Evaluation of the Final Morphology of HIPS Based on the Architecture of the Compatibilizer Graft Copolymer PBd-*g*-PS

Carlos de Anda,[1] *Graciela Morales,**[1] *Pablo Acuña,*[1] *José Sosa,*[2] *Dave Knoeppel,*[2] *Jimmy W. Mays*[3]

Summary: High Impact Polystyrene (HIPS) was synthesized by radical bulk polymerization at 70 °C using 6% w/w of total rubber and 0.01% w/w of azobisisobutyronitrile (AIBN) as radical initiator, where the total rubber was composed by polybutadiene (PBd) and model graft copolymers PBd-*g*-PS. Different ratios in weight percent of PBd to PBd-*g*-PS were used in order to evaluate the effect of the graft copolymers on the morphology development of the rubber particles during the HIPS synthesis reaction. The morphology of the final material was evaluated by Transmission Electron Microscopy (TEM). The model graft copolymers used with controlled architecture and molecular weight were synthesized previously by high vacuum anionic polymerization. Results show that increasing the content and changing the architecture of the graft copolymer significantly affects the phase inversion point.

Keywords: A_2B graft copolymers; HIPS; rubber particles size distribution

Introduction

High Impact polystyrene (HIPS) is one of the most important thermoplastics materials; it combines the rigidity of polystyrene with the toughness of polybutadiene. The improvement in impact strength in this material is due to the presence of rubber particles dispersed into the polystyrene matrix.[1]

In a HIPS reaction, styrene monomer reacts to produce polystyrene (PS) in a solution containing dissolved polybutadiene (PBd). At the beginning of the reaction, once the polymerization of styrene has started, there exists a phase separation due to the incompatibility between the PS and the PBd, resulting in two phases system; a continuous solution of styrene/PBd and a disperse solution of styrene/PS. In the styrene/PBd phase, it takes place the grafting reaction resulting in graft copolymers of PBd-*g*-PS, meanwhile in the styrene/PS phase; it only occurs the polymerization of styrene. Both phases coexist dispersed in each other in the form of an oil-oil emulsion, which is stabilized by the grafts generated onto the PBd chains. After a certain styrene conversion, the system presents a co-continuity between the phases and at the moment where their viscosities are equal and under an appropriate shear stress, the phase inversion takes place and the morphological structure of the rubber particles is established. After the phase inversion, the phase of styrene/PS is the continuous phase, while the styrene/PBd phase is the disperse phase.[2]

About the morphological structure formation, the PS grafted onto the PBd backbone can stabilize the emulsion and depending on the molecular characteristics of the graft copolymer formed *in situ* during the synthesis of HIPS, the interfacial tension between the two incompatible

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[1] Centro de Investigación en Química Aplicada, Saltillo, México 25253
E-mail: gmorales@ciqa.mx
[2] Research and Technology Center, Total Petrochemicals USA, La Porte, TX 77571
[3] Department of Chemistry, University of Tennessee, Knoxville, TN 37996

phases can be modified leading to the formation of different morphologies.[3]

Since HIPS is obtained by free radical polymerization, the architecture of the resulting graft copolymer is difficult to control due to the nature of the propagating species, where the final morphology of the material can be interpreted as a result of a mixture of different copolymers with a variety of architectures.[4]

It is important to note that the chains with two PS grafts are located in the interphase between the particles and the continuous phase stabilizing the emulsion; meanwhile the chains with only one PS graft or more than two PS grafts, remain in the styrene/PBd phase forming micelles (simple or inverse micelles). In the case of micelles with more than two grafts, the formation of particles of lower size is induced presenting a dot type morphology.[5]

With the aid of some model graft copolymers synthesized *ad-hoc*, this work deals with the study of the effect of the PBd-*g*-PS architecture on the phase inversion point and the development of the rubber particle morphology during the synthesis of HIPS.

Experimental Part

Materials

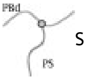
Styrene monomer and polybutadiene rubber ($M_n = 100{,}000$–$110{,}000$ g/mol) were supplied by Total Petrochemicals USA and used as received. The radical initiator azobisisobutyronitrile (AIBN) (Sigma-Aldrich) was recrystallized from ethanol.

Graft copolymers with 1 PS graft onto the PBd backbone were synthesized by using the technique of high vacuum anionic polymerization employing specially made glassware apparatus. These copolymers can be visualized as a 3-arm star (A_2B type). The synthesis of the graft copolymers was carried out using chlorosilane chemistry. The initiator used was sec-BuLi for all the reactions, while benzene was used as the solvent.[6,7] After the copolymers were synthesized, they were characterized by Size Exclusion Chromatography (SEC) using a Hewlett Packard chromatograph fit with a set of ultra-styrogel columns (of nominal pore 10^5, 10^4, and 10^3 Å) to obtain the molecular weight M_n of the arms. Also, the copolymers were characterized using a Precision Detector PD-2040 with two angle light scattering detector (15° and 90°) for static scattering measurements to determine the absolute molecular weight of the copolymer. The molecular characteristics of the copolymers obtained are shown in Table 1.

HIPS Synthesis

HIPS synthesis was carried out by using a multi-reactor system (Argonaut Endeavor) equipped with 8 reaction vessels of 15 mL capacity, with controlled temperature and shear rate. Several HIPS were synthesized using different reaction conditions (see Table 2), where the main variable that was manipulated was the amount of graft copolymer used in each reaction. The amount of graft copolymer was measured as a percent of the total rubber used in each polymerization, which was 6% w/w for all the

Table 1.
Characteristic of the graft copolymer used in the HIPS synthesis

 Samples	M_n PS_{graft}[a] (g/mol)	M_n PBd_{total}[b] (g/mol)	M_n COP[c] (g/mol)	Microstructure[d]		
				PS %	1,4-PBd %	1,2-PBd %
COP1	68 k	66 k	134 k	49	44	7
COP2	66 k	102 k	171 k	37	57	6

[a] Molecular weight values for the PS graft obtained by Exclusion Chromatography;
[b] Molecular weight values obtained by Exclusion Chromatography for the PBd backbone calculated using the molecular weight of the copolymer and the PS graft;
[d] Absolute molecular weight values for the graft copolymer obtained by Two Angle Laser Light Scattering;
[d] Microstructure of the polymer obtained by ^{1}H NMR.

Table 2.
Experimental conditions used for the synthesis of HIPS

Material	St (g)	PBd (g)	PBd-*g*-PS (g)	Copolymer (% w/w)[1]	Copolymer Type	PI time (h)	Conversion (%)
HIPS1	47.00	3.00	–	–	–	2	11.33
HIPS2	47.30	2.70	0.40	7	COP1	3	16.94
HIPS3	27.92	1.53	0.54	15	COP1	5	22.83
HIPS4	23.43	1.39	0.17	7	COP2	3	15.94
HIPS5	46.70	2.70	0.69	15	COP2	4	20.48

[1]% w/w of model graft copolymer related to the total rubber used in the HIPS synthesis.
[2]a total rubber concentration of 6% w/w was used in all reactions and involves the rubber from PBd and the rubber from PBd-g-PS.

reactions. It was also selected 0% graft copolymer for a control HIPS material, and two rubber compositions for the HIPS synthesis were selected: a) 7% graft copolymer/93% PBd, and b) 15% graft copolymer/85% PBd. The use of the graft copolymer in the reaction of HIPS doesn't affect the values of monomer conversion, since it is not involved during the polymerization. Although the viscosity of the reaction solution can be affected by the use of the graft copolymer, affecting the polymerization rate. AIBN was used as the initiator since the grafting reactions by hydrogen abstraction is minimized in its presence, to ensure that the grafting degree would only be the result of the amount of graft copolymer used.[8] Temperature (70 °C) and shear rate (250 rpm) were constant for all the reactions. Samples taken at predetermined periods of time were analyzed by physico-chemical methods and the rest of the sample was polymerized to total conversion at 150 °C for 12 hours. Once the polymerization was complete, samples were taken for TEM characterization. Electron microscopy analysis was performed in a JEOL STEM at 30 kV, on samples cut with a LEICA ULTRACUT ultra microtome and treated with osmium tetra oxide (OsO_4). Rubber Particle Size distribution and rubber particle size was determined from samples taken from the reaction mixture using a Malvern Mastersizer 2000.

Results and Discussion

The experimental conditions used of the HIPS synthesis using only PBd (HIPS1) as the rubber or PBd/PBd-*g*-PS (HIPS2 to HIPS5) with different amount of graft copolymer are shown in Table 2.

Since, it is needed that the phase inversion (PI) takes place in the polymerization of HIPS for the rubber particles to be formed, it is of highly interest to determine the moment at which the rubber becomes the disperse phase. The phase inversion was followed by analyzing the Rubber Particle Size (RPS) distribution, where the presence of a narrow distribution indicates that the phase inversion has occurred and the rubber particles are established.

From the RPS results, it can be observed that for HIPS1 the phase inversion takes place after 2 hours of reaction (Figure 1). Meanwhile for HIPS2, the phase inversion occurs after 3 hours. In the case of the HIPS3 and HIPS5, which contain a greater amount of graft copolymer, independently of the molecular weight of the PBd backbone, the time for phase inversion is higher (see Figure 2 for HIPS3 and Figure 4 for HIPS5). This behavior is attributed to the lower interfacial tension obtained in the presence of 15% of COP1 or COP2 that yields a larger interval of conversion values for the co-continuous morphology to be disturbed (greater amount of PS necessary to invert the phases) and for the PI to take place in accordance to literature.[9]

Once the point of phase inversion in each series of reactions monitored by RPS was reached, the solutions were taken to complete monomer conversion and the final material was analyzed by TEM. The results previous obtained were corroborated

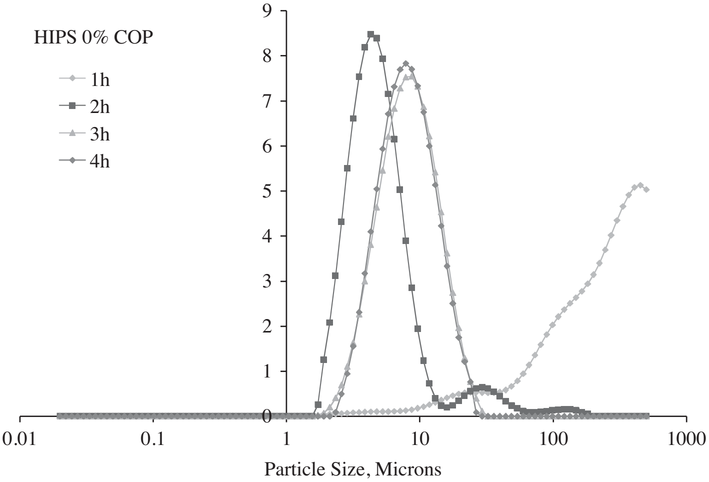


Figure 1.
Rubber Particle Size distribution for the synthesis of HIPS1 with 0% of graft copolymer.

through the characterization of the corresponding morphology by TEM. From Figure 3, it can be observed that HIPS1 and HIPS2 presents a very well defined salami type morphology with small occlusion of PS, while HIPS3 analyzed at the reaction time of 4 hours has not reached the phase inversion and presents a co-continuous phase.

The average size of rubber particles for HIPS1 can be attributed to the radical initiator used, since AIBN tends to minimize the grafting reaction, resulting in bigger particles size due to a higher interfacial tension as a consequence of the absence of graft copolymer able to compatibilize the two phases. When 7% of COP1 is added to the reaction during the synthesis of HIPS, the average rubber particle size is 1.87 μm, only a slightly difference between the reaction with 0% COP ($Dp = 1.82\,\mu m$), due to the small amount of the interfacial agent (PBd-*g*-PS) present during the particle formation. In the case HIPS2, this sample presents a population of small rubber particles ($Dp = 1.22\,\mu m$ estimated from the particles with a diameter less than 2 μm), which are attributed to the presence of the graft copolymer, which forms small microphases resulting in the development of rubber dots morphology.

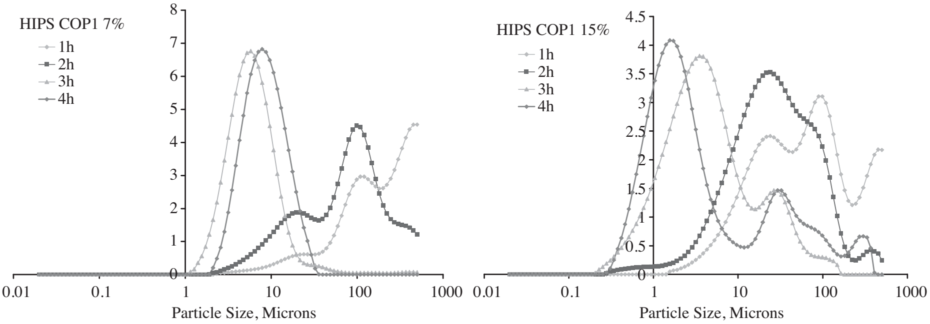


Figure 2.
Rubber Particle Size distribution for the synthesis of HIPS2 with 7% and HIPS3 with 15% of graft copolymer COP1.

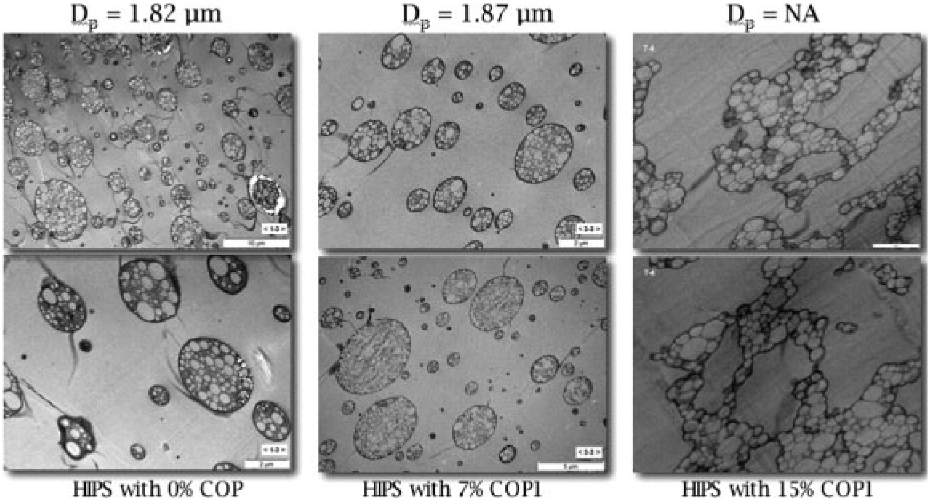


Figure 3.
TEM micrographs for the different HIPS synthesized using COP1 (HIPS1 - 0% COP, HIPS2 - 7% COP1, HIPS3 - 15% COP1) at the reaction time when the phase inversion occurred as reported in Table 2.

Once it was established that the amount of model graft copolymer used cannot be higher than 15% of the total rubber, according to the previous results, a different model graft copolymer with longer PBd backbone (higher M_n) chain was used for the synthesis of HIPS under the same experimental conditions.

In these cases (HIPS4 and HIPS5), the phase inversion occurs after 3 and 4 hours of reaction time (Figure 4). The higher reaction time for the phase inversion to take place, in comparison with the HIPS synthesized with the 0% of COP, is explained by the higher molecular weight of the polybutadiene, thus presenting a solution with a higher viscosity, which requires a greater amount of PS to reach the co-continuous point after which the phase inversion can occur.

After these series of reactions were taken to total monomer conversion, TEM micrographs were taken (Figure 5). HIPS4 presents an average rubber particle size of 1.5 μm, which is bigger than the 1.04 μm of HIPS5. It can be assumed that by using of a greater amount of graft copolymer in the HIPS reaction, the interfacial tension

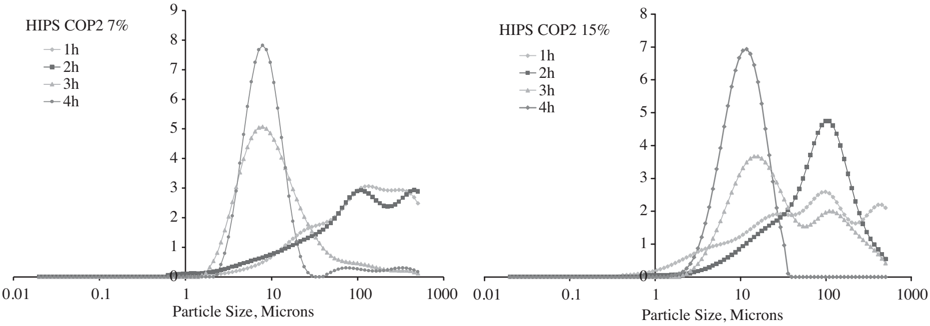


Figure 4.
Rubber Particle Size distribution for the synthesis of HIPS4 with 7% and HIPS5 with 15% of graft copolymer COP2.

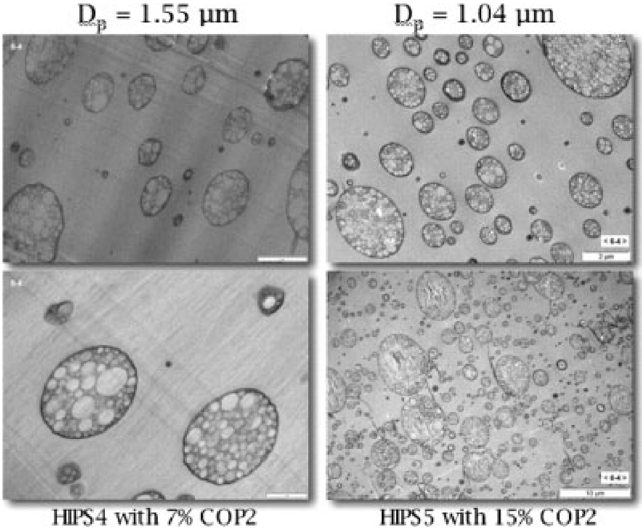


Figure 5.
TEM micrographs for the different HIPS synthesized using COP2 (HIPS4 - 7% COP2, HIPS5 - 15% COP2) at the reaction time when the phase inversion occurred as reported in Table 2.

between the PS phase and the PBd phase is decreased resulting in smaller rubber particles. It the case of HIPS5, it can be observed that a large quantity of small rubber particles are present, meaning that the COP2 tends to form small micelles at the first step of the reaction, forming small rubber microphases. Also, for both cases, the average rubber particle size is smaller than the materials obtained with COP1.

For the HIPS with 7% of COP1 (HIPS2) and COP2 (HIPS4), it is observed that the TEM micrograph for HIPS2 presents a higher number of small particles in comparison with HIPS 4. This is explained as consequence of a higher number of graft copolymer molecules in the reaction resulting in the formation of small micelles, since for the same concentration of 7% of copolymer, more molecules of COP1 are needed due to the smaller molecular weight of the PBd backbone. Also, the chemical composition of the copolymers has a role in the particle formation, affecting the interfacial tension between the two phases. The rubber particle size of the HIPS synthesized is bigger for the reactions obtained using COP1 (HIPS2 and HIPS3), as a consequence of the copolymer molecules forming micelles, thus leaving less amount of copolymer to be located at the interphase between the PS and the PBd increasing the interfacial tension.

Conclusions

HIPS with salami type morphology were obtained using different model graft copolymers during their synthesis (COP1 and COP2). By increasing the amount of graft copolymer used (with respect to the total rubber amount), the time to reach the phase inversion point shift to higher values of reaction time, as a consequence of a decrease in the interfacial tension between the 2 phases (HIPS2 and HIPS3). The same results were obtained when the graft copolymer presents a longer PBd backbone chain (HIPS4 and HIPS5). The average particle size for the HIPS samples was decreased by the presence of the graft copolymer with higher molecular weight of the PBd backbone (COP2) in the reaction in comparison with the reaction without copolymer. Also, by increasing the amount of graft copolymer from 7% to 15%, the average rubber particle size was decreased (COP2).

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