DOI: 10.1002/masy.201300213

SB-S Core-Shell Particles in Semicontinuous Seeded Emulsion Polymerization and their use as Impact Modifier

*Nilva R. Uliana, Ricardo A. F. Machado, Claudia Sayer, Pedro H.H. Araújo**

Summary: The impact resistance of polymeric materials can be modified by the addition of polymer particles with core shell structure, in which the core consists of a rubber phase and the shell of a glassy phase. In this work, the synthesis of core-shell particles (polybutadiene-rich phase / polystyrene rich phase) by emulsion polymerization and their use as impact modifiers in crystal polystyrene, PS, was investigated. Reactions were followed by gravimetry and dynamic light scattering analysis and core-shell morphology was determined by transmission electron microscopy. This latex, after dried, was incorporated into a PS matrix in a single screw extruder. The impact resistance increased with the incorporation of the core-shell particles and with the number of passes through the extruder.

Keywords: core-shell particles; emulsion polymerization; impact modifier; polybutadiene; polystyrene

Introduction

Core-shell polymer particles are multi-component particles where the core of the particle presents a different composition of the shell. Polymeric materials based on core-shell particles present final properties that depend not only of the composition of each polymer phase but also on the morphology of these particles creating a versatile class of materials. This characteristic opens the possibility for tailor-made properties for each application as, for instance, polymer particles with soft core and hard shell resulting in particles suitable to act as impact modifiers, or latex polymer particles with hard core and soft shell resulting in water-born paints with low film formation temperature.[1–7]

Several heterogeneous polymerization techniques as emulsion, miniemulsion, dispersion and suspension polymerizations can be employed to obtain polymer particles with core-shell structures allowing to get incompatible polymers into one particle or to add functionality either into the core or into the shell.[8–11] Each technique leads to the formation of particles in a specific size range that can affect the kinetic control of the polymerization. As the final morphology depends on both thermodynamic and kinetic aspects, as quite frequently the equilibrium morphology may not achieved due to kinetic control of the morphology development, the choice of the operation conditions and the heterogeneous polymerization technique is decisive.

Emulsion polymerization is quite frequently employed to obtain particles with core-shell morphology in the submicrometric range. To obtain core-shell particles it is necessary to operate on semicontinuous mode where the feed composition is changed abruptly allowing the formation of a new polymer phase on the pre-existing polymer particle nucleated at the begging of the reaction. Another frequently used technique is seeded emulsion polymerization, in which the particles are synthesized in a two step procedure. In this way, a seed is synthesized in the first stage by

---

Department of Chemical Engineering and Food Engineering, Federal University of Santa Catarina, Postal Code 476, 88040 900 Florianópolis, Brazil
E-mail: pedro@enq.ufsc.br

conventional emulsion polymerization and in the second stage the seed particles are fed at the initial charge and a different monomer is fed during the reaction to form the shell.[12–16] In this type of polymerization, the polymer of the second stage is build up on the surface of the seed particles and has the advantage of a better control of the final particle size distribution. Alternatively, depending on the interfacial tensions, the seed polymer may form a continuous shell around the second stage polymer resulting in inverted core-shell particles.[17]

ABS (terpolymer of acrylonitrile-butadiene-styrene) core-shell particles obtained by emulsion polymerization are commercially employed to improve the impact resistance of PVC as the acrylonitrile-polystyrene hard shell improves the compatibility between the discrete elastomeric particles and the PVC matrix increasing the impact strength. Formulations with rubber compounded into the general purpose polystyrene (GPPS) are effective to improve the impact resistance. However, better results could be obtained when grafting the elastomeric particles into the continuous polystyrene phase as occurs during the synthesis of high impact polystyrene (HIPS) in bulk/solution or suspension polymerization.[18] In this sense, adding a polymer particle with a elastomeric core grafted to a polystyrene shell could be effective to improve the impact resistance of GPPS.

Rubbery latex particles of styrene-butadiene copolymer (SB) with a high concentration of butadiene are commercially obtained by emulsion polymerization. However, due to its low glass transition temperature this SB latex forms a continuous film after drying, with loss of desired morphology (spherical rubbery particles). To prevent the deterioration of elastomer particle morphology during drying and to further increase the compatibility with the PS matrix, this work intends to study the synthesis of SB-S core-shell particles by semicontinuous seeded emulsion polymerization to be used as impact modifiers in PS.

Experimental Part

The materials used in this work were: styrene (STY, Merck), divinylbenzene (DVB) as crosslinker, latex Taktene® S62 (Lanxess) composed by styrene/butadiene (SB) copolymer with high amount of butadiene (80%) and solids content of 68 wt.%, potassium persulfate PA (KPS, Vetec) as initiator and sodium lauryl sulphate (SLS, Vetec) as emulsifier.

Seeded Emulsion Polymerization

Semicontinuous seeded emulsion polymerization reactions were conducted in a jacketed glass reactor with an initial charge of SB latex S62 and with two feed streams. One feed was composed of styrene and crosslinking agent (DVB) and the other of initiator, emulsifier and water. The feed streams were maintained constant during the first two hours and the reactions were conducted at 80 °C during the first 3 hours and at 90 °C in the last hour of reaction. Table 1 presents the formulation used.

Samples were collected at regular time intervals of 20 min for the determination of conversion by gravimetric analysis and particle size measurements (z average particle diameter) by dynamic light scattering (Zetasizer Nano S from Malvern Instruments). Chromatographic measurements were performed on a gas chromatograph model GC - 2010AF coupled to a headspace sampler (model Shimadzu AOC - 5000). Particle morphology of samples stained

Table 1.
Formulation of semi-continuous seeded emulsion polymerization reactions.

	Amount (wt.%)
Initial Charge	
Water DDI	60.74
KPS	0.09
Latex S62	9.00
Feed 1	
STY	18.40
DVB	0.37
Feed 2	
KPS	0.09
SLS	0.06
Water DDI	11.25

with osmium tetroxide was observed by transmission electron microscopy (JEOL JEM -1011). Solid-liquid extractions using methyl ethyl ketone as solvent were performed in a Soxhlet extractor to determine the gel content (insoluble polymer). The extraction stage lasted 24 hours and the gel content was determined by gravimetric analysis from the ratio between the mass after and before extraction.

Incorporation of Core-Shell Particles in PS

The core-shell latex was dried at 37 °C, macerated and incorporated in polystyrene (PS) in a single-screw extruder. The composition in the extruder was 70 wt.% of PS and 30 wt.% of core-shell particles. The temperature zones range from 150 °C to 170 °C with constant rotation at 45 rpm. In order to compare the incorporation during extrusion and, thus, the effect on the impact strength of the material, samples with two or three passages were produced by extrusion.

The product obtained after extrusion was milled in a vertical mill granulator and the specimens for Izod impact analysis were prepared using a thermopress at 185 °C. Specimen dimensions (64 mm x 12.7 mm x 5.0 mm) and Izod impact test conditions (VI - notch angle 45° and 2.54 mm deep in the center of the specimen) followed ASTM D256. Impact tests were performed using the impact pendulum method by IZOD - EMIC (AIC).

Results and Discussion

Results in Figure 1 shows the instantaneous and total conversion during semicontinuous seeded emulsion polymerization. The instantaneous conversion shows that the reaction was not performed on starved conditions and the polymerization proceeded following monomer and initiator feeding. At the end of the feeding time (120 min), reaction rate started to decrease and at 180 min conversions around 96% were achieved according to gravimetric results. The residual monomer content after 240 min, determined by head-space gas chromatography was around 0.09 wt.%, indicating a higher conversion than by gravimetry. The difference observed on gravimetric conversion can be explained by a small monomer loss during reaction due to volatilization.

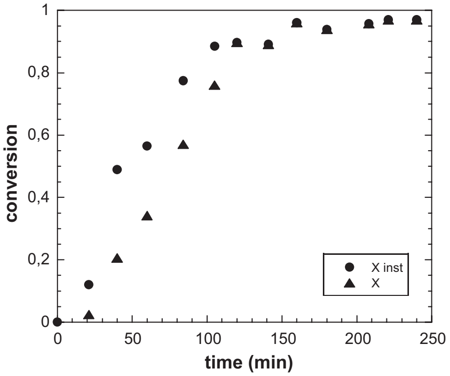

Figure 1.
Evolution of instantaneous (X inst) and total (X) conversion during semicontinuous emulsion polymerization.

Figure 2 shows the intensity particle size distributions (PSD) of the SB polymer seeds (latex S62), and of the particles produced in the semicontinuous seeded reactions, both measurements were performed by DLS. The PSD of the polymer seeds is bimodal. It is a usual procedure to decrease the viscosity of the latex with high solids content (68 wt.%), while the final

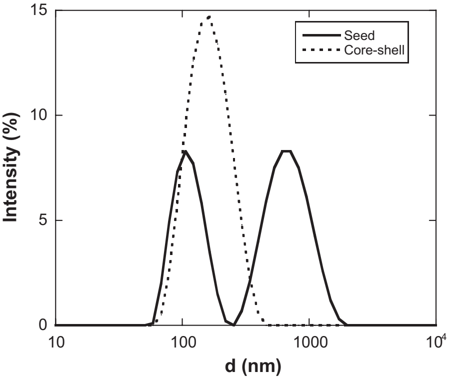

Figure 2.
Particle size distribution of the seed (latex S62) and the core-shell particles after the semi- continuous emulsion polymerization reaction.

distribution of the core-shell particles, with a solids content of 27 wt.%, showed an unimodal shape with an average diameter larger than the first mode of particles (smaller particles) of the seed latex. These results indicate that the bigger particles present in the seeds grew much slower during the reaction than smaller particles due to the effect of radical compartmentalization. Since the number of small particles in the seed is much higher than that of big particles and due to the faster polymerization and growth of the former, the contribution of the population of big particles to the PSD decreased during polymerization.

Figure 3 shows TEM images of the seed latex particles and of the final core-shell polymer particles. In Figure 3a it can be seen that the seed latex (S62) is composed of a small number of very large particle sizes (500 nm–1 μm), and a lot of smaller particles (~100 nm) corroborating the DLS analysis. In the image of the final polymer particles after the semicontinuous seeded reaction (Figure 3b) the presence of large particles was not observed (due to their smaller amount) and the particle size range is between 100–200 nm. This TEM result shows good agreement with the PSD curve obtained by DLS (Figure 2). To allow a better visualization of the internal morphology of the particles, samples were selectively stained with osmium tetroxide that reacts with the double bonds of PB in the polymer seeds, so the rubber -rich phase becomes darker. In Figure 3c it can be observed with a greater detail the formation of a PS shell around the darker SB core indicating the formation of core-shell (SB-S) particles.

Table 2.
Gel content (soxhlet extraction, in duplicate) of pure polystyrene, seed particles and core-shell particles.

Material	Gel content (%)
Polystyrene (PS)	0
SB Seed particles S62	87
Core-shell (SB-S) particles	88

Gel contents of pure PS (negative control), SB seed latex (S62) and of the produced core–shell particles were measured by Soxhlet extraction. Extractions were performed in duplicate and the results are shown on Table 2. For pure polystyrene, as expected the amount of insoluble material was null. The SB seed latex (S62), on the other hand, presented a gel content around 87% due to the high fraction of butadiene (80%) in the copolymer obtained by free radical polymerization. The core-shell particles (SB-S) produced had a gel content (88%) similar to that of seed SB particles due to the use of a crosslinker (DVB) in the reaction.

In order to evaluate if the prepared core-shell particles composed of a SB core and a PS shell could be used as impact modifier, dried core-shell particles were incorporated into PS in a single-screw extruder with a 70/30 weight ratio of pure PS to core-shell particles. The results of the impact strength obtained by the Izod impact test are shown in Table 3

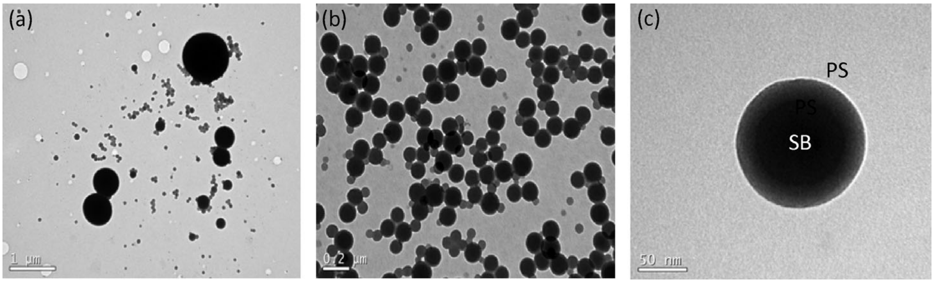

Figure 3.
TEM images of the seed latex S62 (a), and the core-shell particles formed in the reactions semi – continuous seeded emulsion polymerization (b, c).

Table 3.
Impact strength (Izod impact) of pure polystyrene and of polystyrene after the incorporation of the core-shell SB-S particles with 2 or 3 extrusions.

Material	Extrusions	IS (J/m)
PS	-	21,8 ± 2,3
PS with SB-S	2	26,1 ± 3,4
PS with SB-S	3	37,2 ± 0,4

and compared to that of pure PS. While the increase in impact strength after the incorporation of the SB-S core-shell particles after two extrusions was only minor (not significant), a further extrusion step led to a more pronounced increase in impact strength compared the pure PS. This behavior can be explained by the improved dispersion of the core-shell particles in the PS matrix with the increase of the number of passages through the extruder. This is a quite promising result, since the incorporation of 30 wt% of the core-shell particles led to an increase of the impact strength of PS by 70% and, thus, showed potential as impact modifier.

Conclusion

With the present results it can be concluded that it was possible to form particles with a core-shell structure composed of polystyrene shell and elastomeric core (styrene-butadiene copolymer) in semicontinuous emulsion polymerization reactions using styrene-butadiene copolymer seeds. The incorporation of 30 wt.% of the core-shell particles into a polystyrene matrix increased the impact resistance of the PS by 70%.

Acknowledgements: The authors thank the financial support from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), LANXESS for providing the latex used as polymer seed and TEM analyses from Laboratório Central de Microscopia Eletrônica of UFSC (LCME).

[1] Q. Gu, Q. Lin, C. Hu, B. Yang, *J. Appl Polym Sci* **2005**, 95, 404–412.
[2] O. H. Gonçalves, R. A. F. Machado, P. H. H. Araujo, J. M. Asua, *Polymer* **2009**, *50*, 375–381.
[3] I. D. Lee, T. Ishikawa, *J. Polym. Sci. : Poly Chem.* **1983**, *21*, 147–154.
[4] J. Pusch, A. M. Van Herk, *Macromolecules* **2005**, *38*, 6909–6914.
[5] O. D. Velev, K. Furusawa, K. Nagayama, *Langmuir* **1996**, *12*, 2385–2391.
[6] Z. Zhenqian, B. Yongzhong, H. Zhiming, W. Zhixue, *J. Appl. Polym. Sci.* **2009**, *111*, 1659–1669.
[7] C. Sayer, P. H. H. Araujo, 2. Synthesis of Polymer Particles with core- shell morphologies. In: V. Mittal, Ed., *Advanced Polymer Nanoparticles: Synthesis and Surface Modifications*, Taylor & Francis, **2010**, 29–59
[8] D. C. Sundberg, Y. G. Durant, *Polym. React. Eng.* **2003**, *11*, 379–432.
[9] M. K. Lenzi, F. M. Silva, E. L. Lima, J. C. Pinto, *J. Appl. Poly. Sci.* **2003**, *89*, 3021–3038.
[10] O. H. Gonçalves, J. M. Asua, P. H. H. Araújo, R. A. F. Machado, *Macromolecules* **2008**, *41*, 6960–6964.
[11] M. Koskinen, C. E. Wilén, *J. Appl. Poly. Sci.* **2009**, *112*, 1265–1270.
[12] C. Ferguson, G. T. Russel, R. G. Gilbert, *Polymer* **2002**, *43*, 6371–6382.
[13] D. L. Chicoma, V. Carranza, R. Giudici, *Macromol. Symp.* **2013**, *324*, 124–133.
[14] V. Nelliappan, M. S. El-Aasser, A. Klein, E. S. Daniels, J. E. Roberts, *J. Polym. Sci. : Poly Chem.* **1996**, *34*, 3183–3190.
[15] J. M. Stubbs, D. C. Sundberg, *J. Coat. Technol. Res.* **2008**, 2, 169–180.
[16] J. Stubbs, J. Tsavalas, D. C. Sundberg, *Macromol. React. Eng.*, **2010**, *4*, 424–431.
[17] C. Ferguson, G. T. Russel, R. G. Gilbert, *Polymer* **2003**, *44*, 2607–2619.
[18] G. R. Meira, C. V. Luciani, D. A. Estenoz, *Macromol. React. Eng.* **2007**, *1*, 25–39.