The Impact of Thermal Stability on the Performance of Polymeric Dispersants for Boiler Water Systems

Zahid Amjad, Ph.D. and Robert W. Zuhl, P.E.
Lubrizol Advanced Materials, Inc.*
9911 Brecksville Road
Cleveland, OH 44141

Carbosperse™ K-700
Water Treatment Polymers**
Introduction

The quality of feed water available for the efficient operation of a large number of boiler and steam plants is extremely poor. This, coupled with the lack of adequate treatment, often leads to boiler tubes failures and system breakdowns. Thus, from the perspective of efficient operation of steam generation plants, feed water has to be properly treated in order to minimize damage to boiler equipment and to eliminate unforeseen production losses. The major challenges facing the water technologists that seek to provide high levels of steam purity from boilers include prevention of scale and deposit on heating surfaces; corrosion control in the boiler, steam lines, and condensate system; and minimizing carryover. Table 1 below presents an overview of boiler water system pressure categories, corresponding temperatures, feedwater types, and water treatment challenges.

Table 1 - Boiler Water Systems Overview

<table>
<thead>
<tr>
<th>Type (psig)</th>
<th>Temp.</th>
<th>Feedwater Types*</th>
<th>Water Treatment Challenges</th>
</tr>
</thead>
</table>
| Low Press. (<150) | <177°C (351°F) | SN and/or RO or SN/RO and/or DM | • Hardness- (leakage) and iron-(condensate & corrosion) based deposit control.  
• Corrosion control.  
• Shutdown & lay-up procedures. |
| Medium Press. (>150 and <600) | >177°C (351°F) & <25°C (483°F) | SN and/or RO or SN/RO and/or DM | • Hardness- (leakage) and iron-(condensate & corrosion) based deposit control.  
• Process contamination.  
• Corrosion control.  
• Shutdown & lay-up procedures. |
| High Press. (>600) | >251°C (483°F) | DM | • Process contamination.  
• Corrosion control.  
• Shutdown & lay-up procedures. |

* Key to feedwater types above: SN = Softened, RO = Reverse Osmosis, DM = Demineralized

Boiler water treatment programs incorporate a variety of additives to achieve the following desired performance objectives of boiler systems:

- Scale inhibitors [e.g., poly(acrylic acid), poly(maleic acid)] are used to prevent the precipitation of hard minerals as scale on heat transfer surfaces, economizers, pumps, etc.
- Polymeric dispersants/sludge conditioners are employed to condition sludge and render it non-adherent to boiler surfaces so that it can be easily removed in via blowdown.
- Corrosion control in the boiler is achieved by eliminating dissolved oxygen from water, alkalinity, and deposit control additives to prevent under deposit corrosion.
- Corrosion control in boiler condensate systems is generally achieved by adjusting the boiler feedwater pH and adding neutralizing and filming amines to the steam and condensate lines.

Over the years a variety of treatment programs have been developed to treat boiler systems. These treatment programs include:
• “Precipitation”
  o “Carbonate cycle” programs depend upon dispersion of calcium carbonate as boiler sludges. Normally, natural organic polymers such as starch and lignin derivatives are used in carbonate cycle programs.
  o “Phosphate cycle” programs rely on the precipitation and dispersion of calcium phosphate sludge (ideally hydroxyapatite) to minimize accumulations on heat transfer surfaces. Synthetic polymers are used to ensure that the sludge remains fluid until removal via blowdown.
  o “Coordinated phosphate” programs are typically used in boilers operating at least 800 psig. Alkaline and acid phosphates (e.g., mono-, di-, and trisodium) are used to control free caustic that accumulates in restricted flow areas. Neutralizing amines and oxygen scavengers are used (usually fed separately) as appropriate. Synthetic polymers are used to disperse iron-containing suspended solids and stray calcium compounds.

• “Chelant” programs typically use chelating agent such as EDTA or NTA to complex feed water calcium or magnesium so it can not form boiler scale. Synthetic polymers are employed to disperse suspended iron compounds and any salts that precipitate as a result of fluctuations in feed water hardness and/or treatment program upsets.

• “All Polymer” programs rely on the stabilizing properties of polymers as alternatives to EDTA and NTA in chelant programs. Polymers also disperse iron and other suspended solids in these programs.

Accordingly, deposit control agents as components of boiler water treatment programs have multi-functional roles including sludge conditioning, particulate dispersion, and hardness stabilization.

Natural and Synthetic Polymeric Dispersants

The earliest dispersants used in boiler water systems were naturally occurring polymers such as starches, alginates, lignins, tannins, and cellulose derivatives. Subsequently, modifications of these materials such as lignosulfonates were used to treat boiler systems. Occasionally, one may still find these natural materials used to treat some boiler systems particularly those operating at less than 100 psig. However, natural materials are effective for dispersing calcium carbonate scale but they perform poorly as calcium phosphate dispersants. Thus, as phosphate treatment program have gained more popularity, the need for new synthetic polymers was realized and most of natural polymers have now been replaced with more effective synthetic polymers especially in higher (>100 psig) pressure boiler applications.

The use of synthetic polymers (i.e., polyacrylates, polymethacrylates, hydrolyzed polyacrylamides, acrylic acid/acrylamide copolymers) dates back to the 1950s. The early synthetic polymers used were high (>100,000) molecular weight homopolymers of acrylic acid. With the passage of time, lower molecular weight (<100,000) polyacrylates as well as polymethacrylates and polymaleic acids were found to be more efficacious. Researchers have shown that polyacrylate molecular weight is an important consideration relative to performance. Eventually, copolymers of acrylic acid, methacrylic acid, and/or maleic acids...
with a variety of other co-monomers [e.g., sulfonated styrene, 2-acrylamido-2-methyl propane sulfonic acid, (SA), substituted acrylamides] were found to provide improved performance characteristics in various applications including, boiler, cooling, geothermal, oil field, and desalination (thermal and membrane based) processes.\textsuperscript{4,5}

Thermal degradation of polymers is a well studied area. However, there is little information available of real value to a water technologist concerned with using low molecular weight polymers. Polymers used in boiler water treatment programs should be able to sustain high temperature and pressure environments normally associated with boiler operations. Denman and Salutsky\textsuperscript{6} briefly examined the thermal stability of a sodium poly(methacrylate) under dry conditions and they found no change to 316°C after one (1) hour but some charring at 371°C.

In 1982, Masler presented Noveon’s initial research efforts on the thermal stability of several homopolymers [i.e., polyacrylic acids (PAAs), polymethacrylic acids (PMAAs), polymaleic acid (PMAs)] commonly used in boiler applications.\textsuperscript{7} These homopolymers were (before and after thermal stress) (a) characterized by various analytical techniques and (b) evaluated for their performance. It was demonstrated under the conditions employed [pH 10.5, 250°C (592 psig), 18 hr] that PAA, PMAA, and PMA all underwent some degradation. In terms of molecular weight loss, PMAA lost slightly less molecular weight than PAA which lost considerably less than PMA. Additionally, PAA and PMAA had minimal performance changes whereas PMA displayed a substantial loss in performance.

Several years latter, Amjad used a similar test methodology to evaluate the thermal stability of several co-polymers. The results of this study,\textsuperscript{8} showed that the performance of polymers subjected to thermal stress is affected both by temperature level and exposure time. This paper is a continuation of Noveon’s efforts to understand the impact of thermal stress on polymer structure and the resulting changes in performance profiles. The polymer compositions and molecular weight were characterized and performance evaluated before and after thermal treatment. The goal of the work and data presented herein is to provide guidance to industrial water technologists seeking to design water treatment programs for applications such as boiler water treatment where thermal stability and/or performance retention during thermal stress for deposit control polymers is a critical performance criterion.

**Experimental**

Noveon spoke with several individuals in an effort to define the types of deposit control polymers and boiler water system operating conditions of interest to most AWT member companies. This resulted in the characterization of a typical low to medium pressure boiler water systems operating up to 200°C (equivalent to 241 psig) as the basis for Noveon’s laboratory testing simulating typical boiler water conditions discussed herein.

**Sample Preparation**

A solution of polymer was prepared containing 10% polymer (as active solids) at pH 10.5 using sodium hydroxide to neutralize the polymer. Sodium sulfite was added as an oxygen scavenger. A known amount of polymer solution was retained for characterization and performance testing. The balance was charged to a stainless steel tube. The headspace was purged with nitrogen followed by tightening the fittings. The tube was then placed in the oven
maintained at the required temperature [either 150°C (84 psig) or 200°C (241 psig)]. After 20 hr, tubes were removed from the oven, cooled to room temperature, and solution transferred to vials for characterization and performance testing.

**Polymer Characterization**

The molecular weights of polymers were determined by GPC method according to procedure described previously. Nuclear magnetic resonance (NMR) spectra of polymers before and after thermal treatment were obtained on a Brubaker AV-500 NMR spectrometer at 500.13 MHz for spectra detection. Attenuated total reflectance infrared (FT-IR) of all samples were acquired on a Nicolet Magna 560 Fourier Transform Infrared (FT-IR) spectrometer, equipped with the Pike MIRacle.

**Performance Tests**

The iron oxide dispersion, calcium phosphate inhibition, and calcium ion compatibility tests were carried out according to the procedures described in previous studies. The water chemistry for the calcium hydroxyapatite (HAP) dispersion tests included 105 mg/L Ca, 31 mg/L Mg, 353 mg/L Na, 209 mg/L SO₄, 116 mg/L HCO₃, 599 mg/L Cl, 23°C, and pH 7.8. To the 100 mL solution, 2,500 mg/L of HAP was added along with 5 ppm polymer dosages. Ca-HAP dispersion was monitored by measuring the solution transmittance at 3 hr.

The polymers used in this study were commercial polymers and their analytical characteristics are shown in Table 2. The polymers tested fall into the following three (3) categories:

- Homopolymers of acrylic, maleic, and methacrylic acids
- Copolymers of acrylic acid and sulfonic acid
- Terpolymers of acrylic acid and sulfonic acid and either sulfonated styrene or a non-ionic monomer

**Table 2 - Polymers Evaluated**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Polymer Type*</th>
<th>Acronym</th>
<th>Mol. Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignosulfonate</td>
<td>Sodium-lignosulfonate</td>
<td>SLS</td>
<td>&lt;20,000</td>
</tr>
<tr>
<td>GRK732 **</td>
<td>Solvent polymerized poly-AA</td>
<td>GRK732</td>
<td>≈5,000</td>
</tr>
<tr>
<td>GRK7058 **</td>
<td>Water polymerized poly-AA</td>
<td>GRK7058</td>
<td>≈5,000</td>
</tr>
<tr>
<td>BS161</td>
<td>Poly(AA) with phosphinate groups</td>
<td>PAA-P</td>
<td>&lt;2,000</td>
</tr>
<tr>
<td>BC200</td>
<td>Poly-MA</td>
<td>PMA</td>
<td>&lt;2,000</td>
</tr>
<tr>
<td>GRK766 **</td>
<td>Poly-MAA</td>
<td>GRK766</td>
<td>5,000</td>
</tr>
<tr>
<td>TRC233HS</td>
<td>Poly(AA:SA) copolymer</td>
<td>CASA</td>
<td>&gt;10k &amp; &lt;40k</td>
</tr>
<tr>
<td>GRK776 **</td>
<td>Poly(AA:SA) copolymer</td>
<td>GRK776</td>
<td>&gt;10k &amp; &lt;40k</td>
</tr>
<tr>
<td>AC3100</td>
<td>Poly(AA:SA:NI) terpolymer</td>
<td>CASN</td>
<td>&lt;10,000</td>
</tr>
<tr>
<td>GRK781 **</td>
<td>Poly(AA:SA:SS) terpolymer</td>
<td>GRK781</td>
<td>&lt;10,000</td>
</tr>
</tbody>
</table>

* Key to polymer type abbreviations (in table above):
  - AA = acrylic acid
  - MAA = methacrylic acid
  - MA = maleic acid
  - SS = sulfonated styrene
  - SA = sulfonic acid or 2-acrylamido 2-methylpropane sulfonic acid
  - NI = non ionic monomer

** Good-Rite® K-700 polymer supplied by Noveon, Inc. **
Results and Discussion

Polymer Performance Evaluation

Iron Oxide Dispersion

Among many dissolved impurities present in natural waters, iron-based compounds are among the most problematic to the efficient operation of industrial water systems. Sources of iron-ion impurities include boiler condensate, corrosion products (from heat transfer equipment, pipelines, pumps, etc.), biological activity (transformation of iron during bacterial processes), and water treatment residuals or by-product (e.g., excess iron-based flocculating agents). Regardless of the source, soluble iron can and does precipitate under certain conditions to form troublesome scales and deposits [e.g., Fe₂O₃, Fe₃O₄, Fe(OH)₃, FePO₄]. For this reason polymer treatment is necessary to keep the iron oxide particles dispersed and transported in the boiler water system. This dispersant activity results from the adsorption of polymer onto the surface of iron oxide particles thereby changing particle charge characteristics and minimizing agglomeration. Iron oxide dispersion by polymers is affected by various parameters (e.g., pH, temperature, hardness, etc.).

Due to ubiquitous and problematic nature of iron in water system, iron oxide dispersion is a key performance parameter for evaluating deposit control polymers. Thus, the iron oxide dispersancy was evaluated for several homo-, co-, and ter-polymers.

Figure 1 presents performance data for several polymers under standard test conditions (200 ppm iron oxide, 1 ppm active polymer, 3 hr, 7.8 pH, 100 mg/L Ca, 30 mg/L Mg, 314 mg/L Na, 200 mg/L sulfate, 571 mg/L Cl, 60 mg/L bicarbonate, 23°C). As shown in Figure 1, the homopolymers (GRK732, GRK7058, PAA-P, GRK766) before thermal treatment provide relatively poor (<50%) iron oxide dispersion. Furthermore, the iron oxide dispersion values for both heat treated and non-heat treated homopolymers are very similar. This indicates that thermal stress (exposure of aqueous solutions of these homopolymers to 200°C) has a negligible detrimental effect on the dispersing ability of the polymers. While the absolute performance levels of these homopolymers are poor it is interesting to that the solvent polymerized PAA (GRK732) performs better than the water polymerized PAA (GRK7058) and is comparable to PAA-P that is promoted in boiler water applications for iron stabilization.

Comparative dispersion data on several co- (CASA and GRK776) and ter-polymers (CASN, GRK781) are also presented in Figure 1. As illustrated, both the co- and terpolymers in the absence of thermal stress exhibit excellent (>80%) iron oxide dispersion. However, when these co- and terpolymers are exposed to thermal stress (200°C for 20 hr), the iron oxide dispersion decreases drastically (by a factor 4). For example, “% iron oxide dispersion” values obtained for CASN and K781 before heat treatment were both >85% compared to 18% and 26%, respectively after thermal stress. It is interesting to note that the performance of heat treated terpolymers is similar to that obtained for homopolymers.

Iron oxide dispersion data for SLS (sodium lignosulfonate) are also presented in Figure 1. As shown, the SLS exhibits good performance before (70%) and after (55%) thermal stress only losing ~20% of it dispersing power due to heat treatment. Although SLS exhibits good iron
dispersion, it is not used very often today for several reasons: inconsistent quality, breakdown products may deposit on boiler surfaces, poor calcium phosphate inhibition and dispersion.

The influence of temperature level on the thermal stability of polymers was also investigated at both 150 and 200°C (equivalent to 84 and 241 psig, respectively). The performance data presented in Figure 2 indicate excellent thermal stability for the sodium polymethacrylate (GRK766) and two polyacrylates (GRK7058 and PAA-P) evaluated at both 150 and 200°C. The baseline performance (without thermal treatment) for the two acrylate terpolymers is better than for the homopolymers tested.

Figure 2 also shows a comparison of the two acrylate terpolymers that have the same baseline performance before thermal stress. The data indicate that thermal stability (as determined by retention of performance following thermal treatment) of GRK781 is better than the CASN. Although two (i.e., AA and SA) of the three monomers used to manufacture these acrylate terpolymers are the same, the functionality of third monomer (as will be shown later) plays a key role in explaining the performance difference between two terpolymers.

**Hydroxyapatite Dispersion**

As discussed previously, the precipitation methods used for internal boiler water treatment programs rely on the use of alkalinity (carbonate) and phosphates as hardness precipitation agents. Calcium carbonate and calcium phosphate sludges are formed or precipitated (usually in the presence of organic dispersants) so they can be easily removed via boiler blowdown. Both orthophosphates and polyphosphates (that revert to orthophosphates in the boiler) are used for creating calcium phosphate sludges that are typically calcium hydroxyapatite (HAP) or a relatively soft, non-adherent material that can be removed by boiler blowdown.

The calcium HAP dispersing ability of several commercial polymers was investigated using the test method described earlier. Figure 3 presents the calcium HAP dispersion data on homo, co-, and terpolymers before and after thermal treatment at 200°C for 20 hr. As shown in Figure 3, there is a significant performance difference between the homopolymers and the co- and terpolymers tested. Among the homopolymers, GRK732 exhibits the best calcium HAP dispersion. By comparison, the non-thermally stressed co- and terpolymers (i.e., CASA, GRK776, CASN, and GRK781) exhibit good calcium HAP dispersion activity with varying degrees of performance loss for the thermally treated polymer samples. It is also interesting to note the following pertaining to calcium HAP dispersion:

- SLS (shown in Figure 1 to be a good iron oxide dispersant) performs poorly.
- Thermally treated AA:SA copolymers and the CASN terpolymer perform similar to that obtained for homopolymers.
- GRK781 provides the best performance before thermal stress and is superior to the other polymers tested after thermal stress.
Calcium Phosphate Inhibition

A. Polymer Composition

The influence of heat treatment on the performance of polymers as calcium phosphate inhibitors was evaluated by conducting a series of experiments under standard test conditions (9 mg/L PO₄, 140 mg/L Ca, pH 8.5, 10 ppm active polymer, 50°C, 22 hr) as discussed in according to the procedure described previously.³ Figure 4 details the performance of various polymers under two test conditions (i.e., without heat treatment and with heat treatment or 200°C).

It is evident from Figure 4 that exposure of polymer solutions have varying effect on polymer performance. For example, heat treatment of carboxylic acid containing homopolymers (i.e., GRK732 and PMA) has no negative impact on the performance of these polymers indicating that there is no significant loss of carboxylic acid group. However, for the copolymers containing both carboxylic acid and sulfonic acid groups (i.e., GRK776 and CASA) the situation is dramatically different as both polymers lost ~90% inhibitory power. This suggests that SA component of the AA:SA copolymers underwent essentially complete degradation leading to the formation of poly(acrylic acid). The poor performance (<8% Ca/P inhibition) exhibited by thermally treated copolymers is consistent with the performance of high (>10,000) molecular weight PAA.¹¹ Furthermore, the observed decrease in performance by the AA-SA copolymers is consistent with the calcium hydroxyapatite dispersion data presented in Figure 3.

Figure 4 also presents calcium phosphate inhibition performance data for the two terpolymers (i.e., CASN and GRK781). As shown in Table 2 the primarily difference between these two terpolymer compositions is the third monomer [i.e., non-ionic for CASN and sulfonated styrene (SS) for GRK781]. It is interesting to note that CASN lost more inhibitory power (~73%) compared to ~60% loss for GRK781. The data clearly indicate that SS is more stable than the non-ionic monomer present in CASN.

B. Polymer Dosage

To further demonstrate the impact of composition on performance after thermal stress (20 hr and 200°C), a series of experiments were carried out with varying dosages of heat treated polymers. The three polymers selected were the GRK776 copolymer and the two (2) terpolymers (i.e., CASN and GRK781) which in the absence of thermal stress (as shown in Figure 4) provide similar Ca/P inhibition. The results of thermal stress shown in Figure 4 are amplified in Figure 5 wherein GRK781 dramatically outperforms both the GRK776 copolymer and the CASN terpolymer at the baseline 10 ppm dosage and to a greater extent as the polymer dosage is increased from 10 to 20 ppm. The excellent performance shown by the heat treated GRK781 may be attributed to the superior thermal stability of SS component.

C. Polymer Solution Temperature

Several experiments were performed to study the influence of different temperatures (i.e., 150 and 200°C) on the thermal stability of polymers. Figure 6 presents the Ca/P inhibition performance data for the two terpolymers (i.e., CASN and GRK781) in the presence of 0 and 1.0 ppm Fe (III) before and after various levels of thermal stress. As shown in Figure 6,
compared to CASN, GRK781 is a more effective Ca/P inhibitor in the presence of iron and after thermal stress than CASN. Thus, GRK781 is more tolerant to both iron and thermal stress than is CASN. Polymer thermal stability is a key consideration to ensure optimum performance of boiler water treatment programs.

**Calcium Ion Compatibility**

It has been reported that a polymer’s ability to complex hardness ions is affected by polymer molecular weight.\(^\text{12}\) Higher molecular weight polymers typically exhibit better complexing ability than the low molecular weight polymers. However, polymers that complex hardness can also, if not properly dosed, form insoluble calcium salts which exhibit inverse solubility.\(^\text{12}\)

Calcium ion compatibility of several polymers exposed to thermal stress (200°C for 20 hr) was studied using a standard test method (1,000 ppm Ca, pH 9.0, 25°C).\(^\text{9}\) The results shown in Figure 7 indicates that thermal treatment of acrylic acid homopolymers (i.e., GRK732, GRK7058, and PAA-P) does not significantly impact the compatibility of these polymers with calcium ion. The data presented in Figure 7 also suggests that all SA-containing co- and terpolymers are affected by thermal treatment. With the exception of GRK781, all co-and terpolymers became significantly less tolerant to Ca. For example, Ca ion tolerance values obtained for GRK776 and CASA are >100 ppm before thermal stress compared to ~1 ppm obtained when these polymers are subjected to thermal stress (200°C for 20 hr). Because the resultant polymer in both cases (GRK776 and CASA) is a P-AA, the poor compatibility obtained for both polymers is consistent with high molecular weight water polymerized P-AA.\(^\text{9}\)

Figure 7 also illustrates that the terpolymers (i.e., GRK781 and CASN) before thermal stress show excellent calcium tolerance (>100 ppm). However, the situation is quite different in the case of thermally treated terpolymer solutions. As demonstrated in Figure 7, GRK781 exhibits ~10 times more tolerance to Ca than CASN when both polymers were exposed to heat treatment at 200°C for 20 hr. The observed poor Ca ion tolerance of CASN reflects that essentially all of sulfonic acid and non-ionic monomers underwent complete degradation in the thermally treated CASN sample. The high Ca tolerance may be attributed to the superior thermal stability of sulfonated styrene in GRK781.

**Polymer Characterization**

**A. Molecular Weight**

In the present study we have used GPC to measure the molecular weight of the polymers tested. GPC gives relative molecular weights, not absolute molecular weights as in the case of primary methods such as vapor phase osmometry, membrane osmometry, and light scattering. However, by using the calibration standards with accurately known molecular weights, GPC yields molecular weights that match molecular weights determined by primary methods.

It is well known that molecular weight of a polymer has profound effects on its performance in industrial water systems. For example, a low molecular weight (2,000 to 10,000) polymers [e.g., poly(acrylic acid), acrylic acid:sulfonic, etc.], are effective scale control and dispersing agents whereas high (>100,000) molecular weight polymers are poor scale control agents but may be effective flocculants.
All polymers (synthetic and natural) degrade as a result of exposure to elevated temperature and pressure. The extent of degradation depends upon several factors including temperature, duration of heat treatment, and polymer architecture. The polymers used in the present study lost molecular weight as a result of their thermal treatment. Figure 8 depicts the “% molecular weight loss” for homo, co- and terpolymers. The data show that there is relatively small loss of molecular weight for homopolymers (i.e., GRK732, PAA-P, PMA, and PMAA) after heating at 200°C. Figure 8 also shows that terpolymers are degraded to a lesser extent than AA:SA copolymers. For example, the molecular weight loss obtained for terpolymers was ≈11% compared to ≈22% loss in the case of copolymers. It is interesting to note that the natural dispersant (SLS), lost ≈75% of its molecular weight compared to a 22% molecular weight loss for GRK781.

**B. FT-IR Spectroscopy**

Before and after thermal treatment FT-IR spectra of GRK732, GRK776, and CASN are shown in Figures 9, 10, and 11, respectively. Figure 12 shows the FT-IR spectra for GRK781 before as well as after both 4 and 20 hr of thermal treatment at 200°C.

In all cases, polyacrylic carboxylate salt carbonyl, which is near 1,565 cm\(^{-1}\) shifted to a 7-8 cm\(^{-1}\) lower frequency after thermal stress. The reason(s) for this is not fully understood, but may reflect a change in pH caused by the heat treatment.

For those samples containing sulfonic acid (i.e., Figures 10, 11, and 12), the amide carbonyl band near 1,655 cm\(^{-1}\) diminishes and eventually diminishes during heat treatment, as the amide functionality is oxidized. As the amide carbonyl diminishes, a complementary carboxylate salt band near 1,565 cm\(^{-1}\) grows; this band is indistinguishable from the carboxylate salt band observed in polyacrylate salt type products (i.e., GRK732). As the SA component is degraded, the primary sulfonate salt asymmetric SO\(_3\) stretch band near 1,195 cm\(^{-1}\) shifts to an approximately 15 cm\(^{-1}\) higher frequency. The position of asymmetric SO\(_3\) stretch band near 1,047 cm\(^{-1}\) is essentially unchanged. However, the relative intensity of this band is somewhat less in heat-treated samples than in the untreated samples.

The spectra in Figure 12 indicate that the majority of the thermal degradation occurred after only 4 hr. Furthermore, the greater thermal stability of GRK781 vs. CASN is evident by comparing the spectra in Figures 12 and 11, respectively.

**Summary**

The thermal stability of several homo-, co-, and terpolymers under simulated boiler water conditions has been investigated. The polymers evaluated include homopolymers (GRK732, GRK7058, PAA-P, PMA, PMAA), copolymers (CASA and GRK776, and terpolymers (CASN and GRK781). The results show that all polymers undergo some degradation under the conditions employed in this study.

For polymers before thermal stress, the co- and terpolymers provide significantly better iron oxide dispersion than the homopolymers. However after thermal stress, GRK781 is clearly a better overall iron dispersant than CASN which performs better than both AA:SA copolymers.
Iron oxide dispersion data also suggest that thermal treatment of all the homopolymers tested does not significantly degrade their performance.

As calcium hydroxyapatite dispersants, there is a significant performance difference between the homopolymers and the co- and terpolymers tested. The non-thermally stressed co- and terpolymers (i.e., CASA, GRK776, CASN, and GRK781) exhibit good calcium HAP dispersion activity vs. poor performance for the homopolymers. Thermal stress causes varying degrees of performance loss such that the AA:SA copolymers and the CASN terpolymer are similar to homopolymers. GRK781 provides the best performance before thermal stress and is superior to the other polymers tested after thermal stress.

Polymer composition plays a significant role in calcium phosphate inhibition performance. After thermal treatment, GRK781 retains more inhibitory power than CASN which performs better than the AA:SA copolymers both in the presence and absence of Fe(III). Ca/P inhibition data also suggest that thermal treatment for all the homopolymers tested has very limited adverse impact on their performance.

The calcium-ion compatibility exhibited by the polymers tested ranged from poor for the homopolymers to excellent for the SA-containing co- and terpolymers. However, thermal stress had a profound impact on the calcium-ion compatibility of all the copolymers tested reducing all but GRK781 to performance levels similar to the homopolymers.

Thermal stress testing data indicate that homopolymers lost slightly less molecular weight than terpolymers which lost less molecular weight than copolymers. Furthermore, polymers that are susceptible to thermal degradation experience molecular weight and performance loss as the thermal stress is increased from 150 to 200°C.

The FT-IR and NMR analysis of the polymers exposed to heat treatment reveal that the AA:SA copolymers and the CASN terpolymer (AA:SA:NI) underwent more severe degradation than AA:SA:SS terpolymer (GRK781) containing SS.

When selecting deposit control polymers as component of boiler water treatment programs it is important to understand the operating conditions of the system and the thermal stability of the polymers. Operating conditions such as boiler pressure (or temperature), residence time, pH, and polymer dosage should be part of the deposit control polymer selection criteria.

Acknowledgements

The authors would like to thank Harold Paine for polymer preparation in thermal stability experiments and for running the GPCs, Dr. George Benedikt who performed the NMR analyses, Dr. Robert Williams for the FT-IR work, and finally the Noveon, Inc. for permission to carry out the studies and present the results to Association of Water Technologies.
References


Figure 1 - Iron Oxide Dispersion for Polymers before and after Thermal Stress

Figure 2 - Iron Oxide Dispersion for Polymers before and after vs. Varying Thermal Stress
Figure 3 - Calcium HAP Dispersion by Polymers before and after Thermal Stress

Figure 4 - Ca/P Inhibition by Polymers before and after Thermal Stress
Figure 7 - Calcium Ion Compatibility of Polymers before and after Thermal Stress

Figure 8 - Polymer Molecular Weight Loss Due to Thermal Treatment (200 deg C)
Figure 9
FT-IR Spectra of GRK732 before and after Thermal Stress (20 hr @ 200 °C)

Figure 10
FT-IR Spectra of GRK776 before and after Thermal Stress (20 hr @ 200 °C)
Figure 11
FT-IR Spectra of CASN before and after Thermal Stress (20 hr @ 200°C)

Figure 12
FT-IR Spectra of GRK781 before and after Thermal Stress (200°C for 4 & 20 hr)
For additional technical information pertaining to Lubrizol’s Carbosperse™ (formerly Good-Rite) K-700 Polymers, please contact us as follows:

Lubrizol Advanced Materials, Inc.
9911 Brecksville Road
Cleveland, OH 44141-3247, U.S.A.

Phone: 1-800-380-5397 or 216-447-5000
FAX: 216-447-6315 (USA Customer Service)
216-447-6144 (International Customer Service)
216-447-5238 (Marketing & Technical Service)

E-mail: coatings.csr@Lubrizol.com
Web Site: www.carbosperse.com

™ Trademark of The Lubrizol Corporation