

Evaluation of the final morphology of HIPS based on the architecture of the compatibilizer graft copolymer PBd-g-PS

De Anda, C. ^{*}, Morales, G. ^{*}, Acuña, P. ^{*}, Sosa, J. [¥], Knoeppel, D. [¥], Mays, J. W. [†]

^{*} Departamento de Síntesis de Polímeros, Centro de Investigación en Química Aplicada, Saltillo, México 25253

[¥] Research and Technology Center, Total Petrochemicals USA, La Porte, TX 77571

[†] Department of Chemistry, University of Tennessee, Knoxville, TN 37996

gmorales@ciqa.mx:

1. Summary

High Impact Polystyrene (HIPS) was synthesized by radical bulk polymerization using 6% w/w of total rubber and AIBN as a radical initiator, at 70°C, where the total rubber was composed by polybutadiene (PBd) and model graft copolymers synthesized *ex profeso*, in different relation in weight percent in order to evaluate the effect of the graft copolymers on the morphology development. The morphology of the final material was evaluated by Transmission Electron Microscopy (TEM). The model graft copolymers PBd-g-PS used were previously synthesized by high vacuum anionic polymerization with controlled architecture and molecular weight.

2. Introduction

High Impact polystyrene (HIPS) is one of the most important thermoplastics materials that 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. Depending on the molecular characteristics of the graft copolymer formed *in situ* during the synthesis of HIPS, the interfacial tension between the two incompatible phases can be modified leading to the formation of different morphologies [1]. As 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, so the final morphology can be interpreted as a result of a mixture of different copolymers with variety of architectures.

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 development of the rubber particle morphology.

3. Experimental

3.1 Materials

Styrene and polybutadiene ($M_w=100,000-120,000$ g/mol) were supplied by Total Petrochemicals USA and used as received. AIBN (Sigma-Aldrich) was crystallized from ethanol. The model graft copolymers were synthesized by high vacuum anionic polymerization technique following the methods describe elsewhere [2].

3.2 HIPS synthesis

HIPS synthesis was carried out using an Argonaut Endeavor equipment with 8 reaction vessels of 15 mL capacity, with controlled temperature and shear rate. HIPS were synthesized in bulk using 6% w/w of total rubber, where 7% and 15% of the total rubber corresponds to the model graft copolymers. AIBN was used as the initiator due to the absence of grafting reactions by hydrogen abstraction in its presence and to ensure that the grafting degree would only be the result of the amount of graft copolymer used. Temperature (70°C) and shear rate (250 rpm) were constant for all the reactions. Samples taken at predetermined periods of time were physico-chemical analyzed and the rest of the sample was totally polymerized at 150°C for 12 hours. Once the polymerization was complete, samples were taken for TEM characterization. Rubber Particle Size (RPS) distribution was determined using a Malvern Mastersizer 2000.

4. Results and discussion

The experimental conditions and main results from the HIPS synthesis using only PBd (HIPS-1) as the rubber or PBd with different amount of graft copolymer 1 (COP1) (HIPS-2 and HIPS-3) are shown in Table 1. The phase inversion was followed by analyzing the Rubber Particle Size (RPS). From the RPS graphs, the presence of a narrow distribution indicates that phase inversion (PI) has occurred and the rubber particles are established. From Figure 1, it can be observed that phase inversion takes place after 3 hours for the HIPS-1 and HIPS-2 but in the case of the HIPS-3 with a greater amount of graft copolymer, the time for phase inversion is longer. The lower

interfacial tension obtained in the presence of 15% of COP1 yields a large interval of conversion (greater amount of PS necessary to invert the phases) for the co-continuous morphology to be disturbed and the PI can take place, according to literature [3].

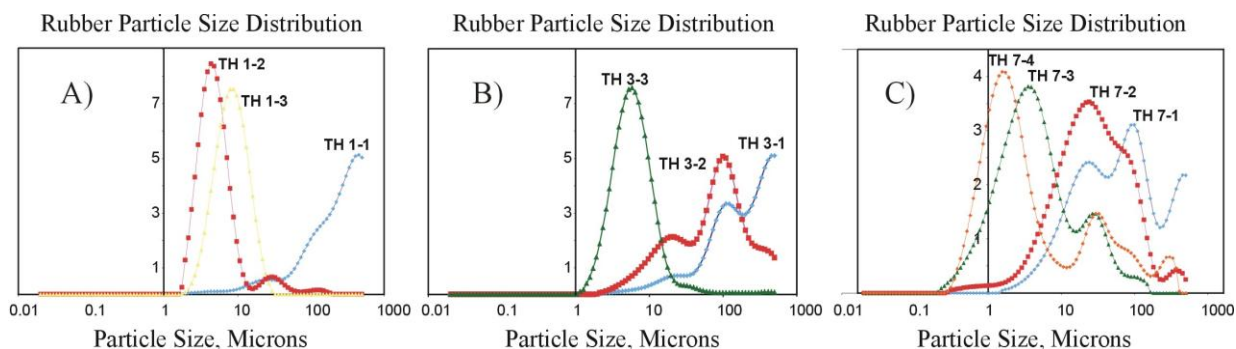
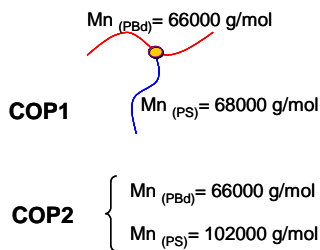


Figure 1: Rubber Particle Size distribution of different HIPS, a) HIPS-1, b) HIPS-2 and c) HIPS-3

Table 1.- Characteristic of the graft copolymer used in HIPS synthesis and experimental conditions

Material	Amount of PBd (g)	Amount of PBd-g-PS (g)	Type of PBd-g-PS	Time for PI (h)
HIPS-1	3.00	0.00	-----	2
HIPS-2	2.70	0.40	COP1	3
HIPS-3	1.53	0.54	COP1	5
HIPS-4	1.39	0.17	COP2	3
HIPS-5	2.70	0.69	COP2	4

Characterisitics of graft copolymers



Once the point of phase inversion was monitored by RPS, and the reactions were taken to complete monomer conversion, the crosslink reaction took place and the final morphology was evaluated (see Figure 2). HIPS-1 and HIPS-2 presents a very well define salami type morphology while HIPS-3 has not reached the phase inversion and presents a co-continuous phase of rubber and PS.

Once it was established that the amount of model graft copolymer can not be higher than 15% of the total rubber according to the previous results, a different model graft copolymer with longer PS graft chain (see Table 1, COP2, HIPS-4 and HIPS-5) was used for the synthesis of HIPS under the same experimental conditions.

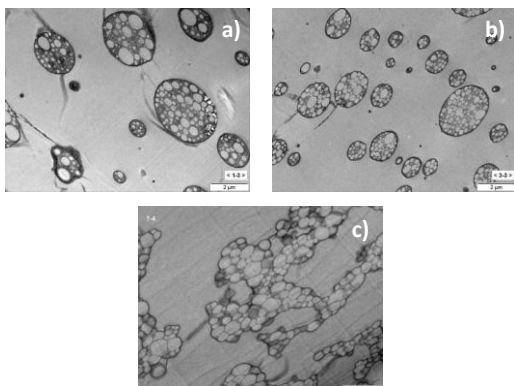


Figure 2: TEM micrographs of different HIPS: a) HIPS-1, b) HIPS-2 and c) HIPS-3

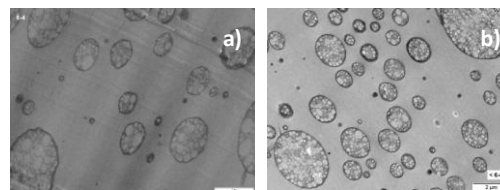


Figure 4: TEM micrographs of different HIPS: a) HIPS-4 and b) HIPS-5

From Figure 3, it can be observed that the phase inversion occurs after 4 hours for both HIPS (HIPS-4 and HIPS-5) which was confirmed by TEM analysis (Figure 4).

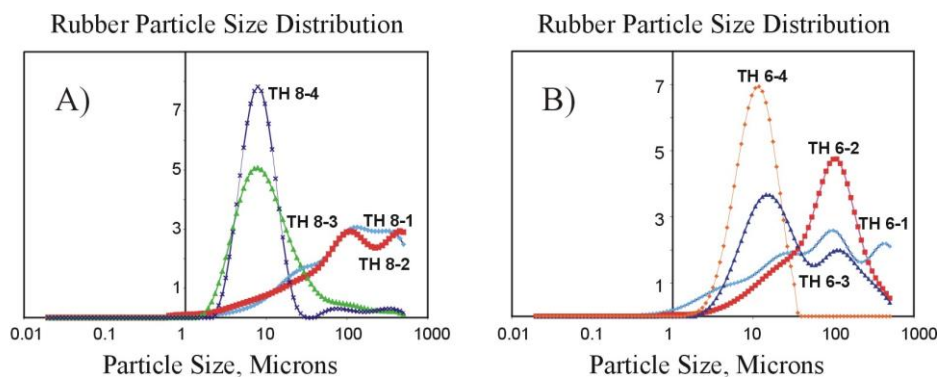


Figure 3: Rubber Particle Size distribution of different HIPS, a) HIPS-4 and b) HIPS-5

5. Conclusions

HIPS with salami type morphology was obtained using different model graft copolymers (COP1 and COP2). By increasing the amount of graft copolymer used of the total rubber amount, the interfacial tension between the 2 phases decreases, and the time to reach the phase inversion point moves to higher values. The same results were obtained when the graft copolymer has a longer PS chain.

4. References

1. Fisher M. and Hellmann G.P., *Macromolecules*, 29, 2498 (1996)
2. Pitsikalis, M., Pispas, S., Mays, J. W., Hadjichristidis, N., *Adv. Polym. Sci.*, 135, 1, (1998)
3. R. Díaz de León, G. Morales, P. Acuña , F. Soriano, *Polymer Engineering and Science*, en prensa