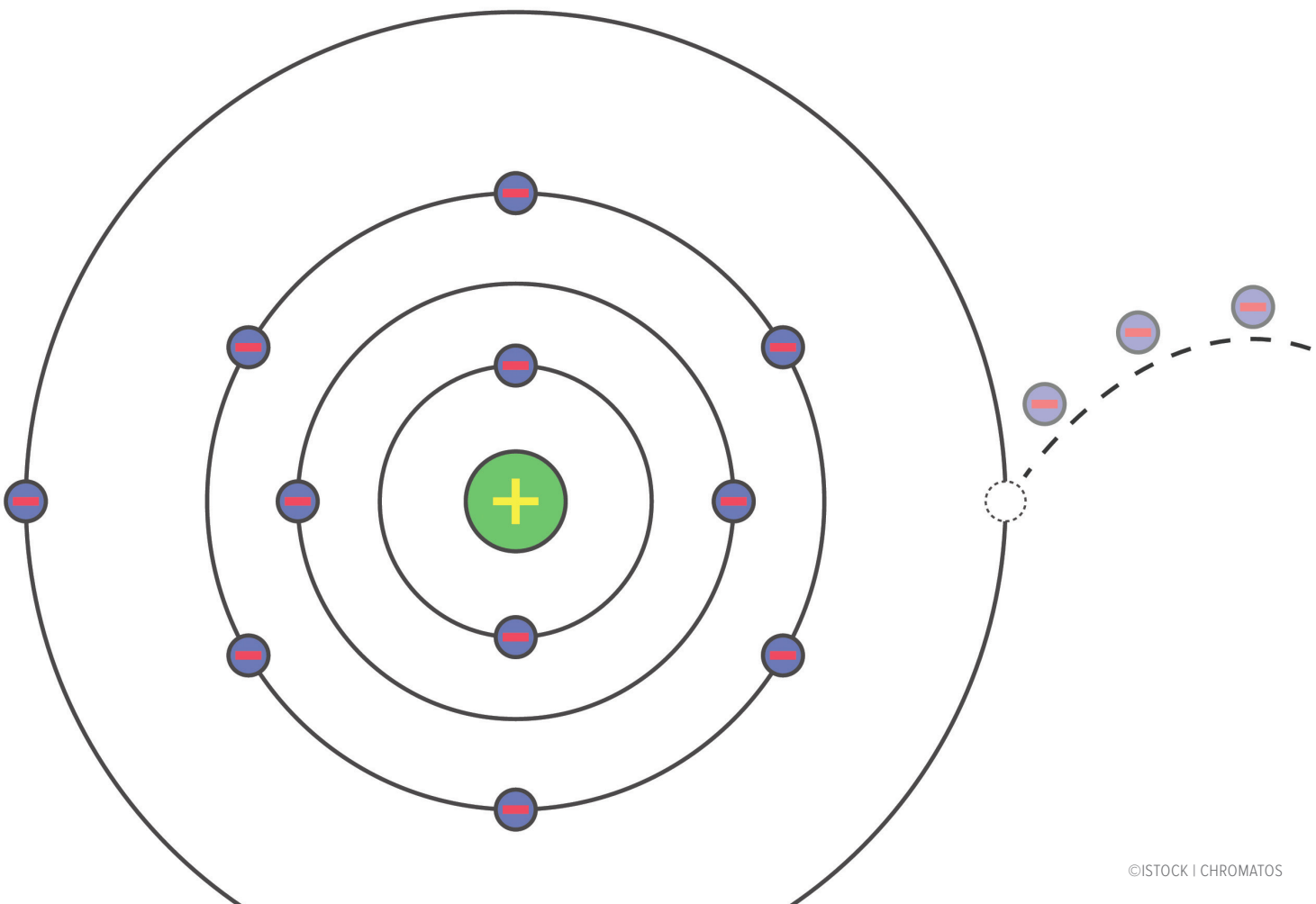
Redox Optimization for Emulsion Polymer Chase to Reduce Cycle Time

By Philip L. Simer, BruggemannChemical U.S., Inc., and Jessica Linker, L. Brüggemann GmbH & Co. KG



Chemically converting monomer via oxidizing and reducing agents (redox) in post-polymerization is a widely used technique; however, little time or effort is typically invested in optimizing this step. Through redox optimization, cost savings can be realized via shortened cycle times while also reducing residual free monomer to non-detectable levels.

While temperature and pH play a major role in the kinetics of redox chemistry, these are variables that often cannot be altered. However, improvements can be achieved regardless of these conditions as well as process or equipment restraints. A few of the variables that impact reaction time in the post-polymerization step that can more easily be optimized include redox pair, dosage/concentration, rate, and method of addition. A series of tests were performed to study the impact of these factors.

METHODS

In each test series, a latex using persulfate to thermally initiate main polymerization was used. In all cases, the polymers were chased with redox expressed as a weight percentage of actives content on total latex. Tertiary-butyl hydroperoxide (tBHP) was used throughout all tests as the oxidizer.

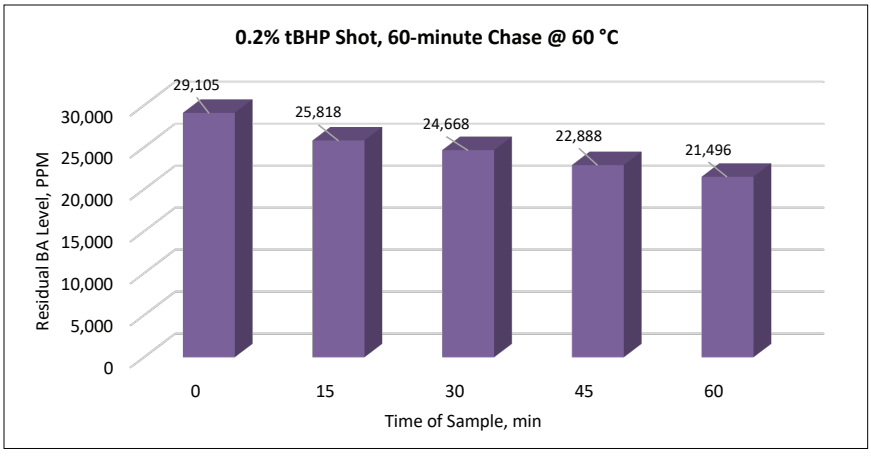
In the first test series, the specifications of the latex were as follows: 41% non-volatiles, 6 °C T_g, pH 2.6, residual monomer before chase of ~30,000 ppm (predominantly BA). The monomer make-up consisted of methyl methacrylate (MMA), styrene (Sty), methacrylic acid (MAA), and butyl acrylate (BA).

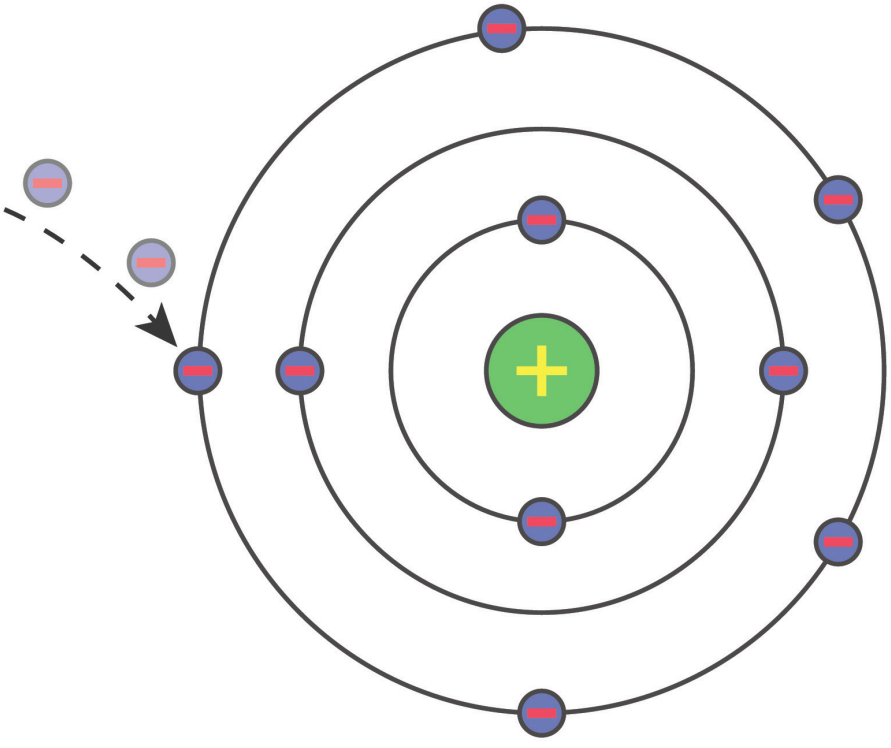
Various redox dosages were tested in this series, as well as several reducing agents, including sodium metabisulfite (SMBS), sodium salt of sulfinic acid derivative (SSIA), sodium salt of sulfonic acid derivative (SSOA), and zinc salt of sulfonic acid derivative (ZSOA).

Different methods of addition were also tested, including simultaneous, continuous feeds at various times and one-shot additions. TBHP was also utilized without any reducing agent as a control, as seen in *Figure 1*. All testing was done at 60 °C and samples were pulled every 15 minutes to test for free monomer via Headspace GC/MS.

In the second test series, the specifications of the latex were as follows: pH 3.5, 40% non-volatiles and chase temperature 80 °C. The monomer make-up consisted of MMA, BA, and 2-ethylhexyl acrylate (2-EHA). The test series

FIGURE 1





Through redox optimization, cost savings can be realized via shortened cycle times while also reducing residual free monomer to non-detectable levels.

FIGURE 2

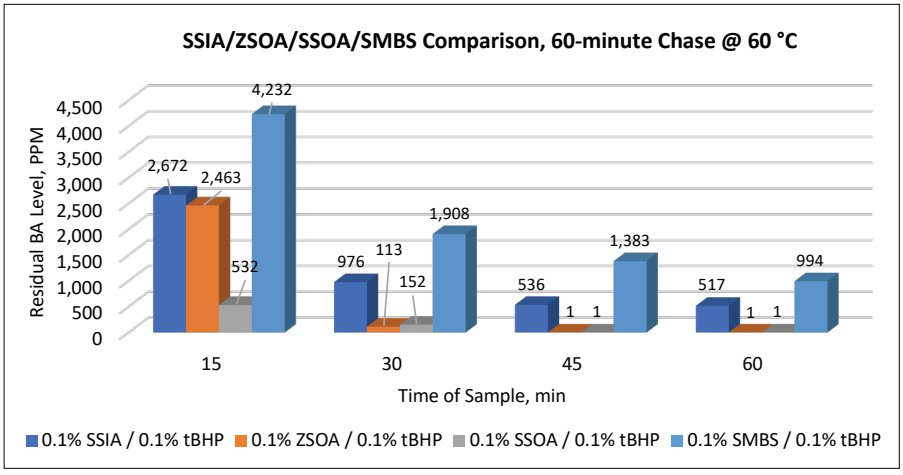


FIGURE 3

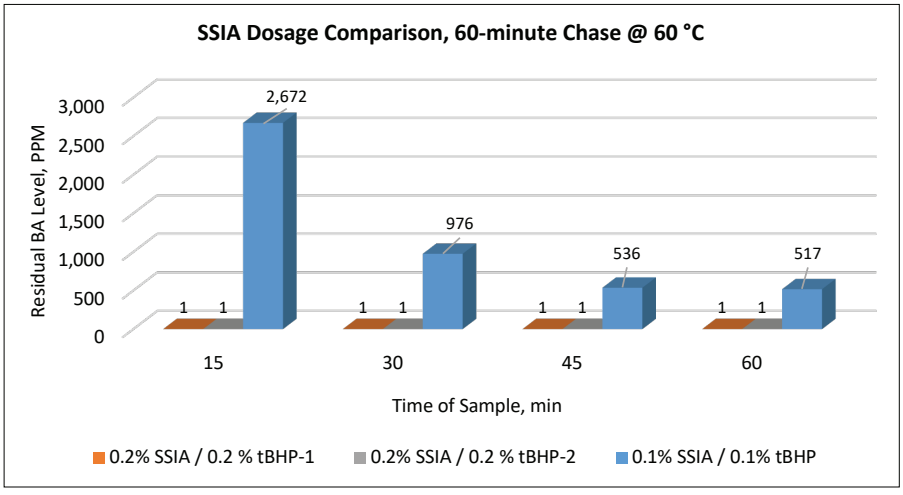
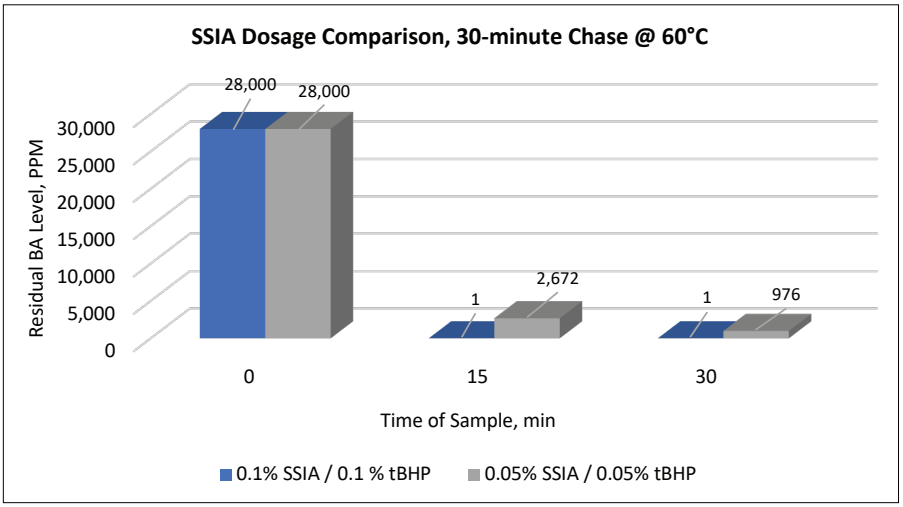


FIGURE 4



utilized tBHP at 0.02% with various reducing agents at 0.015%.

Reducing agents tested included: sodium formaldehyde sulfoxylate (SFS), SSIA, SSOA, modified sodium salt of sulfonic acid derivative (MSSOA), and reduced formaldehyde SFS (RFSFS). The redox pair was charged as one-shot of each component.

The third test series was conducted on a latex with the following specifications: pH 7.5, 50% non-volatiles and chase temperature 80 °C. The monomer make-up consisted of styrene (Sty), 2-ethylhexyl acrylate (2-EHA) and butyl acrylate (BA). Once again, several reducing agents were tested in this series, including SSIA, SSOA, MSSOA, and RFSFS. The redox pair was dosed at 0.1% of each component, however tBHP was charged as one-shot and the reducing agent was fed over 30 minutes thereafter.

It was discovered that the concentration of radicals in situ at any given moment is the primary determinant of monomer propagation, i.e., redox dosage is directly correlated with addition time.

RESULTS

The first test series utilized a 60-minute simultaneous, continuous feed of the redox pairs at 0.1% each. It was found that the less reactive reducing agents, SSOA and ZSOA, performed the best, yielding non-detectable levels of free monomer after 45 minutes as seen in *Figure 2*.

This can be attributed to the low pH of this system where more reactive reducing agents, such as SSIA, will produce radicals at a higher rate creating an environment where kinetics favor recombination and termination over propagation of monomer.

However, it was discovered that the concentration of radicals in situ at any given moment is the primary determinant of monomer propagation, i.e., redox dosage is directly correlated

with addition time. As seen in *Figure 3*, when the dosage of SSIA was doubled to 0.2% while keeping the addition time at 60 minutes, free monomer was reduced to non-detectable levels within 15 minutes.

Furthermore, when the dosage was reduced back to 0.1% and the addition time also halved to 30 minutes, the same results were achieved; non-detectable, free monomer after only 15 minutes as seen in *Figure 4*.

These results were not achieved with any other concentration of redox. Additionally, while the dosage of redox after 15 minutes was 0.05%, a one-shot addition of this dosage will not yield the same results, as seen in *Figure 5*.

Although a one-shot addition was found to not be as effective, the second test series focused on this method as it does minimize cycle time. This series focused strictly on the performance of different reducing agents in this method. It was found that the less reactive reducers, SSOA and MSSOA, performed the best, as seen in *Figure 6*.

Similar to the first test series at low pH, the elevated temperature in this case once again drives the kinetics in favor of a slower oxidizing species. Although this study was comparative in nature, further optimization of redox dosage levels could potentially yield improved performance.

Combining the benefits of the first two series, the third test series utilized a one-shot addition of tBHP followed by a 30-minute feed of reducer. The reducing agents were kept constant between the second and third test series.

It was found that this method was far superior to a one-shot addition of both redox components, yielding non-detectable free monomer levels in 30 minutes with SSIA and MSSOA as well as extremely low levels with SSOA and RFSFS as seen in *Figure 7*.

CONCLUSIONS

The first test series shows that through optimization of redox dosage and addition time, both residual free monomer and post-polymerization cycle time can be greatly reduced. It was shown that non-detectable levels of free monomer can be achieved in as little as 15 minutes.

FIGURE 5

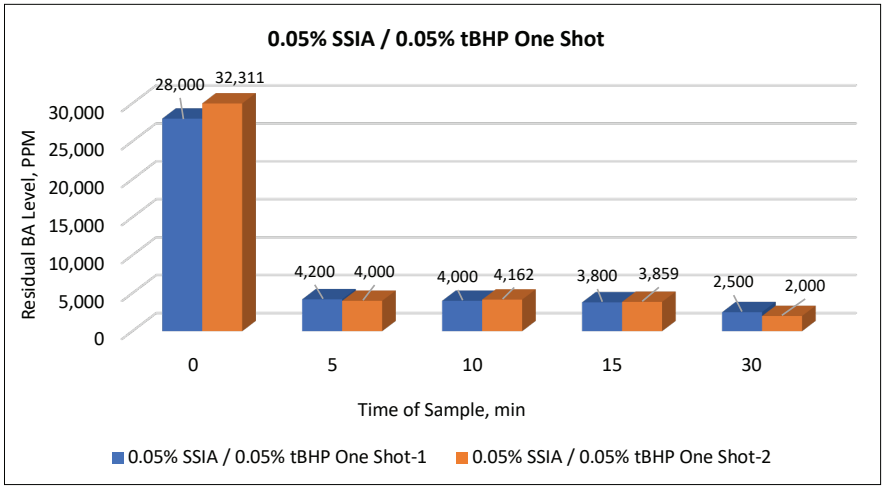


FIGURE 6

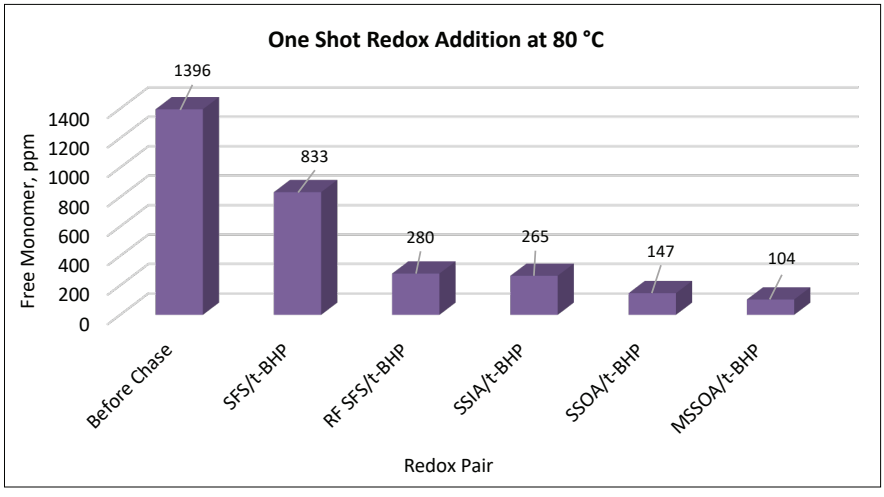
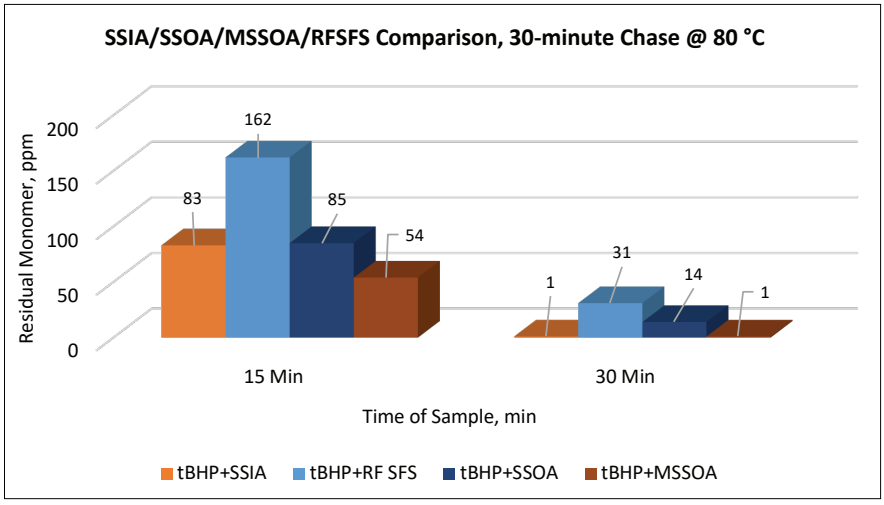


FIGURE 7



If further reduction in cycle time is desired, or if there are process or equipment restraints present, the second test series shows a one-shot addition technique can still be relatively effective when the correct reducing agent is utilized.

As shown in this work, low pH or high-temperature polymerizations favor the use of reducing agents which oxidize more slowly. Furthermore, reducing agents of this nature would be expected to perform better using this technique, regardless of conditions, based solely on reaction kinetics.

In some cases, a simultaneous, continuous feed of redox components is not possible due to production constraints, but improved performance over a one-shot method is desired.

As shown in the third test series, an effective alternative is to charge the oxidizer as one shot, while proceeding to feed-in the reducing agent. Because tBHP is mostly unreactive at waterborne polymerization temperatures, it relies on the reducing agent to chemically form radicals, making this a viable production process.

It has been shown that in various polymerization conditions and with different processes, the post-polymerization or chase, can be optimized to greatly reduce cycle time while still yielding extremely low-residual free monomer levels. ❊

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