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Environmental Technology

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N. Mithil Kumar^a, Sanjay Kumar Gupta^b, Dani Jagadeesh^a, K. Kanny^a & F. Bux^b

^a Composites Research Group, Department of Mechanical Engineering, Durban University of Technology, Durban, South Africa

^b Institute for Water and Wastewater Technology, Durban University of Technology, Durban, South Africa

Accepted author version posted online: 05 Nov 2014. Published online: 09 Dec 2014.

To cite this article: N. Mithil Kumar, Sanjay Kumar Gupta, Dani Jagadeesh, K. Kanny & F. Bux (2014): Development of poly(aspartic acid-co-malic acid) composites for calcium carbonate and sulphate scale inhibition, Environmental Technology, DOI: [10.1080/09593330.2014.984773](https://doi.org/10.1080/09593330.2014.984773)

To link to this article: <http://dx.doi.org/10.1080/09593330.2014.984773>

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Development of poly(aspartic acid-co-malic acid) composites for calcium carbonate and sulphate scale inhibition

N. Mithil Kumar^a, Sanjay Kumar Gupta^b, Dani Jagadeesh^a, K. Kanny^{a*} and F. Bux^b

^aComposites Research Group, Department of Mechanical Engineering, Durban University of Technology, Durban, South Africa;

^bInstitute for Water and Wastewater Technology, Durban University of Technology, Durban, South Africa

(Received 11 June 2014; accepted 13 October 2014)

Polyaspartic acid (PSI) is suitable for the inhibition of inorganic scale deposition. To enhance its scale inhibition efficiency, PSI was modified by reacting aspartic acid with malic acid (MA) using thermal polycondensation polymerization. This reaction resulted in poly(aspartic acid-co-malic acid) (PSI-co-MA) dual polymer. The structural, chemical and thermal properties of the dual polymers were analysed by using scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, differential scanning calorimetry and gel permeation chromatography. The effectiveness of six different molar ratios of PSI-co-MA dual polymer for calcium carbonate and calcium sulphate scale inhibition at laboratory scale batch experiments was evaluated with synthetic brine solution at selected doses of polymer at 65–70°C by the static scale test method. The performance of PSI-co-MA dual polymer for the inhibition of calcium carbonate and calcium sulphate precipitation was compared with that of a PSI single polymer. The PSI-co-MA exhibited excellent ability to control inorganic minerals, with approximately 85.36% calcium carbonate inhibition and 100% calcium sulphate inhibition at a level of 10 mg/L PSI-co-MA, respectively. Therefore, it may be reasonably concluded that PSI-co-MA is a highly effective scale inhibitor for cooling water treatment applications.

Keywords: water treatment; polycondensation polymerization; scale inhibitor; aspartic acid; malic acid

1. Introduction

One of the most promising methods to prevent scale formation involves the addition of scale inhibitors to water in small doses. During the last few decades control of mineral scale formation in industrial waters has been extensively studied and various anti-scaling additives have been proposed. Such additives include polyphosphates, polyacrylic acids, polymethacrylic acids, polyacrylamides, lignin sulphonic acid, hydrolysed polymaleic anhydride and hydrolysed dual polymers as well as their salts. The use of inorganic scale-corrosion inhibitors, polyphosphate salts and their derivatives has received considerable attention since 1990s. These polymers satisfactorily inhibit scale formation; however, these antiscalants usually cause secondary pollution and pose severe challenges to water treatment plants as well as to the environment, especially when discharged. Thus, the concept of ‘Green polymers’ was proposed and ecofriendly scale inhibitors have become an imperative focus to water treatment technology.[1–3] In the late 1990s, the development of non-phosphorous ecofriendly antiscalants drew attention amongst researchers all over the world for industrial water treatment. For cooling water systems, presently polyaspartic acid (PSI), polyepoxysuccinic acid and natural polymers are in use because of their chemically accessible

carboxyl groups, and chelating ability, excellent water solubility and biodegradability.[1] A study by Koskan and Low [4] showed that most of the natural polymer-based green antiscalants have poor stability and low efficiency and are inferior to corresponding synthetic ones in terms of scale inhibition ability and dispersion stability. In recent years, synthetic PSI polymer has attracted more attention as phosphate-free biodegradable, non-toxic polymer that can replace many non-biodegradable polymers.[2,3]

There are currently many synthetic protocols available leading to PSI dual polymers by ring-opening polymerization in the presence of solvent–catalyst systems. Various solvent–catalyst systems such as toluene, DMF, sulpholane and phosphoric acid, and sulphuric acid have been studied as well.[5] The synthesis of PSI and poly-malic acid based dual polymers through ring-opening polymerization has been reported in various studies.[6–11] Though these methods yield high molecular weight polyesters, the synthesis is difficult including repeated purification of the end products. In contrast, direct polycondensation is possible in a one-step reaction and has the advantages of limited or no use of organic solvents in comparison to the conventional polymerizations such as ring-opening reactions.[10,12] Therefore, in recent years, the direct polycondensation synthesis such as ther-

*Corresponding author. Email: kannyk@dut.ac.za

mal heating polycondensation has emerged as a potential route to synthesize 'green' antiscalants.[13–16] These techniques are, therefore, preferred for the production of antiscalants on an industrial scale.[15,17] PSI can be synthesized via thermal polymerization of aspartic acid and has shown to be a promising prospect as a nontoxic, biodegradable water-treatment agent for industrial scale circulated cooling water systems.[18] However, some studies have indicated that the performance of the PSI single polymer as a scale inhibitor is poorer than that of the phosphorus-containing inhibitor.[19,20] Therefore, to overcome these shortcomings and scale-inhibiting capabilities of PSI and to widen its application, attempts have been made to incorporate amino group and a carboxylic group [21] to PSI-based antiscalants.[22,23] Recently, Shogren et al. [5] showed the excellent calcium carbonate scale inhibition efficiency of dual polymers of aspartic acid and aliphatic dicarboxylic acids, which are adipic and sebacic acid. Malic acid is a natural, difunctional monomer that is non-toxic and is also a readily available, inexpensive, biodegradable and safely handling during the synthesis.[24,25] It is a natural monomer used to prepare functional dual polymers. The aim of this study was to improve the calcium carbonate and calcium sulphate scale inhibition performance of aspartic acid by adding malic acid as the modifier agent by thermal polycondensation, which has not been previously studied. The chemical and thermal properties of PSI-co-MA was studied by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and X-ray diffraction (XRD). Morphology analysis was done by scanning electron microscopy (SEM). The effectiveness of this dual polymer for CaCO₃ and CaSO₄ scale inhibition at laboratory scale batch experiments was evaluated with synthetic brine solution at various doses of polymer at 65–70°C.

2. Materials and experimentation

2.1. Reagents and instruments

L-aspartic acid (ASP) (product no. S4913503-137, assay > 99%), DL-malic acid (MA) (product no. 87984, minimum assay 99%) and calcium chloride (product no. 20070) were supplied by S.D. Fine Chemicals Ltd (India). Ethylenediaminetetraacetic acid disodium salt (EDTA) and Eriochrome black T (EBT) was purchased from Capital Lab Supplies (South Africa). All analytical grade chemicals were used in this study as received, without any purification. Ultra-pure water was used during the complete experimental reaction. Instruments used in this study include FITR (MB3000 Model, ABB Company), SDT Q 600 TGA thermal instrument analyser (T.A. Instruments-water LLC, Newcastle, DE, USA) and Carl Zeiss, Evo 15 HD ESEM.

2.2. Synthesis of PSI-co-MA dual polymer

The PSI-co-MA dual polymer systems were synthesized using the following optimized procedure conditions. Six different molar ratios of dual polymer systems were developed (Table 1). Preparation of the dual polymer was achieved by thermal heating polycondensation polymerization. ASP was triturated with different molar ratios of malic acid in ceramic bowls. Subsequently, the fully mingled reactant (ASP and MA) was placed in a heating furnace set at ambient temperature. Initially, the oven temperature was kept at 110°C for 1 h to remove moisture, and then the temperature was increased to 127°C under vacuum conditions for 2 h to initiate the polycondensation reaction avoiding monomer loss (decomposition). The temperature was further raised and constantly maintained at 190°C for approximately 12 h. A dual polymer, yellowish brown in colour was obtained after polycondensation. Finally, the temperature was increased to 250°C for 4 h reacting in a complete conversion to a dual polymer. The developed dual polymers were washed with distilled water several times to remove unreacted monomers and decomposed impurities and to finally yield 80–95% of the product. A similar polycondensation process was used for the synthesis of PSI single polymer.

2.3. Characterizations

2.3.1. Fourier transform infrared spectroscopy analysis

A small portion of solid dried polymer was dispersed thoroughly in potassium bromide (KBr) powder using a mortar and pestle. The KBr dispersion was placed in a stainless steel mould and compressed into pellets by application of a 5-t force. The pellets were scanned (16 scans) in a FTIR spectrophotometer (MB3000 Model, ABB Company, Horizon software). FTIR spectra were recorded in the MB3000 Model with a resolution of 16 cm⁻¹, using KBr pellets (1 mg polymer and as 400 mg KBr). The FTIR spectrophotometer was used to identify the PSI-co-MA dual polymer formation.

2.3.2. Differential scanning calorimetry analysis

Thermogravimetric measurements were carried out using a DSC apparatus (Model: SDT Q 600 DSC, T.A.

Table 1. Composition of single and dual polymers.

Sr. no.	Polymer codes	Amounts of aspartic acid (mM)	Amounts of malic acid (mM)
1	PSI-co-MA ₁	75.13	18.64
2	PSI-co-MA ₂	75.13	24.61
3	PSI-co-MA ₃	75.13	37.29
4	PSI-co-MA ₄	75.13	55.93
5	PSI-co-MA ₅	75.13	74.58
6	PSI-co-MA ₆	75.13	149.16
8	PSI	75.13	–

Instruments-water LLC, Newcastle, DE) instrument. DSC of PSI and PSI-co-MA was studied under the following operational conditions: sample weight 5–13 mg, heating rate 20°C/min and nitrogen flow (100 mL/min).

2.3.3. Thermogravimetric analysis

To determine the degree of degradation of the samples, TGA analyses were conducted using a TGA instrument (T.A. Instruments-water LLC, Newcastle, DE). A heating rate of 20°C/min was applied in the temperature range of 30–600°C under air at a flow rate of 100 mL/min. The 5–13 mg of polymer sample was examined and alumina powder was used as the standard. The pan with the sample was introduced into a thermo balance and further subjected to pre-programmed heating (30–600°C at the rate of 20°C) in the furnace. A profile of weight loss versus temperature was plotted.

2.3.4. GPC analysis

The molecular weight of the polymers was measured by gel permeation chromatography (HPLC: Dionex ultimate 3000 Model). Molecular weight of PSI and PSI-co-MA was studied under the following operational conditions: the solvent used: tetrahydrofuran, the flow rate: 1 mL/min, the temperature of the column and of the detector: column: 45°C, the column: Jordi gel, the detector and wavelength: UV detector and 254 nm. Molar mass and molar weight distribution were calculated with reference to poly(styrene) standards. Molecular weights of poly(aspartic acid–malic acid) dual polymers were investigated as a function of malic acid concentration.

2.3.5. X-ray diffraction analysis

The XRD method was used to identify the formation of polymer network. The samples were dried and finely grounded for XRD. The formation of copolymer network was recorded on a Rikagu diffractometer (Cu k_{α} radiation, $\lambda = 0.1546$ nm) running at 40 kV and 40 mA.

2.3.6. Scanning electron microscopy analysis

The single and dual polymer surface structure, morphology and the fracture surface interface were examined using a Zeiss Scanning Electron Microscope (JEOLJEM-7500F, Tokyo, Japan), operating at an extended pressure and with voltage up to 2 kV. All samples were carbon-coated, prior to examination.

2.4. CaCO₃ scale and CaSO₄ scale inhibition performance of PSI-co-MA dual polymer

All of the single and dual polymers were tested using a modified method of Kumar and Kanny,[26] to establish calcium carbonate scale inhibition performance by the

static test scale inhibition method. In brief, an aqueous solution containing 500 mg/L Ca²⁺ and 1000 mg/L HCO₃ was prepared in a screw cap reagent bottle (capacity 1 L). A quantity of 10 mg/L of PSI single polymer and PSI-co-MA copolymer was mixed into the solution. The solution was allowed to react in a water bath at 65–70°C for 16 h. Simultaneously, a set of blank solution without polymeric additive was also processed. At the end of the reaction, the solution was cooled to room temperature and the residual Ca²⁺ in the supernatant solution was measured by the EDTA titrimetric method. The scale inhibition efficiency of the PSI-co-MA scale inhibitor against CaCO₃ scale was calculated as follows [27]:

$$\begin{aligned} & \text{CaCO}_3/\text{CaSO}_4 \text{ scale inhibition efficiency}(\%) \\ &= \frac{\text{Ca}_i - \text{Ca}_b}{\text{Ca}_c - \text{Ca}_b} \times 100 \end{aligned} \quad (1)$$

where η (%) is the scale inhibition ratio, Ca_c (mL) is the EDTA volume consumed by all calcium cations in the solution, Ca_b (mL) is the EDTA volume consumed by certain calcium cations in the solution without the scale inhibitor after incubation at 65–70°C for 16 h and Ca_i (mL) is the EDTA volume consumed by certain calcium cations in the solution with the scale inhibitor at 65–70°C for 16 h.

The CaSO₄ scale inhibition test was performed using the following conditions: sample solution with 7500 mg/L of Ca²⁺ and 10,200 mg/L of SO₄²⁻. The experimental conditions were as follows: temperature 65–70°C, solution pH 8.0 and a reaction time of 16 h. The experimental conditions of the static scale test are shown in Table 2 and the composition of brine solution is shown in Table 3.

2.5. Feed analysis

A 50 mL of calcium brine solution and 50 mL of distilled water were taken in a 250-mL Erlenmeyer flask and mixed properly. Thereafter, 10 mL of polymer solution was added to the above solution. A 5 mL aliquot of this mixture was then taken and a drop of 0.05 M MgCl₂ solution and 2 mL of ammonia buffer was added to it and immediately titrated with 0.01 M of EDTA and EBT was used as the indicator.

Table 2. Test conditions for calcium carbonate and calcium sulphate inhibition experiments.

Ca	500 ppm as CaCO ₃
NaHCO ₃	1000 ppm as CaCO ₃
CaSO ₄	7500 ppm as CaCO ₃ (10,200 ppm as CaSO ₄)
Temperature	65–70°C
Duration	16 h

Table 3. Composition of anion and cation brine.

Test	Composition	Concentration
Calcium carbonate test	2.94 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	1 mL = 2 mg Ca as CaCO_3
	3.36 g/L NaHCO_3	1 mL = 2 mg NaHCO_3 as CaCO_3
Sulphate test	7.5 g/L NaCl + 11.1 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	1 mL = 7.55 mg Ca as CaCO_3
	7.5 g/L NaCl + 10.66 g/L Na_2SO_4	1 mL = 7.51 mg SO_4 as CaCO_3

3. Results and discussion

3.1. Chemical characterization and structural analysis

Figure 1 shows the FTIR spectra of PSI-co-MA dual polymer (Figure 1(a)), pure ASP (Figure 1(b)) and MA (Figure 1(c)). The FTIR spectrum of dual polymer showed a large absorbance peak at 1710 cm^{-1} , corresponding to the carbonyl stretching in the (PSI) succinimide residues [5,28] and a strong wide peak at 3510 cm^{-1} may be attributed to the carboxyl groups (MA). This was attributed to the presence of ASP and MA functional groups in the dual polymer system.[29–31] The latter confirms the functional groups of a dual polymer when compared with pure MA and ASP spectra.[29–31]

Figure 2 shows the DSC thermograms of a single polymer (PSI) and dual polymers (PSI-co-MA₂, PSI-co-MA₄, and PSI-co-MA₆). DSC of the single polymer and dual polymers gives glass transition temperature (T_g) of 357°C , 342.53°C , 322.66°C and 320°C , respectively. The T_g decreases with the increase of malic acid content in the dual polymer. This was due to the incorporation of malic

acid units (aliphatic), which provided more flexibility and chain degradation to the biodegradable dual polymers.

Thermogravimetric analysis was done to evaluate the thermal stability of developed PSI and PSI-co-MA dual polymers. TGA plots (Figure 3) showed that dry polymers are thermally stable up to 110°C making them suitable for high-temperature application. Only 4.5% weight loss was observed up to 110°C , which was possibly due to loss of moisture. The results show differences in the thermal behaviour between the dual polymer and the single polymer. TGA of the PSI-co-MA₆ indicated two-stage weight loss: the first stage ranged between 70 and 140°C and showed 4.5% loss in weight, this was mainly attributed to residual water and the elimination of impurities. The second stage of weight loss started at 150°C and continued up to 590°C during which time 79.3% weight loss resulted. This corresponded to the degradation of malic acid, some oligomers, carbon dioxide, nitrogen and polymer main chain, respectively. For single polymer (PSI), 65.8% weight loss between 250 and 590°C resulted. All

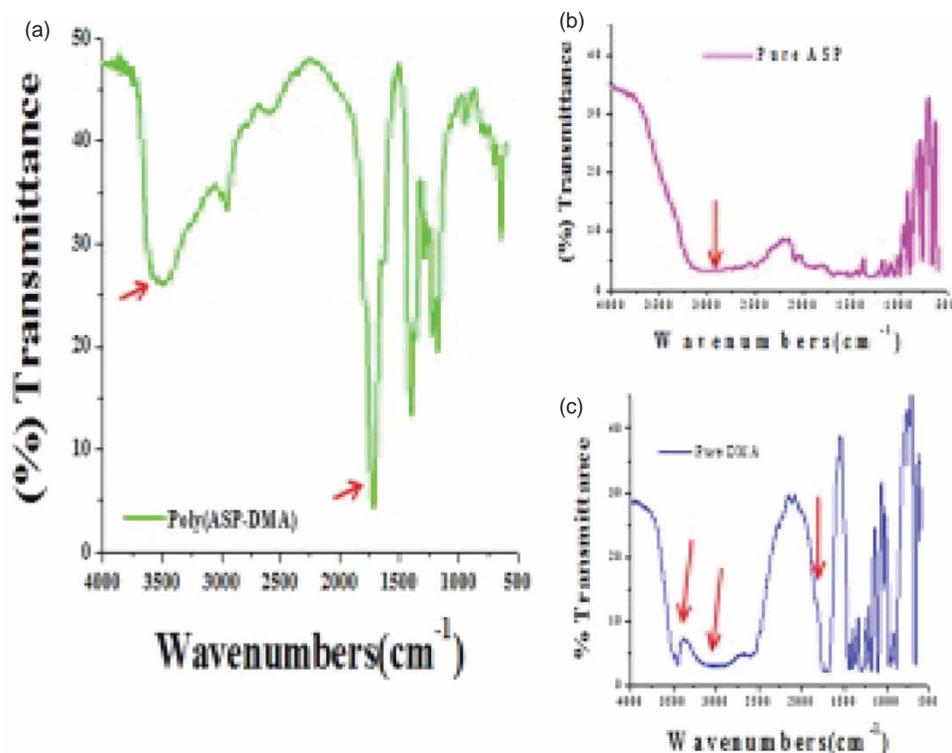


Figure 1. FTIR spectra of (a) poly(aspartic acid-co-malic acid) [PSI-co-MA₆], (b) aspartic acid (ASP) and (c) malic acid (MA).

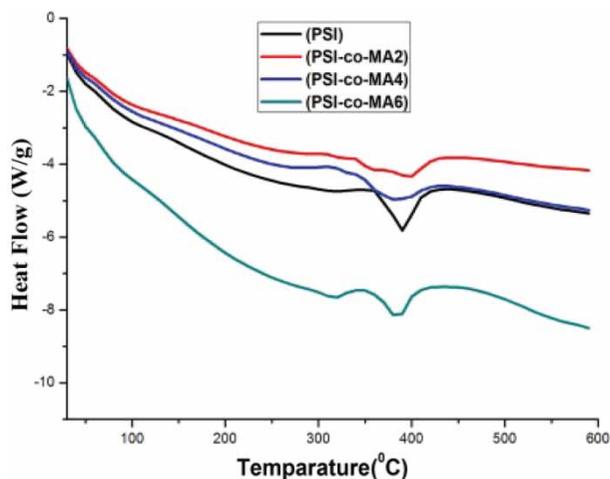


Figure 2. DSC spectra of single polymer (PSI) and dual polymers [PSI-co-MA2, PSI-co-MA4 and PSI-co-MA6].

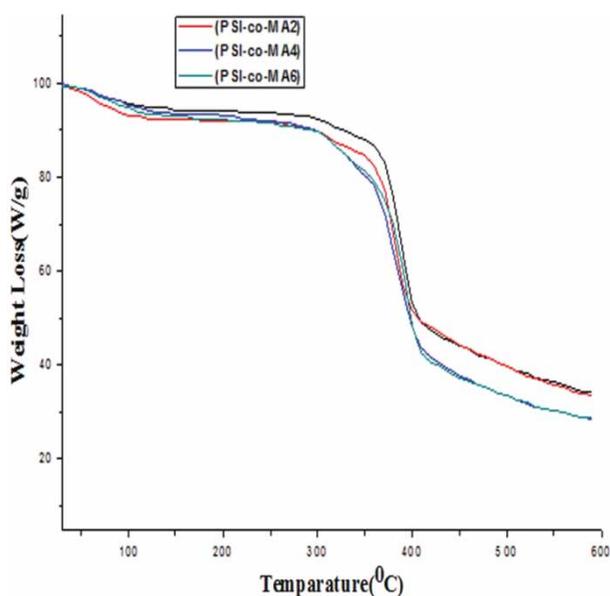


Figure 3. TGA spectra of single polymer (PSI) and dual polymers [PSI-co-MA2, PSI-co-MA4 and PSI-co-MA6].

of the dual polymers were crystalline in nature. Insertion of malic acid fragments into the PSI structure caused a decrease of dual polymer thermal stability.[32]

Table 4 shows the molecular weight of the single and dual polymers. The high molecular weight (M_w) of 1005 g/mol was obtained for the single polymer. The molecular weights of the dual polymers decreased with the increased amount of MA.[33] The resultant single polymer had a polydispersity of 1.31, whereas polydispersity of dual polymer decreased from 1.31 to 1.23. When the ASP was reacted with MA, the resulting dual polymers showed a narrow molecular weight distribution. The molecular weight distribution and the CaCO_3 and CaSO_4 scale inhibition of both single and dual polymers are shown in Table 4.

Table 4. Molecular weights of single (PSI) and dual polymers [PSI-co-MA₁ and PSI-co-MA₆].

Sample	M_w (g/mol)	Polydispersity (PDI)	CaCO_3 scale inhibition (%)	CaSO_4 scale inhibition (%)
PSI	1005	1.31	54.71	75
PSI-co-MA ₁	898	1.31	56.91	87.5
PSI-co-MA ₄	855	1.26	65.0	95.0
PSI-co-MA ₆	821	1.23	85.36	100.0

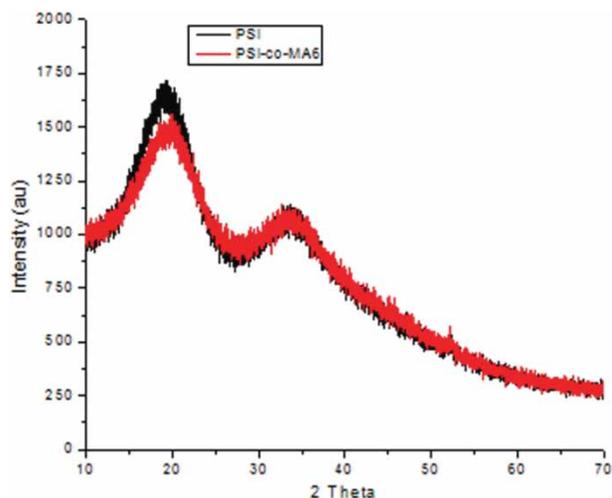


Figure 4. XRD spectra single polymer (PSI) and dual polymer [PSI-co-MA₆].

The XRD patterns of the single polymer and dual polymer are presented in Figure 4. Two broad peaks at 18.92° and 33.54° corresponding to the single polymer can be observed. A further two peaks corresponding to the dual polymer can be seen at 20.12° and 34.69° . These peaks, however, have a higher intensity than that of the single polymer, which may be due to the incorporation of malic acid (dicarboxylic organic acid) as it has more flexible (amorphous) nature than dual polymer.

The differences registered in morphological structures of the polymeric matrices studied by SEM analysis and morphological differences between the PSI and PSI-co-MA polymers are shown in Figure 5. In the case of PSI single polymer (Figure 5(a) and (a1)), the large voids network is seen. This may be caused by the gas generated during the drying process. In the case of PSI-co-MA dual polymer (Figure 5(c) and (c1)), a 'solid, smooth non-porous surface' is seen, which supports the hypothesis that PSI polymer was dispersed in the dual polymer systems.

3.2. Determination of calcium carbonate scale inhibition efficiency of PSI-co-MA

Several studies have been done on the removal of various kinds of organic [34,35] and inorganic contaminants

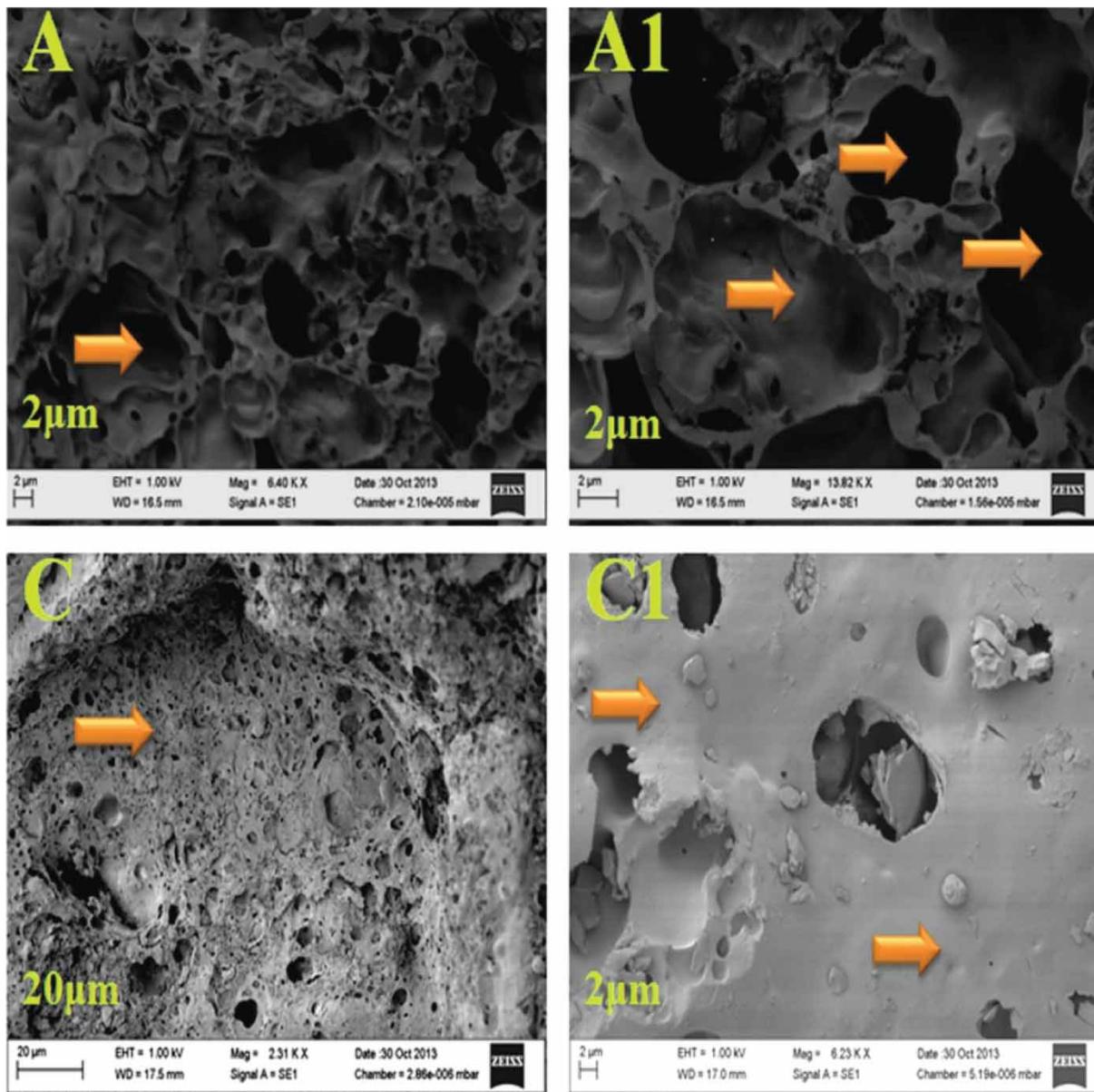


Figure 5. SEM images of single polymer (a, A1 = PSI) and dual polymer (c, C1 = P(ASP-MA6)).

[36,37] from industrial wastewater; however, carboxylic-based polymers have been widely used as CaCO_3 scale inhibitors. PSI polymers containing carboxylic groups were found to be effective in calcium carbonate and sulphate scale growth inhibition.[27] In this study, the calcium-scale inhibition power was investigated by performing the EDTA potentiometric titration against PSI single and PSI-co-MA dual polymer solutions. MA was chosen mainly because it has carboxyl and hydroxyl groups, which are responsible for the inhibition of mineral scale precipitation. The highest amount of reactant used was 30 g, made up of 10 g of ASP and 20 g of MA. The CaCO_3 and CaSO_4 scale inhibition efficiencies were evaluated at 10 mg/L concentration of each composition. The CaCO_3

and CaSO_4 scale inhibition efficiency of PSI-co-MA₁, PSI-co-MA₂ and PSI-co-MA₃, PSI-co-MA₄, PSI-co-MA₅, PSI-co-MA₆ and PSI are presented in Table 5. All inhibitors reduced scale deposition when compared with the blank (without polymeric inhibitor).

Table 5 shows the variation in the CaCO_3 scale inhibition efficiency with an optimal concentration of all the scale inhibitors. The results clearly indicated that the effectiveness of polymers increased with increasing MA proportions due to increase in carboxyl functional groups on the polymer backbone. The CaCO_3 scale inhibition efficiency increased from 59.74% to 85.36% as the carboxyl content (MA) increased from 3.3 to 20 g. The findings revealed that PSI was not a particularly effective Ca-carbonate precipitation inhibitor (Table 5). The inhibitory performance

Table 5. Test conditions for calcium carbonate and calcium sulphate inhibition experiments.

Ca	500 ppm as CaCO ₃
NaHCO ₃	1000 ppm as CaCO ₃
CaSO ₄	7500 ppm as CaCO ₃ (10,200 ppm as CaSO ₄)
Temperature	65–70°C
Duration	16 h

of the PSI-*co*-MA₅ dual polymer was substantially better, whereas PSI-*co*-MA₆ dual polymer attained the best performance in this system as it achieved > 85% inhibition of Ca-carbonate precipitation for 16 h or within 16 h. It could be explained that the polymeric inhibitors with a higher degree of carboxyl group prolong the induction period for crystallization because of the ability of the anionic carboxylate groups to get adsorbed on the calcium carbonate crystal surfaces. Several investigations have indicated that polymeric-descaling agents that exhibit an inhibitory effect on the crystallization kinetics of soluble salts are highly substituted with functional carboxylate groups.[38] Apparently, the larger number of carboxylate functional groups increases the ionic attractive interactions between the polymeric adsorbate (COO⁻) and the positive sites of Ca-scale (Ca²⁺) in the solution interface. However, in the aqueous media, the carboxylate groups of MA are negatively charged; they act as an antiscalant to the formation of the insoluble precipitate and prevent or minimize the scale formation.

Tables 1 and 5 show that when MA concentration increases by eightfold, the inhibition efficiency increases only by 28.45%. This suggests that the incorporation of large amounts of anionic (MA) and non-ionic (ASP) monomer groups increases the calcium ion tolerance of polymers. The PSI-*co*-MA dual system possesses more negative charges that can effectively adsorb at the faces of CaCO₃ scale nuclei and delay the formation of precipitation. This may be due to its carboxylic functional groups in the main polymeric chain of the dual polymer, which enhance its complexing abilities for Ca²⁺. The cations bound to the polyaspartate dual polymer may be explained by the ion exchange model. The positive effect of the foregoing investigated biodegradable polymers may be ascribed to the behaviour of the functional carboxylate groups (anionic nature) containing a biodegradable polymer to inhibit the scale formation.

The molecular weight has a great effect on the ability of the poly(aspartate-diacid) dual polymer to inhibit precipitation of calcium carbonate and calcium sulphate scale in supersaturated aqueous solutions. In addition to that charge, polymeric size and structures, functional groups and amount of co-monomers present in dual polymers affect the interactions that occur between polymeric inhibitors and metal ions. The evaluation of PSI-*co*-MA showed that the molecular weight of polymers plays an important role in the inhibition of CaCO₃ scale deposition.

The PSI-*co*-MA₆ was the best of the polymer antiscalants, which was due to the lower molecular weight of this product. The effect of the molecular weight can also be seen in the results of single polymer (PSI) and dual polymers (PSI-*co*-MA₁ and PSI-*co*-MA₆) with the molecular weights of 1005, 898, 855 and 821 g/mol, respectively (Figure 6). The findings are consistent with the conclusions of Loy et al. [39] that the smaller polymer components diffuse and adsorb faster than the larger ones. With the high molecular weight, PSI does not reduce the scaling effectively. This low value of scale inhibition for PSI tests may be explained by an inhibition of the CaCO₃ nucleation, decreasing the number of active sites available for the formation of calcium carbonate scale. It was obvious that decreasing the molecular weights of the polymers resulted in the increased inhibition performance of the biodegradable polymer. The inhibiting ratio at the optimal concentration of PSI-*co*-MA₆ was 85.36% under the following conditions: 500 mg/L of Ca²⁺, 1000 mg/L of HCO₃⁻ and 10 mg/L of inhibitor, which was higher than that of PSI single polymer. Therefore, it can be concluded that the order of effectiveness of polymers with different molecular weights was as follows: PSI-*co*-MA₆ > PSI-*co*-MA₁ > PSI.

The mechanisms of action of the PSI-*co*-MA dual polymers are completely different from PSI single polymer. While comparing the structures of PSI and PSI-*co*-MA, it is noteworthy that the PSI-*co*-MA has functional carboxylate groups on both sides of the polymer backbone due to MA comonomer, whereas PSI has one. This indicates that there are functional carboxylate groups (anionic nature) regularly on both sides of the PSI-*co*-MA polymer backbone even if the stereochemistry of the polymer is not controlled. The functional carboxylate groups escalate the anionic nature of poly(aspartate-*co*-malic acid) dual copolymer, which effectively prevents scale deposition by binding to the surface of growing scale. Indeed, as shown in Table 5, a high CaCO₃ scale inhibition was observed for the PSI-*co*-MA₆. The PSI-*co*-MA₆ might act on nucleation by reducing the number of calcium carbonate scale growth sites by its two active groups (carboxyl and hydroxyl) in comparison to the PSI single polymer. These active groups can bond with Ca²⁺ in the solution to form chelates, which can be adsorbed on the surface of the CaCO₃ scale. More the number of these active groups of PSI-*co*-MA₆, the bonding efficiency for the Ca²⁺ ions increase resulting in an increase in the scale inhibition efficiencies. The bonding strength disorders the normal chemical structure of calcium carbonate scale/crystal, which is helpful to dissolve Ca²⁺; therefore, PSI-*co*-MA₆ has excellent inhibition performance on CaCO₃ scale. These green scale inhibitors decreased the consumption of calcium ions from the bulk, compared with the PSI single polymer test results leading to less CaCO₃ precipitation. Hence, this green PSI-*co*-MA₆ dual polymer leads to higher CaCO₃ scaling inhibition efficiency. On the other hand, the poor performance of PSI

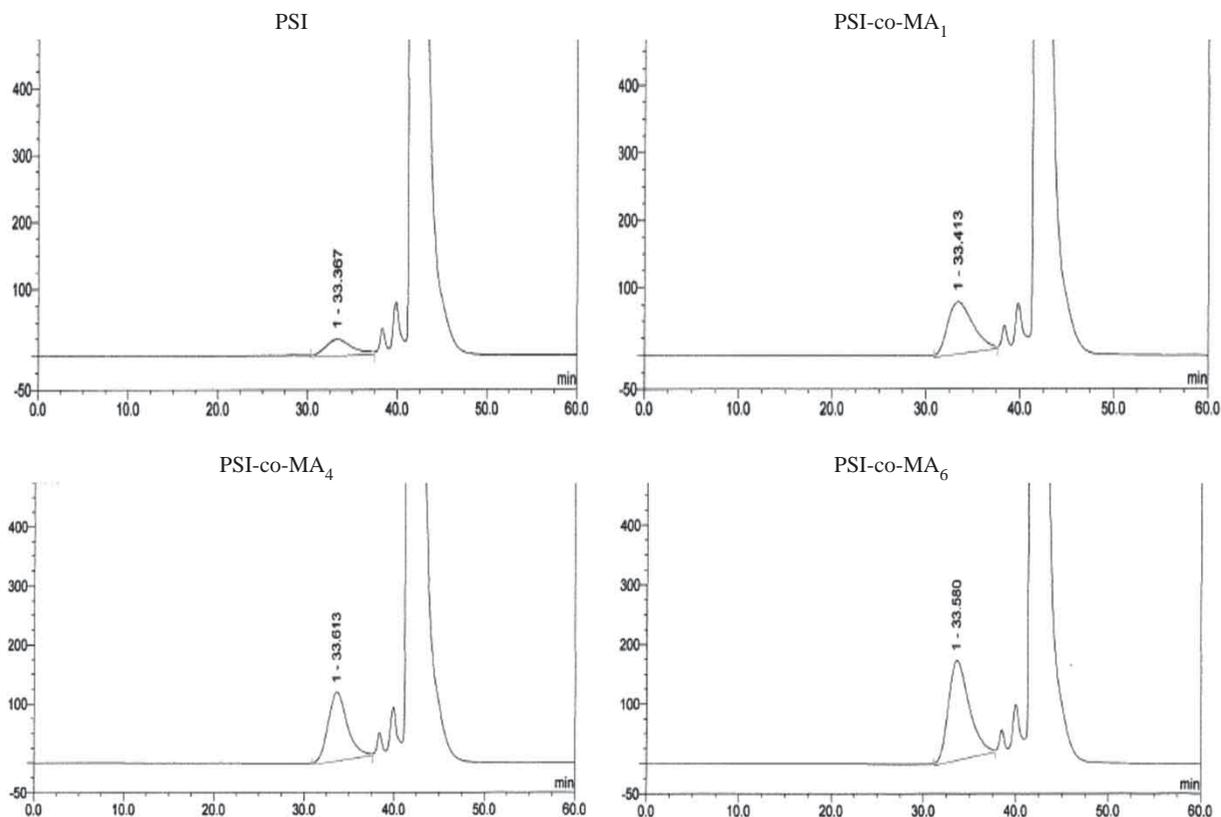


Figure 6. GPC chromatogram of PSI, PSI-co-MA₁, PSI-co-MA₄ and PSI-co-MA₆.

single polymer may be due to their less specific interactions with CaCO₃ scale.

3.3. Determination of calcium sulphate scale inhibition efficiency of poly PSI-co-MA

Reports on the calcium sulphate inhibition by polymers having carboxylate functional groups have been reported earlier by Weijnen and van Rosmalen.[40] In this study, the CaSO₄ scale inhibiting activity of the PSI single polymer and six different molar ratios of poly(aspartic acid-co-malic acid) dual polymers were performed by a static scale test method as explained in the test method. The comparison of CaSO₄ scale inhibition efficiencies of PSI-co-MA₁, PSI-co-MA₂, PSI-co-MA₃, PSI-co-MA₄, PSI-co-MA₅, PSI-co-MA₆ and PSI is shown in Table 5. All six formulations showed varying degrees of CaSO₄ scale inhibition, which ranged from 87.5% to 100% with an average of 95%. The highest calcium sulphate inhibition (up to 100%) was achieved with PSI-co-MA₅ and PSI-co-MA₆, whereas the lowest inhibition (87.5%) was recorded for PSI-co-MA₁ at 10 mg/L concentrations. However, at the same concentrations PSI showed only up to 75% CaSO₄ scale inhibition. The results clearly suggested that all PSI- and MA-based dual polymers with 10 mg/L concentration showed reasonably good inhibition, in which that PSI-co-MA₅ and PSI-co-MA₆ being the most effective. The results strongly

indicated that the efficiency of scale inhibition increased with a corresponding increase in the molar ratio of the MA reactant in the PSI-co-MA compositions.

PSI-co-MA₅ and PSI-co-MA₆ contain good proportions of hydrophilic functional groups such as hydroxyl and carboxyl, which may get adsorbed on the active sites of CaSO₄ surface. This adsorption leads to the chelation on Ca²⁺ ions to form stabilized and dissoluble chelates, which increases the scale inhibition activity. Therefore, during the prolong periods, the hydroxyl and carboxyl functional groups of polymeric inhibitors delay the scale deposition of calcium sulphate. The results depicted that when the functional groups were increased, molecular chain gets extended by the good affinity between the functional groups and water corresponds to the reduced scale deposition. Therefore, PSI-co-MA₆ can sustain a higher stable state for a long time than PSI single polymer, moreover, also improving the dissolution of the precipitation due to the presence of two active functional groups. All PSI-co-MA-based polymers at 10 mg/L concentration were proven as reasonably good inhibitors and PSI-co-MA₆ was most effective and could remove up to 100% of sulphate scaling.

4. Conclusions

Poly(aspartic acid-co-malic acid) dual polymer was developed with six different weight ratios of both ASP and

MA. It was observed that the six different molar ratios of dual polymers, namely PSI-co-MA₁, PSI-co-MA₂, PSI-co-MA₃, PSI-co-MA₄, PSI-co-MA₅ and PSI-co-MA₆ performed well for carbonate and sulphate scale inhibition at 65–70°C and around a pH of 8.0, whereas single polymer showed poor scale inhibition efficiencies for calcium carbonate scale. PSI-co-MA₆ was found to be the most effective in more than 85% of calcium carbonate and 100% sulphate scaling. Remaining other dual polymers showed reasonable inhibition even with low molar concentration levels of MA. The findings suggest that polyaspartic-malic acid based dual polymers could be an attractive alternative for preventing CaCO₃ and CaSO₄ scale in industrial cooling water treatment systems. It may be concluded that PSI-co-MA₆ dual polymer may be used as an effective anti-scalant at higher temperatures (65–70°C) and pH (7.5–8.0) in cooling water systems.

Acknowledgement

The author (N. Mithil Kumar) gratefully acknowledges the financial support of the National Research Foundation of South Africa (NRF) (grant no.: 80437) and the Durban University of Technology.

Disclosure statement

No potential conflict of interest was reported by the authors.

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