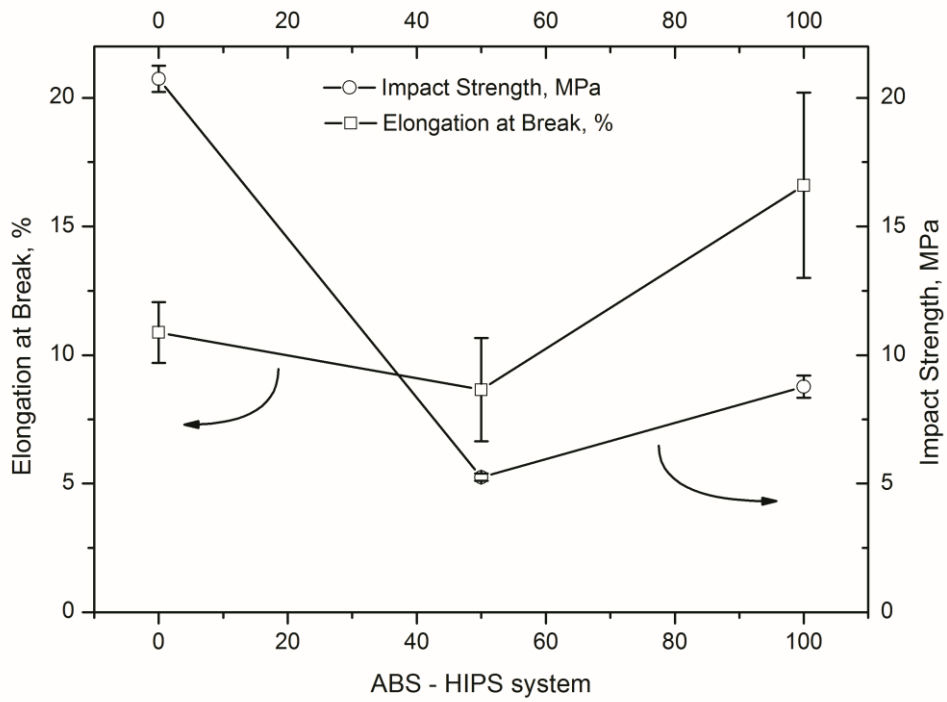


Figure 5.

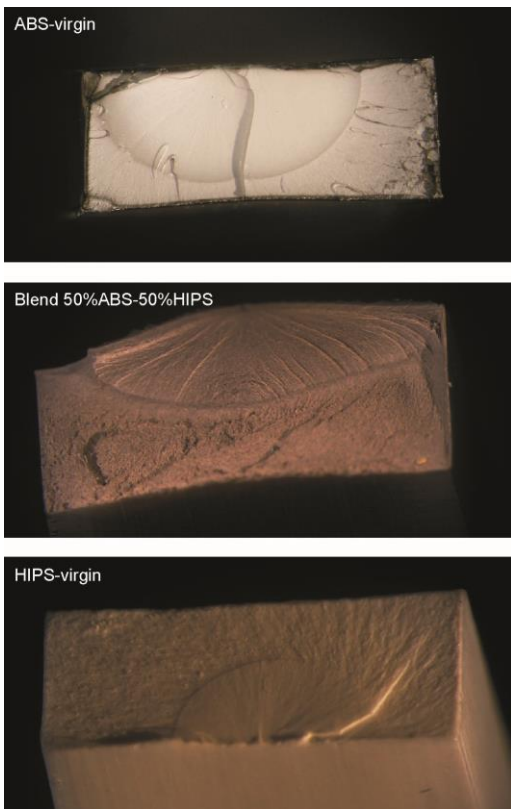


Figure 6.

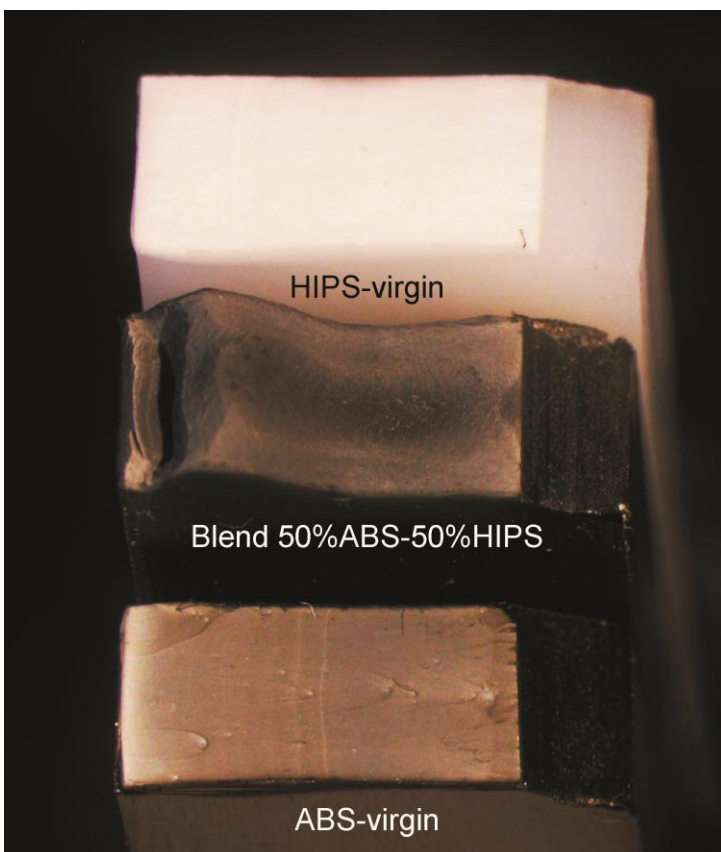


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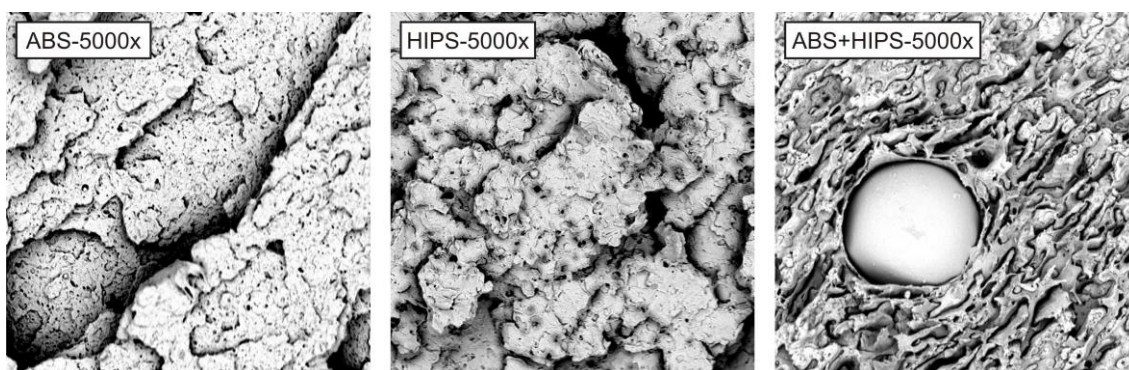


Figure 8.

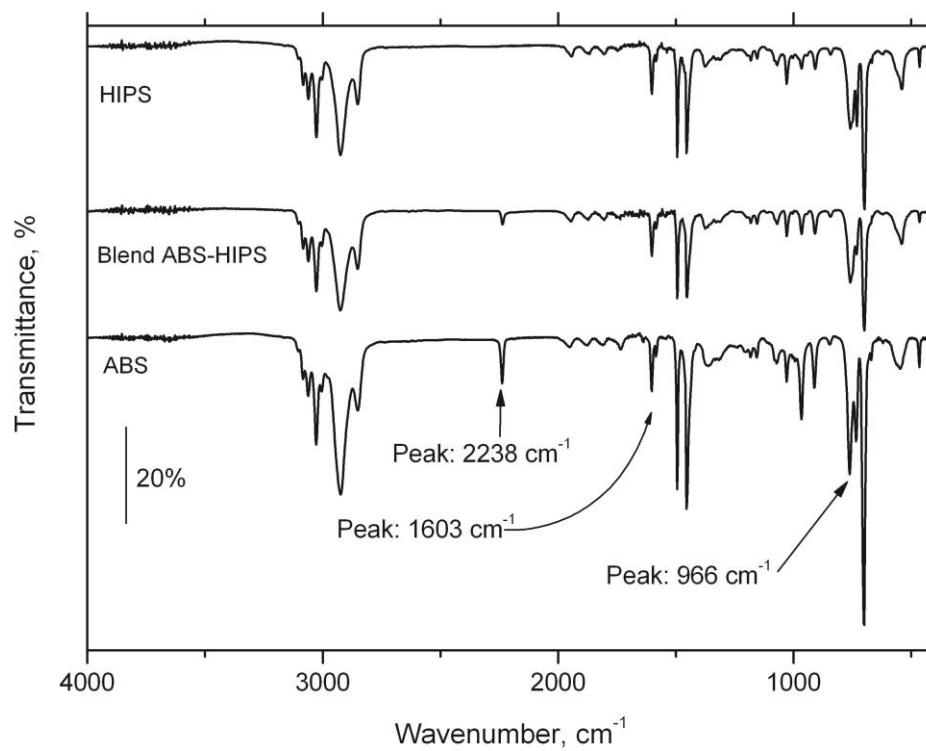


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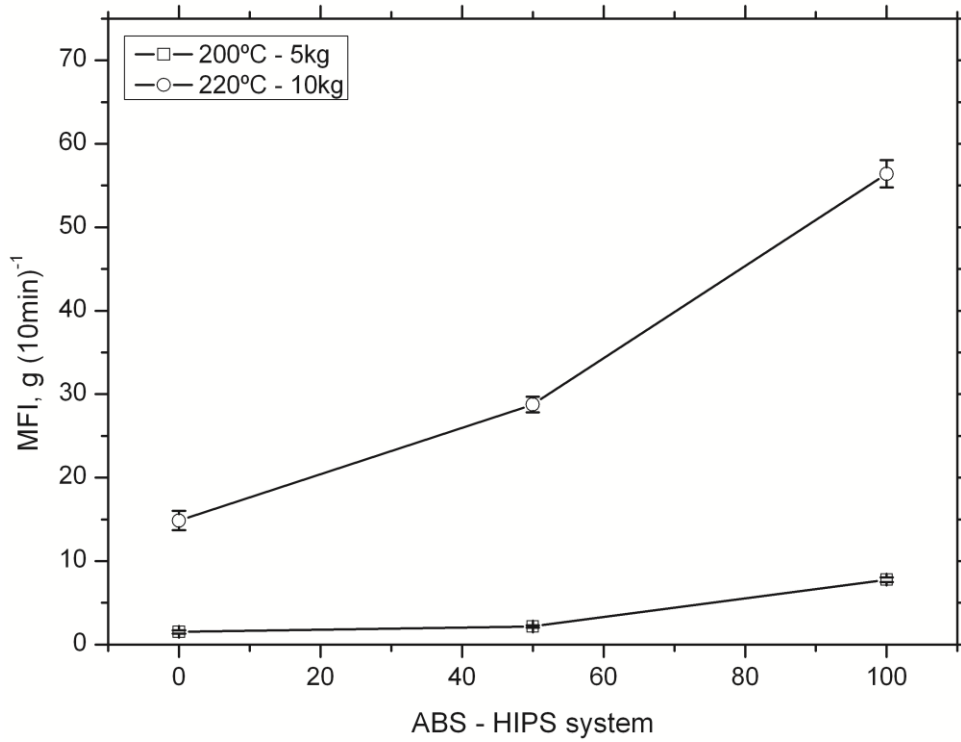


Figure 10.

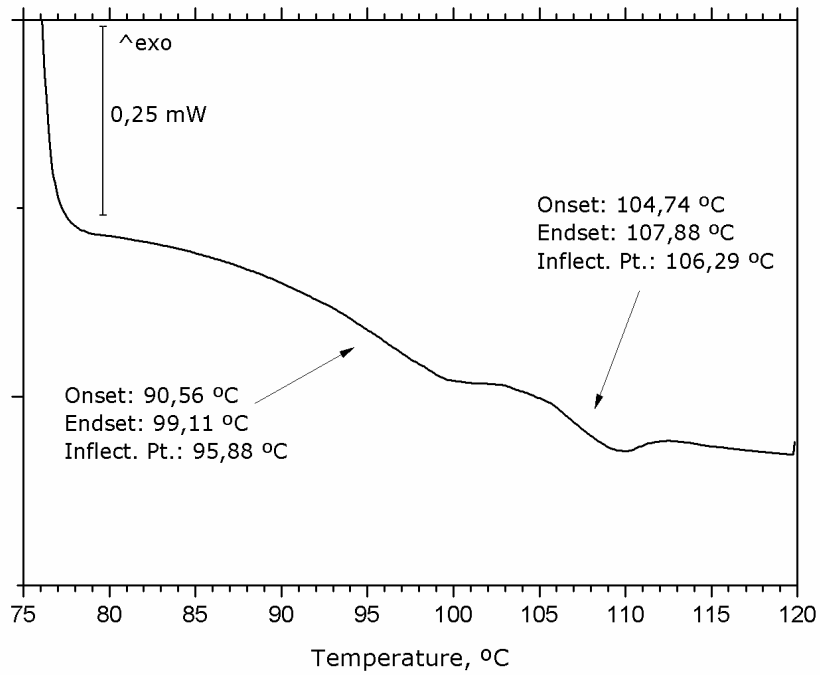


Figure 11.

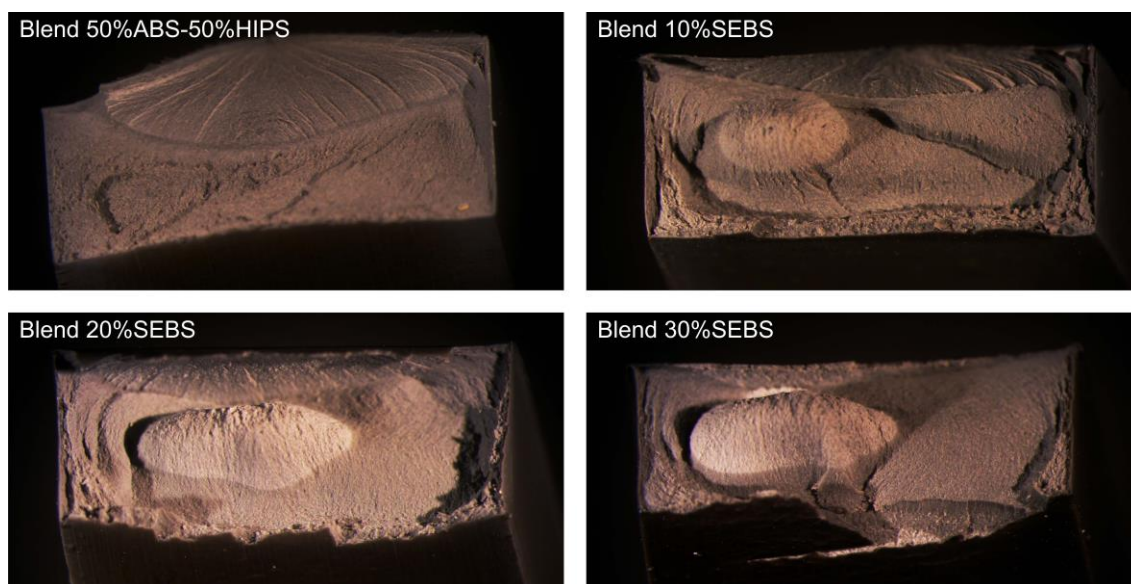


Figure 12.

