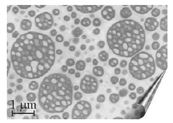
Phase Inversion Prediction during the Bulk Synthesis of High-Impact Polystyrene: A Fluid-Dynamic Approach

Juan M. Maffi[1], Diana Estenoz[2]

[1]Department of Chemical Engineering, Instituto Tecnológico de Buenos Aires (ITBA), Buenos Aires, Argentina.
[2]Instituto de Desarrollo Tecnológico para la Industria Química, INTEC (Universidad Nacional del Litoral - CONICET), Santa Fe, Argentina. E-mail: destenoz@santafe-conicet.gov.ar

Introduction

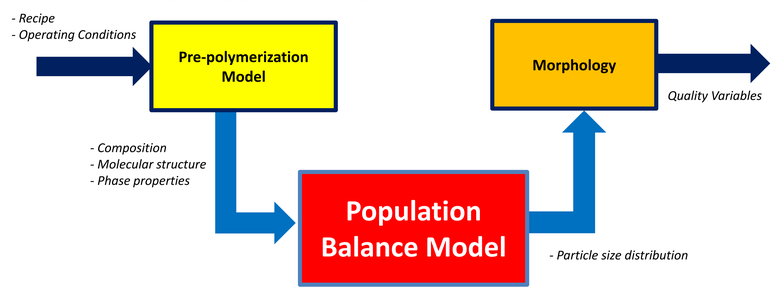


High-Impact Polystyrene (HIPS) is a heterogeneous material constituted by a rubber (PB) particles dispersed in a vitreous polystyrene (PS) matrix.

Two typical morphologies are usually identified: 'salami' (larger rubber particle with several PS occlusions) or 'core-shell' (smaller particle with one large occlusion).

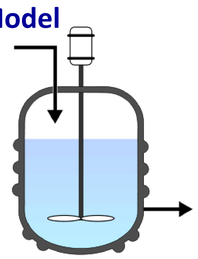
The industrial continuous bulk HIPS process involves four main stages: dissolution, pre-polymerization, finishing and devolatilization. During the pre-polymerization, the mixture consists of a continuous PB-rich phase where PS-rich droplets grow as the reaction proceeds. At a critical point, the dispersed vitreous phase reaches a volume such that it becomes the continuous phase, through a co-continuous transition. This is the phase inversion (PI) point, and the material morphology is essentially defined at this stage, characterized by a sudden drop in the mixture's apparent viscosity.

HIPS Industrial Process Model



Kinetic Mechanism for HIPS Polymerization Model

Proposed kinetic mechanism	Nomenclature	
Initiation	St	Monomer
$3St \xrightarrow{k_{i0}} 2S_1^\bullet$	$S_1^\bullet$	Monomer radical
$I_2 \xrightarrow{f\,k_d} 2I^\bullet$	I_2	Initiator
$I^\bullet + St \xrightarrow{k_{i1}} S_1^\bullet$	$I^\bullet$	Initiator radical
$I^\bullet + B \xrightarrow{k_{i2}} P_0^\bullet$	B	Unreacted butadiene unit
$P_0^\bullet + St \xrightarrow{k_{i3}} P_1^\bullet$	$P_0^\bullet$	Primary radical produced by attack to a butadiene unit
Propagation	$P_1^\bullet$	Copolymer radical with one styrene unit
$S_n^\bullet + St \xrightarrow{k_p} S_{n+1}^\bullet$	$P_n^\bullet$	Copolymer radical with n repetitive units of St in active branch.
$P_n^\bullet + St \xrightarrow{k_p} P_{n+1}^\bullet$	$S_n^\bullet$	Free PS radical with n repetitive units.
Transfer	S_n	PS with n repetitive units.
$S_n^\bullet + St \xrightarrow{k_{fM}} S_n + S_1^\bullet$	P_n	Copolymer with n repetitive St units.
$P_n^\bullet + St \xrightarrow{k_{fM}} P_n + S_1^\bullet$		
$P_0^\bullet + St \xrightarrow{k_{fM}} B + S_1^\bullet$		
$S_n^\bullet + B \xrightarrow{k_{fG}} S_n + P_0^\bullet$		
$S_n^\bullet + P_n \xrightarrow{k_{fG}} S_n + P_n^\bullet$		
Termination		
$S_n^\bullet + S_m^\bullet \xrightarrow{k_{tc}} S_{n+m}$		
$S_n^\bullet + P_m^\bullet \xrightarrow{k_{tc}} P_{n+m}$		
$P_n^\bullet + P_m^\bullet \xrightarrow{k_{tc}} P_{n+m}$		
$P_n^\bullet + P_0^\bullet \xrightarrow{k_{tc}} P_n$		
$S_n^\bullet + P_0^\bullet \xrightarrow{k_{tc}} P_n$		
$P_0^\bullet + P_0^\bullet \xrightarrow{k_{tc}} P_0$		



HIPS polymerization model is based on the macroscopic mass balance equations for each chemical species. Simulations predict the evolution of the chemical species' concentration and detailed polymer molecular structure.

Output Variables

- Solid content
- St grafting efficiency
- Free PS or HIPS molecular weights
- Concentrations of St, initiators, and rubber repeating units
- Phases viscosities
- Interfacial tension

Population Balance Model

Mathematical Model for Particle Size Distribution of Vitreous (PS-rich) Droplets

General Population Balance Equation:

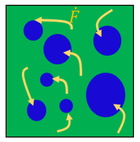
$$\frac{\partial f_{(v,t)}}{\partial t} + \frac{\partial}{\partial v}\left(\dot{V}_{(v,t)} f_{(v,t)}\right)$$
$$= 2\int_v^\infty \omega_{b(v')} f_{(v',t)} \beta_{(v|v')} dv' - \omega_{b(v)} f_{(v,t)} + \frac{1}{2}\int_0^\infty \omega_{c(v-v',v')} f_{(v-v',t)} f_{(v',t)} dv' - f_{(v,t)} \int_0^\infty \omega_{c(v,v')} f_{(v',t)} dv'$$

- v: particle volume (state variable)
- f: number density function
- $\omega_{b(v)}$: fractional breakage rate of particles of volume v
- $\omega_{c(v,v')}$: coalescence rate of pairs of particles of volumes v and v'
- $\dot{V}_{(v)}$: growth rate of particles of volume v

Growth Rate:

Particles shrink due to density difference between St and PS, and grow due to monomer transfer from continuous to dispersed phase.

Mass balance for St in each phase:



$$\dot{m}_{St,v} = -k_{pv}[St_v][S_v^\bullet]V_v M_{St} + \dot{F}$$
$$\dot{m}_{St,r} = -k_{pr}[St_r]([S_r^\bullet] + [P^\bullet])V_r M_{St} - \dot{F}$$

Styrene flow between phases is such that its partition coefficient is 1.

$$[St_v] = [St_r]$$
$$m_{St,v}\left(\frac{m_{PB}}{\rho_{PB}} + \frac{m_{St,r}}{\rho_{St}}\right) = m_{St,r}\left(\frac{m_{PS}}{\rho_{PS}} + \frac{m_{St,v}}{\rho_{St}}\right)$$
$$\dot{m}_{St,v}\frac{m_{PB}}{\rho_{PB}} = \dot{m}_{St,r}\frac{m_{PS}}{\rho_{PS}} + m_{St,r}\frac{\dot{m}_{PS}}{\rho_{St}}$$
$$\dot{F} = \frac{(m_{St,r} + m_{PB})Rp_v V_v + (m_{St,r} - m_{PS})Rp_r V_r}{m_{PB}\frac{\rho_{PS}}{\rho_{PB}} + m_{PS}} M_{St}$$

Then:

$$\boxed{\dot{V}_{(v)} = \left[k_{pv}[St_v][S_v^\bullet]\left(\frac{1}{\rho_{PS}} - \frac{1}{\rho_{St}}\right)M_{St} + \frac{\dot{F}}{\rho_{St}V_v}\right]v}$$

Birth and Death Kernels:

$$\omega_{b(v)} = C_{1b}\varepsilon^{1/3}\,\mathrm{erfc}\left(\sqrt{C_{2b}\frac{\gamma}{\rho_c\varepsilon^{2/3}}\left(\frac{\pi}{6v}\right)^{5/9} + C_{3b}\frac{\eta_d}{\sqrt{\rho_c\rho_d}\varepsilon^{1/3}}\left(\frac{\pi}{6v}\right)^{4/9}}\right)$$

$$\omega_{c(v,v')} = C_{1c}(\lambda_1 + \lambda_2 - \lambda_1\lambda_2)h_{(v,v')}\frac{\varepsilon^{1/3}}{1+\phi_d}\left(v^{2/9} + v'^{2/9}\right)^{1/2}$$

- *Daughter particle size distribution:*

$$\beta_{(v|v')} = 30\left(\frac{v}{v'}\right)^2\left(1 - \frac{v}{v'}\right)^2$$

- *Coalescence efficiencies:*

$$\lambda_{1(v,v')} = \exp\left[-C_{2c}\frac{\eta_c\rho_c\varepsilon}{\gamma^2}\left(\frac{v^{1/3}v'^{1/3}}{v^{1/3} + v'^{1/3}}\right)^4\right]$$
$$\lambda_{2(v,v')} = \exp\left[-C_{3c}\frac{\gamma}{\rho_d\varepsilon^{2/3}}\frac{(v+v')}{vv'}\frac{(v^{2/3} + v'^{2/3})}{(v^{2/9} + v'^{2/9})}\right]$$

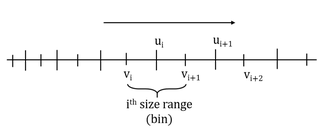
- *Radial distribution function:*

In dense dispersions, to account for the probability of a particle 'seeing' another one.

$$h_{(v,v')} = \frac{1}{1-\phi_d} + \frac{3}{2(1-\phi_d)^2}\xi_{(v,v')} + \frac{1}{(1-\phi_d)^3}\xi^2_{(v,v')}$$
$$\xi_{(v,v')} = 2\left(\frac{vv'}{v+v'}\right)^{1/3}\sum_{i=1}^{N}\hat{N}_i v_i^{2/3}$$

Grid discretization:

Moving pivot technique.

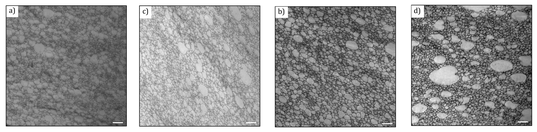


Experimental

A set of batch, bulk polymerizations were performed varying different operating conditions that affect the location of the inversion point: initiator (BPO) concentration, temperature and stirring speed.

Run #	[BPO] (%wt)	Temperature (°C)	Agitation speed (rpm)
1	0.05	80	30
2	0.1	80	30
3	0.05	90	30
4	0.1	90	30
5	0.05	80	60
6	0.1	80	60
7	0.05	90	60
8	0.1	90	60

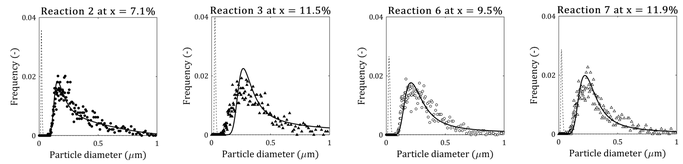
PSDs were determined by an image analysis technique performed on TEM micrographs.



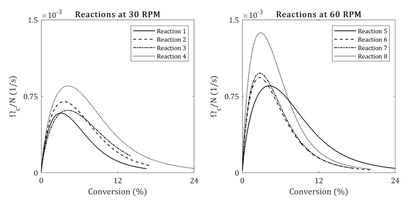
a) Reaction 2, 7.1%, b) Reaction 3, 11.5%, c) Reaction 6, 9.5%, d) Reaction 7, 11.9%

Simulation Results

The PB model was adjusted to fit the PSDs obtained by TEM.



Coalescence frequencies were observed along the reaction, to verify occurrence of inversion point.



No spiking occurs. Coalescence rates naturally decrease along each reaction, due to:

- Increase in phase viscosities
- Increase in dispersed phase density
- Decrease in total particle number
- Increase in interfacial tension attenuated by the presence of graft copolymer

Conclusions

Fluid-dynamic model of HIPS pre-polymerization successfully modeled with a population balance equation. Predicted PSDs are in good agreement with observed by TEM. Theoretical results seem to indicate that phase inversion does not occur by an exponential increase in particle coalescence, as widely suggested.

Further research is required to confirm that a different criterion for phase inversion is required in this system.

Ongoing work will use a PB equation to predict particle morphology at the inversion point.

References

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