

CASE STUDY

Redox Techniques: Optimizing VOC Reduction and Efficiency with Advanced Reducing Agents



Summary

Product type: Advanced Reducing Agents by Brüggemann

End application: Paints | Varnishes | Coatings | Adhesives | Building and construction chemicals | Paper coatings | Textile, paper, mineral bleaching | Polymeric surfactants

Key benefits: Reduces residual monomer level | VOC reduction | Optimizes cycle time | Low-odor | Cost-effective | Low production time

The Challenge

In the formulation of waterborne systems, one of the primary challenges formulators encounter is the **high residual monomer levels** present after the polymerization process. This occurs when not all monomers are converted into polymers or oligomers, resulting in unreacted monomers within the final product. These residual monomers can compromise the quality of the latex, lead to regulatory non-compliance, and pose potential health risks.

To combat this, many formulators turn to **high reducing agent/oxidizer (redox) addition** to minimize residual monomer levels. However, this approach can be difficult, primarily due to deficiencies around the redox package and dosing thereof. The choice of redox pair is critical, as an unsuitable selection can lead to inefficiencies in the polymerization process and impact the performance characteristics of the latex.

High cycle time is another challenge that directly affects the bottom line. The conventional approach to reducing residual monomer levels involves post-polymerization chase techniques using redox pairs. While effective in achieving low levels of residual monomers, without optimization this process can significantly increase production time, add cost through additional chemical consumption and energy usage, and ultimately reduce overall production capacity.

Lastly, the **increased regulations on VOCs** and consumer demand for low-odor products present an ongoing challenge. These regulations and consumer demands place additional pressure on formulators to innovate and adopt solutions that can effectively minimize VOC levels without compromising product quality or performance.

Balancing these requirements while maintaining product performance and economic viability remains a key challenge for formulators.

The Solution

To tackle these complex challenges, Brüggemann conducted a series of successful tests. The aim was to identify practical solutions for reducing VOCs in waterborne systems without compromising on production efficiency or economic feasibility.

The following studies were performed to optimize cycle time and dosage, compare redox components, and reduce VOCs:

- 1. The Impact of Feed Rates and Dosage on Cycle Time**
- 2. Alternative Dosing Techniques**
- 3. Redox Initiation for Main Polymerization**

Now, let's take a closer look at the results of these studies and how they offer potential solutions to the challenges faced by formulators.

Impact of Feed Rates and Dosage on Cycle Time:

This study aimed to optimize the post-polymerization, redox package of a commercial latex which had been thermally initiated with a persulfate for main polymerization. The goal was to reduce residual monomers [methyl methacrylate (MMA), Styrene, methacrylic acid (MAA), and butyl acrylate (BA)] and optimize dosage, cycle time, and redox amount used.

During the post-polymerization assessments, only BA levels, present at approximately 30,000 ppm, were measured as it was found that conversion of MMA, Styrene, and MAA was unproblematic. This approach focused on evaluating redox efficiency.

A series of tests were conducted at Brüggemann lab in Heilbronn, Germany, using various reducing agents such as Bruggolite® FF6M and E28, TP 1646, and Sodium Metabisulfite (SMBS). The oxidizer used was Tertiary-butyl hydroperoxide (t-BHP). The process was tested under three conditions:

- Continuous feed over 60 minutes
- Continuous feed over 30 minutes
- One-shot redox addition at time 0

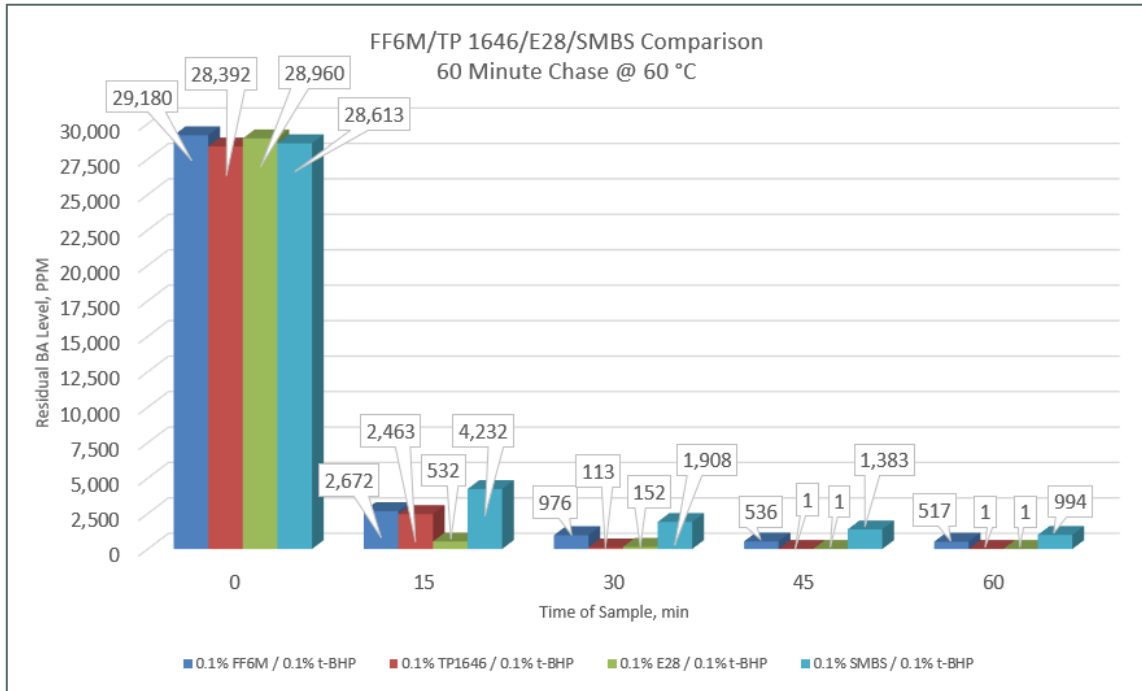


Figure 1: 60 mins chase results

The results in Fig. 1 show a continuous decrease in the levels of residual BA during 60-minute post-polymerization at 60 °C, with the most significant reduction reported with Bruggolite® E28 and TP 1646 reducing agents, reducing the residual BA to below 1 ppm within 45 minutes. However, Bruggolite® E28 shows exceptional results in just 15 minutes by reducing the residual BA level to 532 ppm from 28,960 ppm.

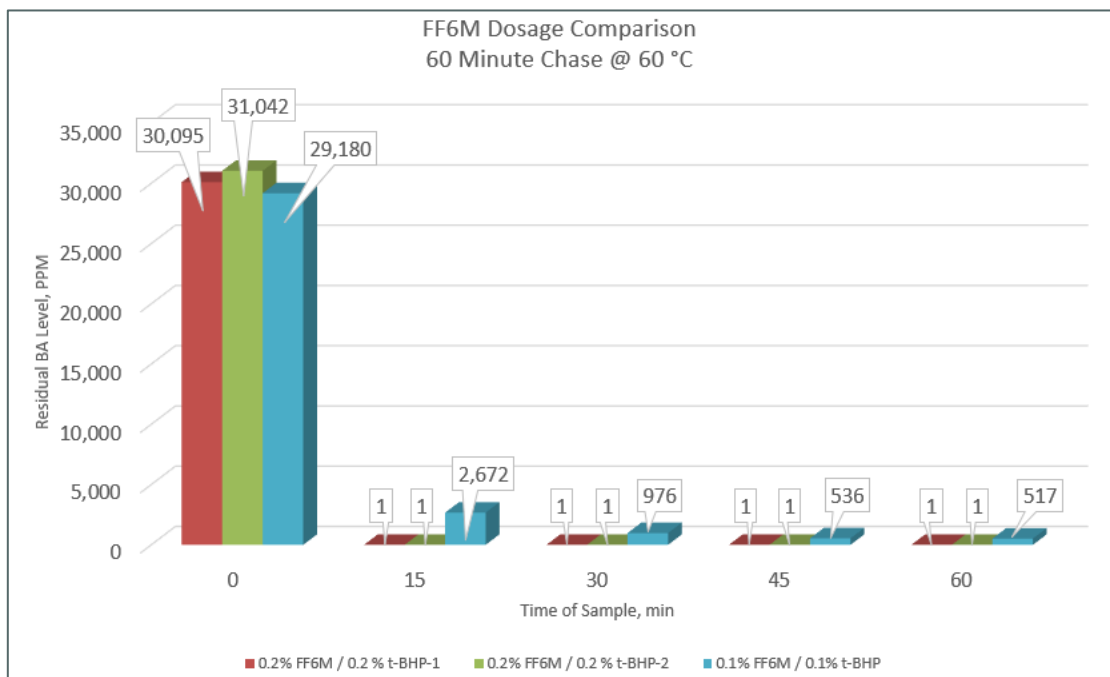


Figure 2: Optimized chase with FF6M dosage for 60 min

Following the initial tests, an optimized 60-minute chase, as shown in Fig. 2, was implemented using Bruggolite® FF6M. This optimized approach demonstrated a remarkable improvement, achieving a reduction in residual BA levels to 1 ppm within just 15 minutes, utilizing dosages of 0.2% FF6M in conjunction with 0.2% Tertiary-butyl hydroperoxide (t-BHP) in two separate tests. Conversely, a lower dosage of 0.1% resulted in a slower reduction, achieving 517 ppm in residual levels over 60 minutes.

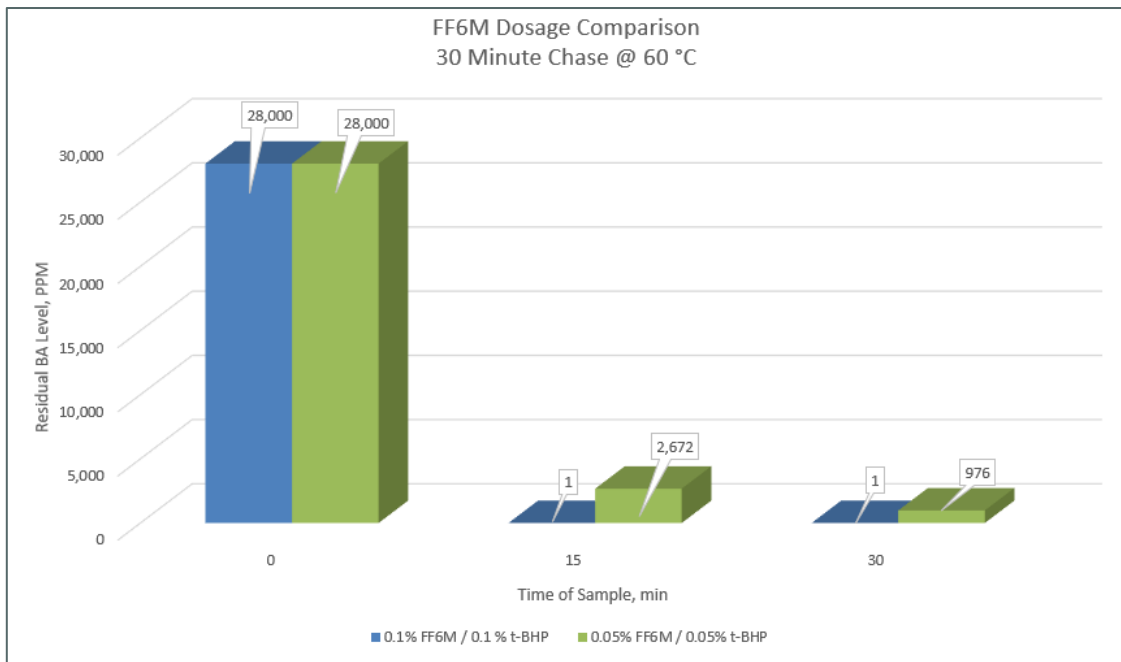


Figure 3: 30 min chase results with FF6M dosage

In a 30-minute chase with Bruggolite® FF6M, as shown in Fig. 3 above, residual BA levels plummeted from 28,000 ppm to just 1 ppm in 15 minutes at a 0.1% dosage, showcasing remarkable efficiency. Recall from Fig. 1, that this same dosage fed over a period of 60 minutes did not achieve these results. From this work, it was discovered that there is a direct correlation between redox dosage and feed time on the efficiency of monomer conversion. Specifically, the level of redox in-situ and present at a given point in time is the most impactful variable on converting residual free monomer.

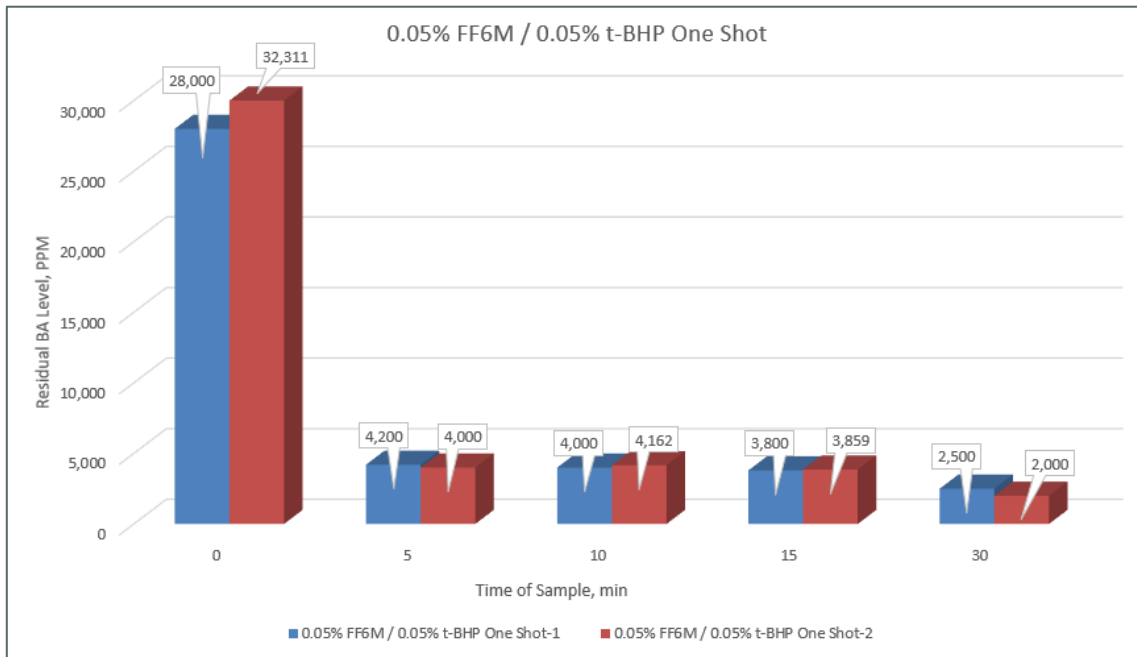


Figure 4: One-shot dosage result

As shown in Fig. 4 above, implementing a one-shot redox addition strategy wherein the oxidizer and reducer are charged entirely at once vs. feeding over time, demonstrated significantly worse efficacy at converting free monomer. As the graph illustrates, this test was duplicated to confirm results.

These results demonstrate that the selection and dosage of reducing agents, coupled with the appropriate application method (continuous feed vs. one-shot addition), significantly influence the efficiency of VOC reduction. It also shows that the residual BA level could be substantially reduced to non-detectable levels in as little as 15 minutes. This meets the stringent industry and consumer standards for low VOC content and addresses the operational need for reduced cycle times and cost savings. The outcomes suggest that the next step would be finding ways to further shorten the cycle time.

Alternative Dosing Techniques:

This study by Brüggemann uncovers an innovative post-polymerization (chase) at conventional temperatures used for thermal initiation and main polymerization. By chasing at 80°C, lengthy production cooldown periods can be eliminated. Furthermore, there are often commercial constraints around utilizing two, simultaneous feeds for redox pairs thus, additional techniques were explored.

Shining a spotlight on the test series, a variety of reducing agents were investigated including Bruggolite® FF6M, Bruggolite® E28, TP 1651, Sodium Formaldehyde Sulfoxylate (SFS), and TP 1646. The oxidizer used in this study was also Tertiary-butyl hydroperoxide (t-BHP). A one-shot redox method was investigated once again vs. a new technique; charging the oxidizer as one shot followed by a continuous reducer feed over 30 minutes.

The latexes were thermally initiated and polymerized at 80°C with ammonium persulfate. Fig. 5 illustrates a one-shot chase process at 80°C on a 40% solids polymer at pH of 3.5 comprised of MMA, 2-Ethylhexyl Acrylate (2-EHA), and BA.

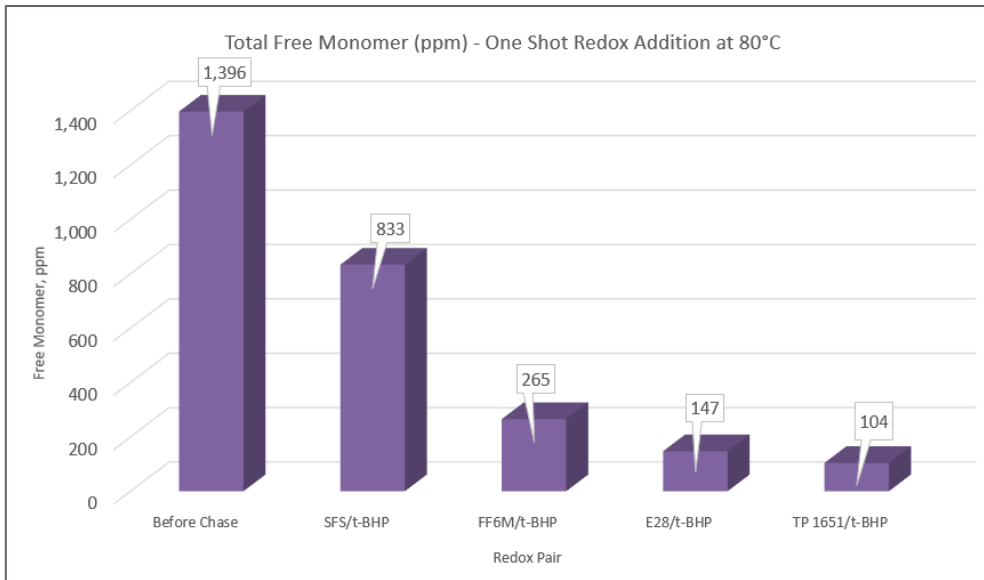


Figure 5: Reducer performance comparison at 80°C

The results indicate an evident difference in performance among Bruggolite® FF6M, E28, TP 1651, and SFS, with TP 1651 showing the least amount (104 ppm) of residual free monomer. Differences in reducer stability vs. reactivity and redox reaction kinetics dictate performance in this technique. The one-shot technique is least favorable for highly reactive reducers such as Bruggolite® FF6M as recombination and termination of radicals becomes more prevalent with a single, large dose of redox.

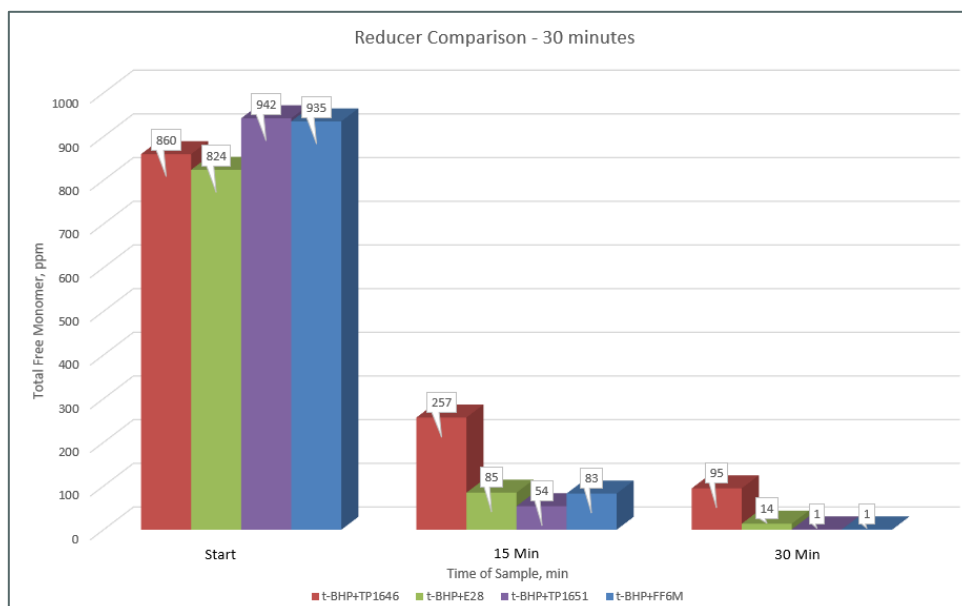


Figure 6: Reducer comparison with continuous feed for 30 minutes at 80°C

Fig. 6 illustrates a second comparative study to reduce free monomers in a latex comprised of Styrene, 2-EHA, and BA at pH of 7.5 to less than 100 ppm from 1,000 ppm. Once again, the polymerization was thermally initiated at 80°C using ammonium persulfate and chased with one shot of t-BHP followed by a 30-minute reducer feed. The results showed a significant decay of monomer residuals over 30 minutes for all reducing agents. Still, t-BHP paired with TP1651 or FF6M appeared to be the most effective by reducing free monomers to non-detectable levels.

It was found that the elevated temperature offset the high pH to deliver excellent results and further solidifies the effectiveness of even one continuous feed over a one-shot redox addition. Taking advantage of these findings can lead to non-detectable levels of free monomer more quickly while eliminating reactor cooling time yielding faster reactor turnarounds.

Redox Initiation for Main Polymerization:

This experiment was designed to compare emulsion polymers with identical compositions and reaction times while varying initiation temperature. The system was a 50% solids BA/MMA latex, with starting temperatures set at 20°C and 40°C for redox initiation, and 80°C for thermally initiation with persulfate.

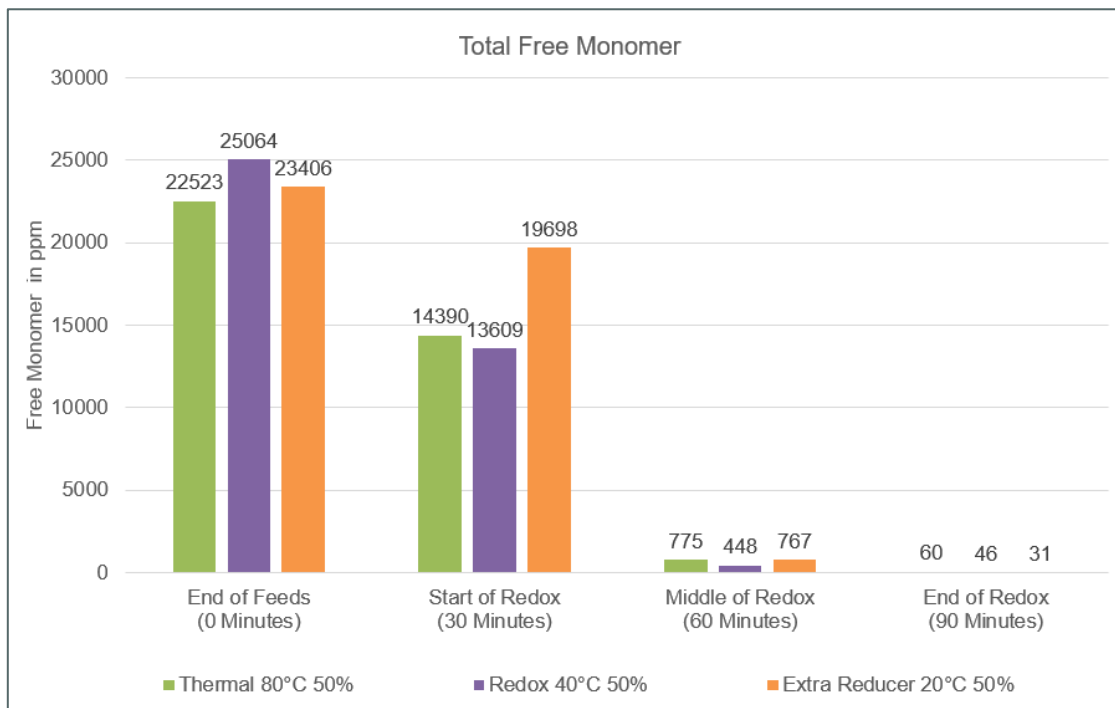


Figure 7: Free monomer comparison

As shown in Fig. 7, the free monomer level comparisons at the end of chase were 60 ppm, 46 ppm, and 31 ppm, respectively for the thermal system, redox initiated at 40°C, and redox initiated at 20°C systems. This illustrates the energy-efficient redox initiation at 20°C was most effective at converting monomer without requiring any heating or cooling. Redox optimization was required for effective initiation at this temperature and as noted in the graph, extra reducer was required at the start of the reaction to achieve this.

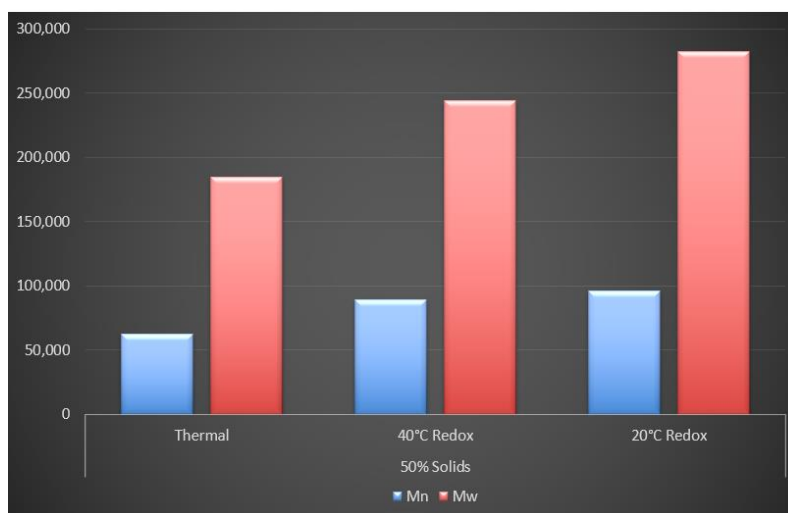


Figure 8: Molecular weight comparison

In Fig. 8 above, the molecular weight comparison highlights interesting findings. The M_n for thermal, 40°C redox, and 20°C redox were 62,755, 89,400, and 96,100 respectively; while M_w showed 184,600, 243,850, and 282,500 respectively. This illustrates that molecular weight can be modified by optimizing the redox process and substantial increases in molecular weight can be achieved by decreasing initiation temperature.

The experiment proved to be efficient at initiating and running polymerization at various temperatures. The key findings include potential process time and energy savings due to the absence of heating or cooling. Higher molecular weights were achieved, and the reactions were cleaner given the lack of required heating, allowing quicker reactor turnaround. This study will help develop better procedures and foster improvements in polymerization processes.

Conclusion

The case study methodically investigates the impacts of various dosing strategies and temperatures on VOC reduction and polymerization processes in latex production. It reveals that strategic selection and application of reducing agents, particularly **Bruggolite® FF6M**, **Bruggolite® E28**, **TP 1651**, and **TP 1646**, significantly optimize VOC reduction, achieving non-detectable levels of free monomers. Highlighting the efficacy of continuous feed over one-shot additions, the studies underscore potential operational efficiencies, including reduced

cycle times, lower VOCs, and cleaner reactions. Lastly, it explores the potential of redox initiation for main polymerization, demonstrating that it can significantly lower energy consumption while increasing molecular weight and improving reaction cleanliness.

Overall, this study presents practical solutions for improving process efficiency and reducing latex production costs while meeting industry standards for low VOC content.

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