

Changes in the mechanical and thermal properties of high impact polystyrene (HIPS) in the presence of low polypropylene (PP) contents

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Abstract The final properties of recycled polymers greatly depend on the presence of impurities, which can be detected by differential scanning calorimetry. For the purpose of the present study a total of five high impact polystyrene (HIPS)/polypropylene (PP) blends (100/0; 97.5/2.5; 95/5; 92.5/7.5; 90/10) were prepared and injected at a temperature in the 220–250 °C range. The subsequent mechanical characterization indicates a reduction of tensile strength, elongation at break and impact strength. Scanning Electron Microscopy (SEM) was used in the morphological analysis of the different blends. Finally the variations in the flow measurements and glass transition temperature were analysed using melt flow index (MFI) and differential scanning calorimetry (DSC), respectively. The presence of impurities may have a negative effect on the mechanical properties of the material, but may improve material performance during processing.

Introduction

Polymeric materials have experienced growing use in different industrial sectors, particularly in the packaging and packing industries. This high consumption of polymers in industrialized countries has in turn generated big amounts of waste, mainly from the packaging and packing industries. The new environmental policies and regulations together with the high price of crude oil as the main raw

material for the manufacture of polymers have led to the development of waste recovery systems.

The companies devoted to polymeric waste recycling have found different problems in the recovery of such materials mainly due to the difficulty in separating the different types of polymers present in the waste. Although different separation systems have been developed, current techniques do not allow the recovery of highly-pure material [1] added to the fact that these new technologies increase the cost of the end product, which becomes non-competitive in comparison to products made from raw material.

In this context, most companies have preferred the option of in-plant waste collection rather than the implementation of separation and recovery systems [2].

Despite the common practice of in-plant waste collection, it is usual to find impurities in the recycled material mainly because many similar products are packed using different raw materials. This is the case of styrene recovery from dairy product packaging waste, in which small amounts of polypropylene have been detected through differential scanning calorimetry techniques. This technique has been widely used for the identification of different polymers [3].

The mixture of different types of polymers often involves a loss of the mechanical properties of the material, mainly due to the incompatibility of the component elements in the blend [3]. Although in certain cases the mixture of two polymers improves the mechanical performance of the resulting material [3], copolymerization affects not only the mechanical performance, but also the thermal properties of the material [4].

The mechanical behaviour of HIPS/PP blends has been analysed by other authors [4] who observed a reduction in the tensile strength and impact strength of the material.

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Other authors have used compatibilisers to balance this negative effect on the properties of the blend [5]. Studies have been developed not only on the mechanical properties, but also on the rheological characteristics of these materials and on the morphological changes resulting from the immiscibility of both copolymers [6–7].

The studies about HIPS/PP blends have analysed the entire system, from 0 to 100% PP, but no study has been found that analyses the effect of small amounts of PP on the performance of HIPS. However, such an analysis is of great importance for material recovery since a better understanding of the performance of low PP content/HIPS blends will allow us to determine the maximum amount of PP for the blend to maintain its good properties for further processing.

One of the current priorities of material-recovery companies is to obtain high-quality recycled material with mechanical and thermal properties similar to those of the raw material. To reach this goal it will be necessary to know the effect of different parameters such as temperature or the presence of impurities, on the material's properties.

The objective of the present work is to estimate the maximum amount of PP that can be added to the blend without significantly altering the properties of the material. Virgin polymeric researches are very important, because the results can be extrapolated to polymeric recovery process. In this case, HIPS/PP blends are interesting to study, because PP usually appears during HIPS recovery process.

For that end, raw polymeric material samples are analysed and the results obtained are used to study recycled HIPS/PP blends.

Experimental

Materials

The PP and HIPS used in the experiment are commercial products HIPS (Empera[®] 514; BP Spain S.A.U., Madrid, Spain) and PP (Isplen[®] PB 180 G2M Repsol YPF, Madrid, Spain).

The samples of the recycled material were supplied by ACTECO, productos y servicios, S.L. Alcoy–Alicante, Spain. This company processes mainly HIPS waste material coming from the packaging industry.

Sample preparation

Sample blends were prepared by varying the PP contents, from 0 to 10% (wt%). Due to the low PP percentages, the blends were directly obtained from the injection moulding machine, at two molding temperatures, with 200 and 250 °C, which define the upper and lower recommended values for HIPS processing.

Mechanical properties measurement

The mechanical properties of the samples were evaluated using an ELIB 30 electro-mechanical universal testing machine by Ibertest (S.A.E. Ibertest, Madrid, Spain), with a load cell of 5 kN. All tests were carried out following UNE-EN ISO 527 standard, at a speed of 30 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 5–7 specimens for each composition.

Scanning electron microscopy (SEM) measurements

The cracks appearing in the material after the tensile strength tests were analysed by Scanning Electron Microscopy with a HITACHI S-3000N Scanning Electronic Microscope (Hitachi Ltd., Japan). Image acquisition was taken after gold sputter coating under vacuum on the surface of the samples.

Thermal characterization

The calorimetric analysis was carried out using DSC Mettler-Toledo 821 equipment (Mettler-Toledo Inc., Schwerzenbach, Switzerland). Samples of weight between 8 and 9 mg have been used. A first heating (30–180 °C at 10 °C min⁻¹) was completed, followed by a cooling process (180–40 °C at 10 °C min⁻¹) to eliminate the thermal history and by a second heating (40 °C–250 °C at 10 °C min⁻¹). The T_g values have been determined from second heating process. The tests were performed in a nitrogen environment (flow rate 50 ml min⁻¹).

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 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 5,000 g weight.

Results and discussion

Mechanical properties

The analysis of the mechanical properties of the material includes different parameters, such as tensile strength, elongation at break and impact strength.

Compatibility between the two polymers of the blend is a major factor that affects the performance of the material; if the polymers are incompatible, a general alteration in the

mechanical properties of the blend can be observed. Incompatibility causes important negative effects on the properties of the material [8–13].

The graphical representation of tensile strength values versus PP content in the different samples shows a similar behaviour of the blends independently of the injection temperature. At both temperatures, tensile strength decreases as the percentage of PP in the blend increases (Fig. 1).

The graphical representation of the elongation at break shows a similar trend to that observed for tensile strength, giving lower elongation values as polypropylene content increases. This trend is observed in the samples injected at 200 °C and at 250 °C.

However, this response of the material to elongation at break depends on the PP content in the blend. Thus, at low PP weight fractions (2.5% and 5% PP), the elongation at break values decrease a little, whereas at higher PP contents (7.5% PP and 10% PP), elongation suddenly drops to 80% of its initial value (Fig. 2).

Immiscibility between two components generates the formation of two well-differentiated phases, a matrix one and a dispersed one; in those cases in which immiscibility results in poor adhesion between the component elements, the application of a load causes the loss of the mechanical properties of the material (tensile strength, elongation at break) mainly due to the stress concentration effect of the impurity as a consequence of the lack of the interaction among the interface.

Impact tests provide information about the performance of polymeric blends. The analysis of the data obtained indicates a decreasing trend in the impact strength values, similar to the results obtained in the tensile strength tests. Although for low PP contents (2.5% PP) impact strength

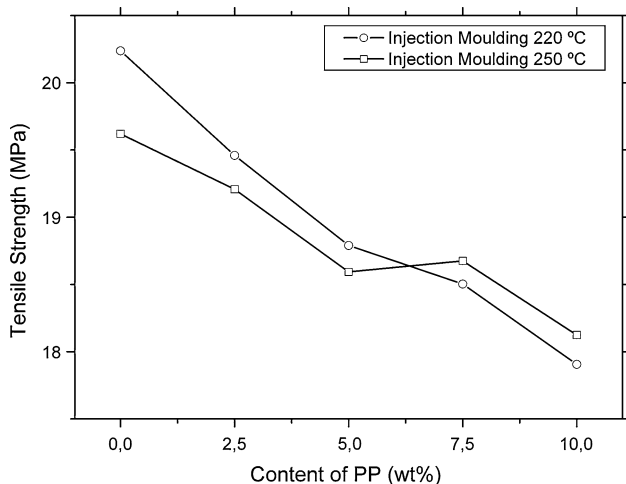


Fig. 1 Variation of tensile strength versus HIPS/PP blends composition

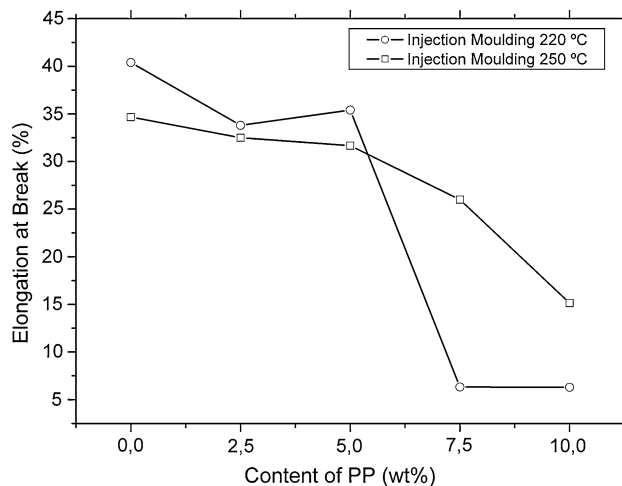


Fig. 2 Variation of elongation at break versus HIPS/PP blends composition

values remain almost constant, for higher PP concentrations (higher than 2.5% PP) impact strength exhibits a sharp drop (Fig. 3).

The presence of PP negatively affects the mechanical properties of the blend, although to different extent depending on the concentration of PP. The addition of PP to the blend reduces tensile strength to 10% of its initial value, whereas elongation at break and impact strength decrease to values lower than 80% of their initial value.

From the results obtained it can be concluded that the maximum concentration of polypropylene allowed in the blend for successful recovery of high-impact polystyrene is 5 wt%, since at higher PP contents the good properties of the material decrease significantly.

Other studies about recycled material have reported the presence of polyolefinic impurities in recycled HIPS. These

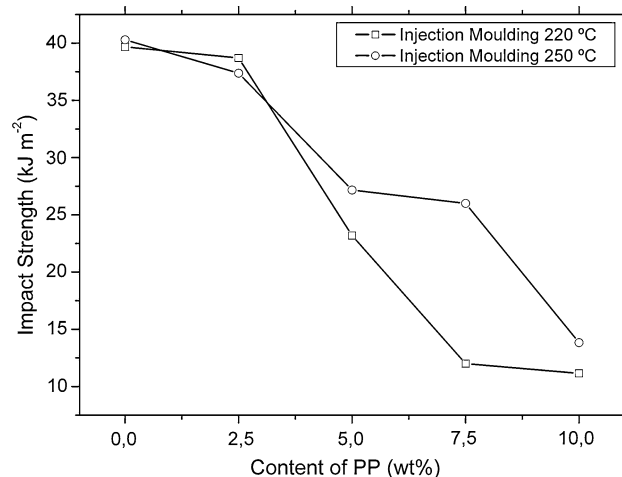


Fig. 3 Variation of Charpy impact strength versus HIPS/PP blends composition

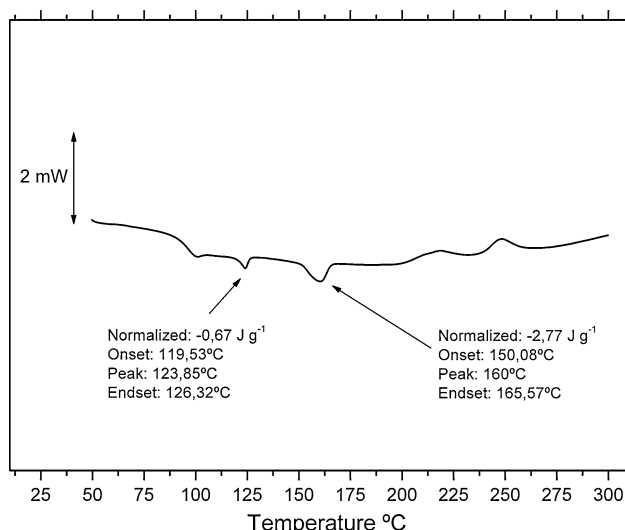


Fig. 4 DSC curves of waste HIPS

impurities were detected by differential scanning calorimetry (DSC), observing two endothermic reactions at about 120 and 160 °C, corresponding to polyethylene and polypropylene, respectively. These impurities appear for different reasons; first, PE appears in recovery process because of its use as colour masterbatch. Second, PP and HIPS use to packaging dairy products, and incorrect separation process causes the presence of polypropylene in recycled HIPS (Fig. 4).

Polypropylene crystallinity can be calculated from the melting enthalpy obtained in the calorimetric analysis and the melting enthalpy for 100% crystalline PP, by means of the following equation [14, 15].

$$\chi_c = \frac{\Delta H_m}{\Delta H_{100\%}} \quad (1)$$

Likewise, a variation in Eq. 1 indicates the amount of polypropylene in a blend in terms of the melting enthalpy of the peak corresponding to polypropylene (ΔH_n) and the melting enthalpy of different raw polypropylenes (ΔH_m) (Table 1).

$$\text{Polypropylene content} = \frac{\Delta H_n}{\Delta H_m} \quad (2)$$

The polypropylene contents found in different samples of recycled HIPS indicate values that range between 2.7 and 4 wt%. These values lie in the limit at which HIPS/PP blends begin to lose their properties.

The PP contents detected do not necessarily involve a loss in the mechanical properties of the material, although the presence of PE in the blend may contribute to reduce the mechanical properties as it is a polymer incompatible with HIPS.

Table 1 Polypropylene content in HIPS waste in terms of PP melting enthalpy

	ΔH_n (J g^{-1})	Polypropylene content (%)	
		$\Delta H_m = 81.77 \text{ J g}^{-1}$ Isplen [®] PB 180 G2M	$\Delta H_m = 100.5 \text{ J g}^{-1}$ [16]
Residue 1	2.77	3.38	2.75
Residue 2	3.13	3.82	3.11
Residue 3	3.33	4.07	3.31
Residue 4	3.32	4.06	3.30

Morphology of HIPS/PP blends

Fractured surfaces generated either during testing or during actual operation of a polymeric piece, provide information about material performance and type of stress. In this sense, fracture in a brittle material greatly differs from fracture in a ductile material. On the other hand, for the same material, the morphology of a fractured surface depends on the type of stress acting on the material.

The specimens used in this work were subjected to tensile stresses, and the morphology of the resulting surfaces depended on whether the sampling material was brittle or ductile.

The analysis of the images obtained by SEM shows significant differences in the blends depending on the PP content. The morphological study corresponding to the samples injected at 220 °C illustrates the presence of two well-differentiated phases; a detailed analysis of the images magnified 500 times reveals the random distribution of small PP spherical particles and the presence of a cavity generated by particle segregation during fracture. This fact confirms the important role played by PP on material fracture due to the lack of interfacial adhesion between the PP particles and the HIPS matrix, as can be clearly observed in the photographs. PP particle size ranges between 1 and 2 μm . The ratio of particles and cavities increases as PP content increases (Fig. 5).

Observe that these phenomena do not occur in low PP content samples (2.5 wt% PP), although the detailed analysis of the magnified images allows the observation of PP particles and cavities (Fig. 6).

This phenomenon also occurs in the samples moulded at 250 °C, although moulding temperature does not affect the resulting surface of fracture (Fig. 7).

The lack of interfacial adhesion between the matrix (HIPS) and the dispersed phase (PP) in the form of spherical particles is the main cause of the reduction in the mechanical properties of the blend, though not so much affecting the properties of strength (tensile strength).

Fig. 5 SEM micrograph of fracture surfaces of HIPS/PP injection moulding temperature at 220 °C (x500): (a) 2,5 wt% PP; (b) 5 wt% PP; (c) 7,5 wt% PP; (d) 10 wt% PP

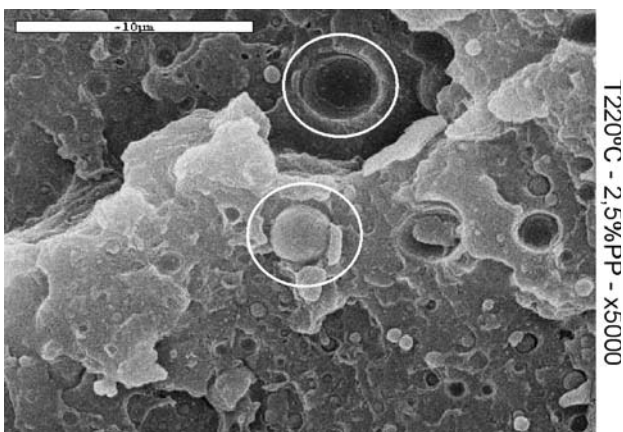
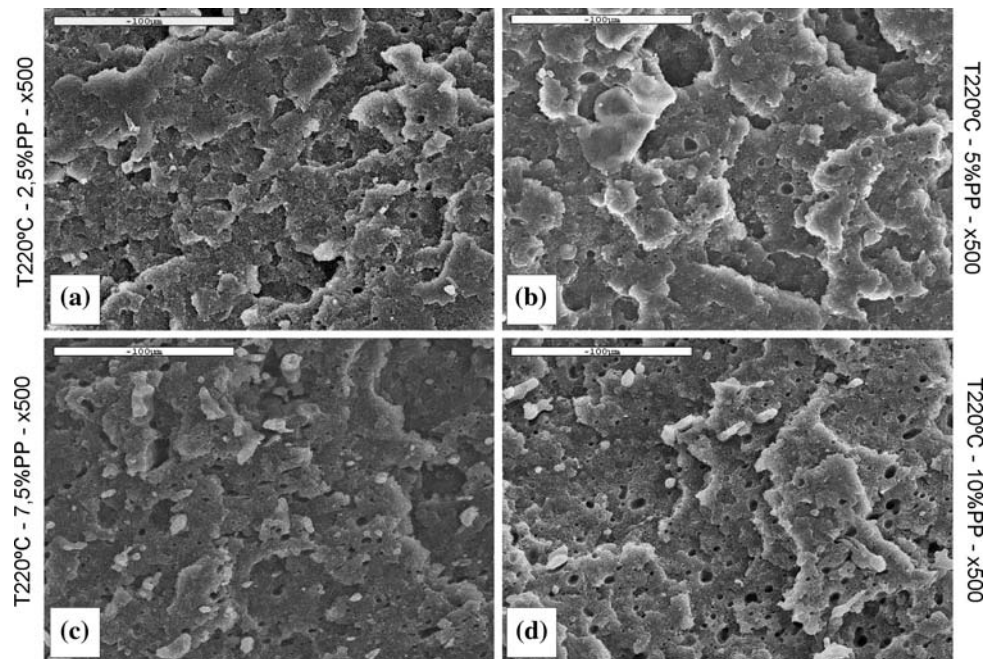


Fig. 6 Micrograph of the structure of a HIPS – PP (97, 5/2, 5% in weight) injection moulding temperature at 220 °C (x5000)

Thermal properties

In the previous section we have described the changes in the mechanical properties induced by the presence of PP, but these are not the only important properties in recycled materials that become affected. Another important effect is the possible alterations in the melt flow index (MFI) of the blend, as this property is important for material processing.

The graphical representation of the results shows a similar evolution of the flow index in the samples injected at 220 and 250 °C. The flow properties of the blends increase as PP content also increases (Fig. 8).

The testing temperature greatly exceeds the melting point of polypropylene (160 °C); under these conditions,

PP is in a state of high fluidity acting as a lubricant for HIPS and favouring extrusion through the injection nozzle.

The flow variations of the material when blended with PP are analysed by differential scanning calorimetry observing the variations in the thermal transitions, as the interaction of the elements causes changes in the T_g of the material [17].

The calorimetric analysis of the blends indicates the presence of three transitions, corresponding to the different component elements of the polymer; a jump of the base line near 100 °C indicates the vitreous transition of styrene; an endothermic peak is observed at 160 °C due to PP melting, and finally an exothermic reaction due to butadiene cross-linking at 180 °C (Fig. 9).

The glass transition temperature indicates the temperature at which chain movement increases noticeably; chain movement can be affected by different factors such as chain length, degree of cross-linking and the presence of other polymers of different nature. In this sense, the analysis of the results reveals that the glass transition temperature increases depending on the PP contents independently of the moulding temperature [18] (Fig. 10).

There are two factors that influence the glass transition temperature, the presence of PP and butadiene. First, the semicrystalline nature of PP, with an amorphous and a crystalline phase, affects chain movement; the presence of crystalline regions, in which the chains are more compacted, reduces chain movement and as a consequence the T_g of the blend increases. Second, the cross-linking reaction of butadiene affects chain movement too, because this reaction causes structural stiffness.

Fig. 7 SEM micrograph of fracture surfaces of HIPS/PP injection moulding temperature at 250 °C (x500): (a) 2,5 wt% PP; (b) 5 wt% PP; (c) 7,5 wt% PP; (d) 10 wt% PP

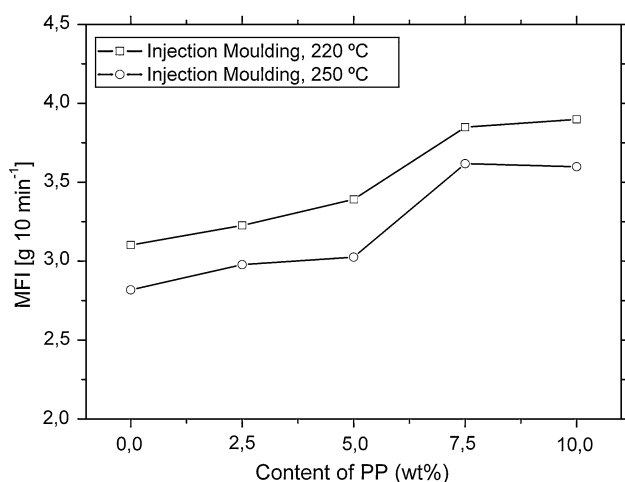
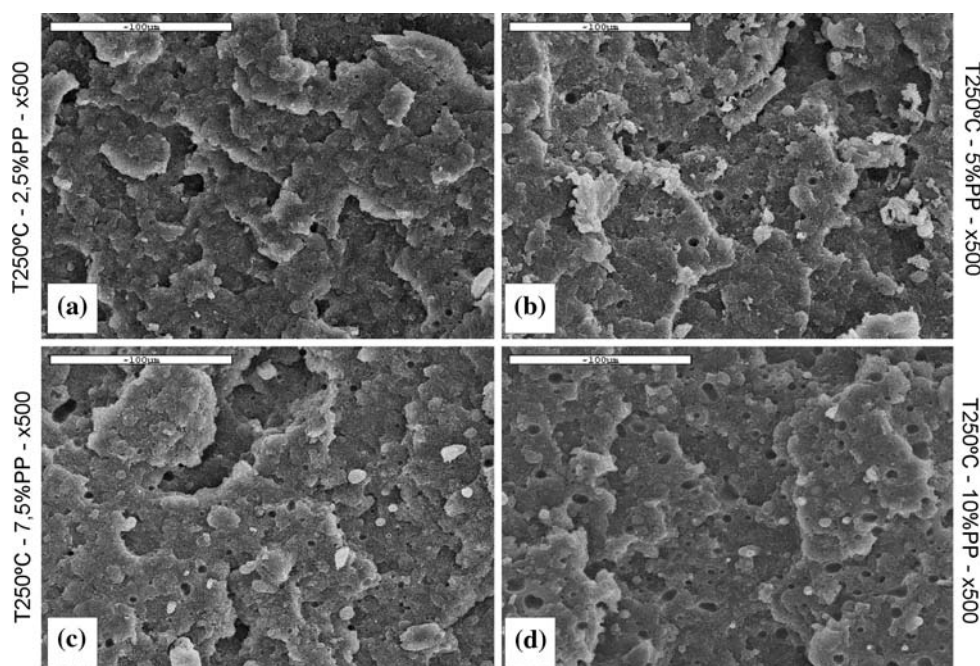


Fig. 8 Variation of melt flow index (MFI) in function of PP presence

Conclusions

The analysis of the different mechanical properties shows a generalized reduction of tensile strength and elongation at break in the samples, with a sharp drop from 5% PP contents.

Blend preparations using immiscible materials exhibit a general loss of mechanical properties, in particular in ductility. This negative effect occurs in samples processed at different moulding temperatures, 220 and 250 °C.

The analysis of the SEM images provides information about the type of fracture, which though not relevant for a quantitative analysis of the materials, adds qualitative information about the behaviour of the samples.

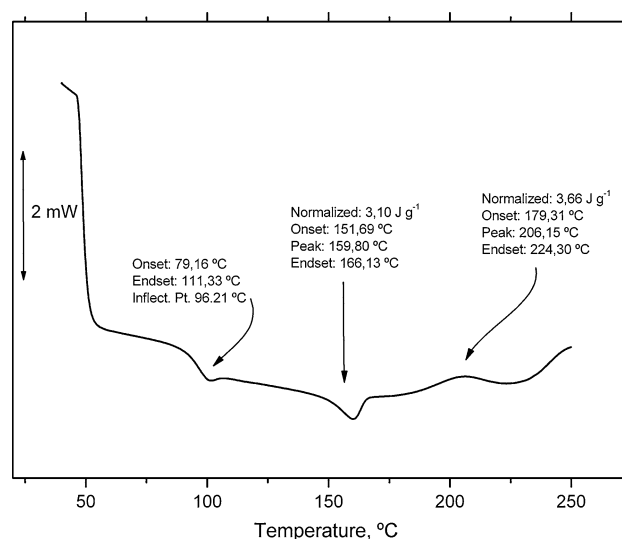


Fig. 9 DSC curve of HIPS/PP (97, 5/2, 5% in weight) injection moulding temperature at 220 °C

The addition of PP generates the appearance of two phases clearly differentiated, the matrix phase formed by the predominant material in the blend, and the dispersed phase by the less abundant material. The immiscibility of both materials, HIPS and PP, promotes the formation of spheres made of the less abundant material in the blend.

The different surfaces generated show the presence of spheres and cavities produced by segregation of the spherical particles. An increase of PP in the blend causes an increase in the ratio of spheres and/or cavities on the fractured surface, acting as weak points of the material.

As a consequence of this structure the material deteriorates because of the immiscibility of PP with styrene, and

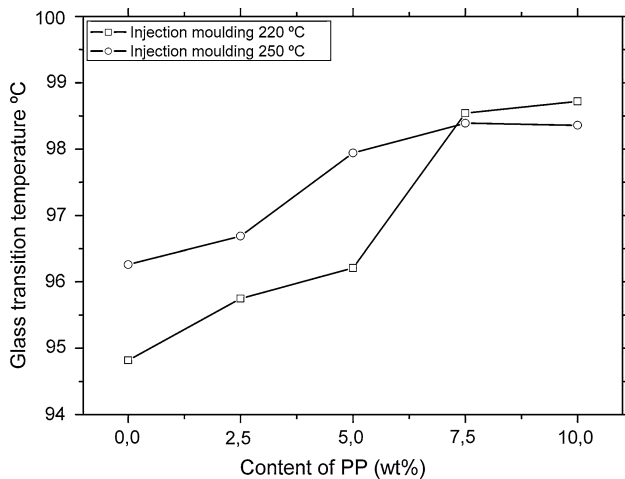


Fig. 10 Changes on T_g values for HIPS in function of PP presence

this little or nil interaction prevents the correct transmission of stresses resulting in the reduction of the mechanical properties of ductility and strength. Since PP does not mix well and does not interact with the styrene phase it acts as a concentrator of stresses.

The combination of materials in a blend not only causes changes in the mechanical properties, but also modifies other properties such as the thermal properties, which are important for material processing. In this sense, the presence of PP increases flow index in the HIPS/PP blend, improving processability.

The presence of PP and butadiene increases T_g in the blends independently of the moulding temperature. Cross-linking reaction of butadiene and chain packing of the presence of the crystalline phase of PP reduce slippage in the structure of the material and consequently produces an increase in T_g .

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