

Synthesis and Characterization of Linear Polycarboxylate Dispersant of Glacial Acrylic Acid–Maleic Acid–Sodium Methallylsulfonate for Ceramics

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In this research, linear polycarboxylate of glacial acrylic acid (GAA), maleic acid (MA) and sodium methallylsulfonate (SMAS) dispersant polymer as a water reducer was synthesized for ceramic applications by using redox free radical initiation system consisting sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and sodium hypophosphite ($\text{Na}_2\text{H}_2\text{PO}_2$) through aqueous solution free radical polymerization. The structural characterizations were done using FT-IR and ^1H NMR. The molecular weight of polymer was analyzed using GPC and residual monomer levels in final product were measured with HPLC. Measured the ceramic flow times, viscosities at dispersant dosage rate 0.30 % (dry slurry based) and the results indicated that linear polycarboxylate showed a good performance at the mol ratios of GAA:MA:SMAS = 60:20:20, ratios of initiator ($\text{Na}_2\text{S}_2\text{O}_8$) and chain transfer agents ($\text{Na}_2\text{H}_2\text{PO}_2$) 2:6 % at 85 °C polymerization temperature and 2 h reaction time.

Keywords: Dispersant, Polycarboxylate, Acrylic acid, Maleic anhydride, Sodium methallylsulfonate, Redox initiator, Viscosity.

INTRODUCTION

A water soluble dispersant is an important additive in ceramic, cement and concrete mixture since a long time [1]. The ceramic industries often utilize dispersants to reduce the slurry viscosity of slip and to operate at low moisture of ceramic body and glaze. It helps to reduce the ball-milling time, improves grinding ability, dryness, improving the pumps and other transfer equipment efficiency [2], hence bringing down the energy consumption and increasing economic efficiency of manufacturing unit. In the initial stage, inorganic ceramic dispersants were represented by soluble glass, organic small molecule, later macromolecular ceramic polymer of different molecular structure represented by polycarboxylates as it improves the dispersion, strengthening effect, excellent durability and non-polluting ability have attracted much [3]. In the 21st century, newly emerged organically synthesized polycarboxylate dispersants have replaced inorganic dispersants owing unique molecular structure and large control on molecular weight, when they wrapped and absorbed clay particles, it proves more efficient than traditional organic water reducers [4]. In early 21st century, the processing of ceramic suspension attracted more attention, as it is an important additive which improves stability of high solid slurry by controlling the colloidal properties. Due to the limitation in molecular structure and molecular weights, it will rule out

the possibilities for traditional ceramic inorganic dispersant producing the desired effects, by adding huge quantity into the harsh conditions, high dispersion of ceramic slurry and high quality ceramic products are not satisfied [5].

In the presence of sodium hypophosphite, thermal decomposition of persulfate is accelerated and the required temperature for the formation of free radicals is reduced *e.g.*, synthesized maleic acid and itaconic acid homopolymers [6], homopolymer of glacial acrylic acid synthesized by using sodium hypophosphite and persulfate [7,8], maleic anhydride and glacial acrylic acid copolymer synthesized with sodium hypophosphite and ammonium persulfate [9], sulfonic acid and acrylic acid copolymers, acrylic acid and maleic acid copolymer, sulfonic acid homopolymers synthesized with sodium hypophosphite [10,11], sodium acrylate synthesized with sodium hypophosphite and persulfate, sodium bisulfate and persulfate combinations [12], sodium methallylsulfonate and acrylic acid copolymer synthesized [13], sodium allylsulfonate and maleic anhydride polymer preparation to control the scale deposition [14], sodium allylsulfonate and acrylic acid copolymer synthesized [15], methallylsulfonates, acrylic acid and maleic acid linear polymer synthesized by using ammonium persulfate [16]. Based on the literature surveyed, a linear polycarboxylate dispersant polymer from acrylic acid, maleic acid and sodium methallylsulfonate can be synthesized using redox initiating system of sodium hypophos-

phite and sodium persulfate through aqueous free radical polymerization method.

EXPERIMENTAL

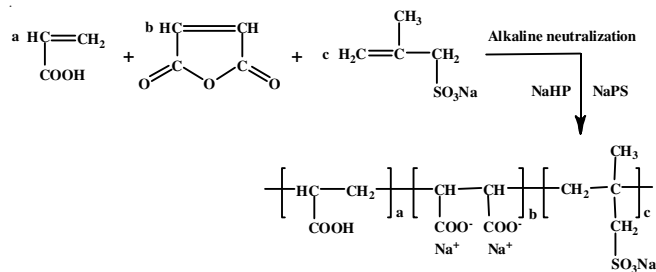
Glacial acrylic acid (BASF, Malaysia), maleic acid (Taiwan Prosperity Chemical Corporation, Taiwan), sodium methallylsulfonate (KOWA, Japan), sodium persulfate and sodium hypophosphite (A.M.P.E.R.E. Industries S.A.S Lyon Ltd., France), sodium hydroxide (ARKEMA, France), water (Millipore water), PC67 superplasticizer & Flosperse 40152 commercial ceramic dispersant (SNF SAS, France). The chemical composition of ceramic composite clay (CLAYRIS Ceramics) is given in Table-1.

Characterization: FT-IR spectra, recorded on Spectrum-100 (Perkin Elmer, USA) in transmission mode: 4000–400 cm^{-1} with average 16 scans. ^1H NMR spectra was recorded on spectrometer BRUKERS, NMR AVANCE III HD 400MHz. Molecular weight of polymer spectra was measured on WATERS-GPC with eluent KH_2PO_4 , flow rate 0.4 mL/min, injection volume 100 μL . High performance liquid chromatography was adopted to measure the free monomer content in final polymer, WATERS-HPLC (alliance e2695-USA) with UV detector-2489.

B4 cup/ford type flow cup (Gabbrielli, Italy) was used to measure the flow times or slip viscosity of ceramic slurry by adding 0.3 % of dispersanting agent (dry slurry based). The ceramic slurry viscosity was measured by digital viscometer (Brookfield-DV2TLV) and the dispersing effect of our dispersant GAA-MA-SMAS based is denoted by 5 times the average value of measured viscosity.

Synthesis: The linear GAA-MA-SMAS polycarboxylate was synthesized through redox free radical initiation system consisting of sodium persulfate and sodium hypophosphite. Weighed 60.9 g of maleic acid was added into 376.4 mL of water and 99.3 g of sodium hydroxide solution, heated to 55 $^\circ\text{C}$ and dissolved, then added 98.2 g of sodium methallylsulfonate (SMAS) to the former solution then transferred into a four-necked 1.5 kg double jacket glass reactor, which was equipped with thermometer (Comark make), stirrer, dosing pipes (Parmer-Master flex dosing pumps) and glass condenser. The solution is heated to initial temperature 85 $^\circ\text{C}$, and then separately 134.26 g of glacial acrylic acid and total 8 % (wt) of redox initiator (sodium hypophosphite and sodium persulfate aqueous solutions) were added dropwise into the reaction mixture (GAA:85 min, $\text{Na}_2\text{S}_2\text{O}_8$:90 min and $\text{Na}_2\text{H}_2\text{PO}_2$:90 min). After the completion of dosage, the resultant substance was to be aged at the same temperature for 30 min then the pH value of polymer was adjusted to 7.0 by adding 126.6 g of NaOH (50 % solution) after cooling the reaction mixture at 60 $^\circ\text{C}$ (Scheme-I) [6-26].

Preparation of slurry: Weighed 250 g of dry blanks proportionally and screened through 4 sieves and should pass through 250 Tyler mesh sieves. To achieve this fineness, the dry blanks to be milled in the ball mill and passed through the sieves and the residue should be < 1 % [16,18].



Scheme-I: Synthesis of GAA-MA-SMAS linear polymer through free radical polymerization

RESULTS AND DISCUSSION

FTIR analysis of dispersant: The FTIR spectrum (Fig. 1) showed the typical absorption bands at 3340.24 cm^{-1} (stretching and vibration of absorption peak of hydroxyl and carboxyl on water molecule), 1550.57 and 1401.52 cm^{-1} (asymmetric and vibration of carboxyl carbonyl appears and its corresponding to absorption characteristic peak of symmetric stretching and vibration), 1451.74 cm^{-1} (asymmetric bending vibration of methylene), 1042.80 and 1171.33 cm^{-1} (sulfonyl symmetric stretching and vibration peak emerges with its corresponding absorption peak of asymmetric stretching and vibration), 624.8 cm^{-1} (stretching and vibration of sulfur oxide), alkene double bond stretching and vibration peak doesn't appear near the wave number 1640 cm^{-1} [16,27]. The ^1H NMR spectrum peaks at 2.6–2.3 ppm is attributed to $-\text{CH}$ (MA), 2.2–2.0 ppm attributed $-\text{CH}$ (GAA), CH_2 in alpha of SO_3H is often around 2.9–3.2 (SMAS) while $-\text{CH}_2$ from polymer backbone attribute 1.8–1.0 ppm and 1.0 ppm attributed $-\text{CH}_3$ [17,27].

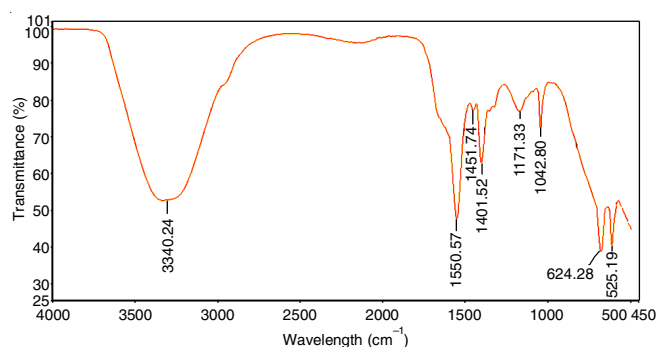


Fig. 1. FT-IR spectrum of linear GAA-MA-SMAS dispersant polymer

GPC analysis: GPC was used to determine molecular weight and polydispersity of GAA-MA-SMAS sample. The molecular weight was found to be 4900 g/mol Daltons and polydispersity was 1.19 (PDI), where polymer has shown excellent slurry viscosities properties [26].

HPLC analysis (residual monomer): High performance liquid chromatography was used to determine the residual monomer presence in the final polymer sample. UV- detector (HPLC Waters, USA), wave length 205 nm, column-Acclaim OA, m250*4.0 mm, 5 μ , injection volume 20 μL , analysis time

TABLE-1
CHEMICAL COMPOSITION OF CERAMIC COMPOSITE CLAY

Clay composition	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	LOI
% Wt	76.81	14.33	0.27	0.4	0.99	1.14	3.42	1.65	0.96

20 min, flow time 0.7 mL/min, work pressure 1800 psi. Chromatogram (Fig. 2) indicated residual monomer levels as maleic acid 0.1 ppm at 7.0 min, SMAS 0.3 ppm at 15.12 min and acrylic acid 1 ppm at 15.926 min.

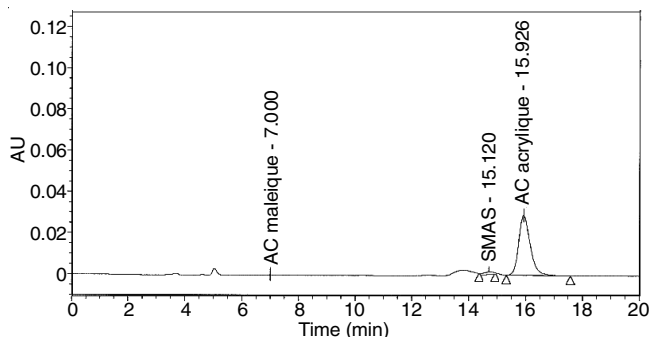


Fig. 2. HPLC chromatogram of linear GAA-MA-SMAS dispersant polymer

Determination of optimum synthesis conditions: The major function of polycarboxylate is to disperse the ceramic clay particles in order to reduce the slip viscosities, improvement of flow and stabilities of ceramic slurry. Slip viscosity test (flow times) was adopted to determine the optimum conditions of GAA-MA-SMAS linear polymer synthesis mole ratios by addition of admixture quantity ratio of dispersant of slurry system 0.3 % (relative-mass ratio of absolutely dry slurry).

Table-2 shows that the best flow time 18 s serves, when the linear GAA-MA-SMAS polycarboxylate monomer mole ratio's was 60:20:20 with 8 % redox initiator ($\text{Na}_2\text{S}_2\text{O}_8$: $\text{Na}_2\text{H}_2\text{PO}_2$ = 2:6) at 85 °C and 2 h polymerization time.

Effect of redox initiator on ceramic slurry viscosity: Molecular weight of the polymer is affected by the speed of radicals generated by the initiating agent. Under the condition of 85 °C polymerization temperature and 90 min polymerization reaction time, the acquired proportion of $n(\text{GAA}):n(\text{MA}):n(\text{SMADS})$ = 60:20:20 and 0.3 % admixture quantity ratio of dispersant. Fig. 3 clearly shows the ceramic slurry viscosities varies with catalyst quantity $n(\text{Na}_2\text{S}_2\text{O}_8):n(\text{NaH}_2\text{PO}_2)$. It is also evident that an increase in dosage of $n(\text{Na}_2\text{S}_2\text{O}_8):n(\text{NaH}_2\text{PO}_2)$, decreases viscosity is least when the mole ratio is $n(\text{Na}_2\text{S}_2\text{O}_8):n(\text{NaH}_2\text{PO}_2)$ = 2:6%. This showed that addition of appropriate quantity of sodium hypophosphite will significantly enhance dispersant performance by controlling molecular weight of polymer, but when dosage is too high, generation of excessive quantity of sodium hypophosphite radicals reduce the chain

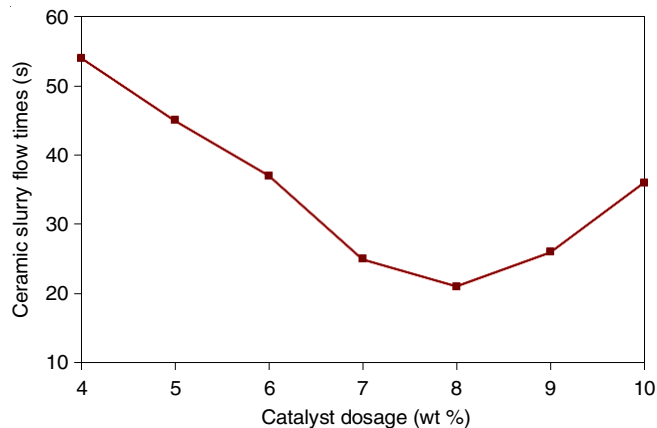


Fig. 3. Tendency of ceramic slurry viscosity varies with catalyst fractions

length within the unit volume and leads to low molecular weight, resulting weakened dispersion performance.

Increasing the dosage of catalyst $n(\text{Na}_2\text{S}_2\text{O}_8)$ initially reduces the viscosity and after a point of time, the viscosity stabilizes. This is due to low generation of free radicals and since the life of these free radicals is short, they stabilize quickly during their life there is no collision or initiation towards the monomer will occur. Thereby increasing the molecular weight of polymer product and hence one can witness a reduction in viscosity effect. Further increase in oxidant dosage results an increase in monomer free radicals and hence drops in degree of polymerization due to mutual competition leading to reduction of molecular weight. When dosage of oxidant is excessively high, the probability of oxidant colliding with chain transferring agent within unit time reduces and utility rate of oxidant also falls, thereby weakening the viscosity effect, resulting in the decline of viscosity effect and hence viscosity stabilizes. Thus, an ideal combination of $n(\text{Na}_2\text{S}_2\text{O}_8):n(\text{NaH}_2\text{PO}_2)$ is 2:6 to be maintained [9,10,19,26,28].

Effect of glacial acrylic acid on ceramic slurry viscosity: Under the conditions of 85 °C polymerization temperature and 90 min polymerization time, acquired proportion of $n(\text{MA}):n(\text{SMADS})$ = 20:20 mol ratio and 0.3 % admixture quantity ratio of dispersant, catalyst quantity 8 % ($n(\text{NaPS}):n(\text{NaHP})$ = 2:6 %). Fig. 4 showed that by varying $n(\text{GAA})$ dosage, the ceramic slurry viscosity also varies. The mol % of $n(\text{GAA})$ slowly increased from 55 to 80 %. From 55 to 60 %, a huge reduction of ceramic slurry viscosity can be noticed, due to $-(\text{COOH})$ group addition to the clay particles, which shortens the flow time. Thus, 60 mol % of $n(\text{GAA})$ stands out to be the

TABLE-2
SYNTHESIS OF POLYCARBOXYLATE WITH DIFFERENT MOLE RATIO AND SLURRY FLOW TIMES

Sample No.	Mole ratio GAA:MA:SMAS	Amount of raw materials			Conc. polymer	Polymer molecular weight (g/mol)	Slurry flow times (s)
		GAA (g)	MA (g)	SMAS (g)			
1	80:10:10	199.25	33.9	54.6	8	40.22	36
2	70:10:20	167.01	32.4	104.7	8	40.11	24
3	60:10:30	133.65	30.3	146.6	8	40.19	40
4	70:20:10	166.67	64.8	52.2	8	40.20	23
5	60:20:20	132.93	60.3	97.2	8	40.30	18
6	50:20:30	106.43	57.9	140.1	8	40.16	36
7	60:30:10	134.01	91.1	49.0	8	40.11	29
8	50:30:20	106.10	86.6	93.1	8	40.15	24
9	40:30:30	80.87	82.5	133.0	8	40.09	45

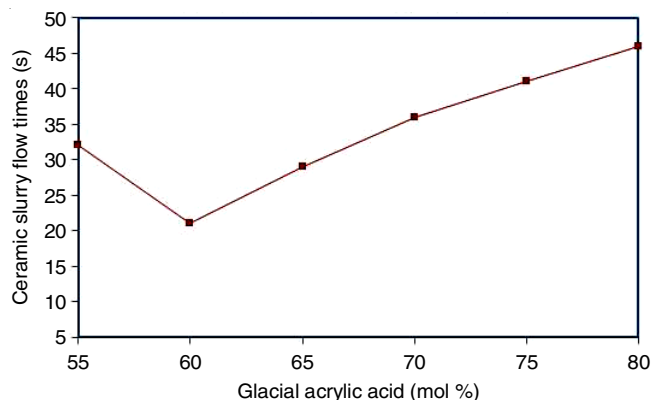


Fig. 4. Tendency of ceramic slurry viscosity varies with GAA mole fractions

inversion point and from this value to 80 mol % of $n(\text{GAA})$ again the viscosity starts increasing due to overloading of the carboxylic group on the clay particles, which forms longer chains hence, increasing the flow time. Hence, 60 mol % is the optimum dosage of glacial acrylic acid for getting the better results on ceramic clay slurry.

Effect of maleic acid on ceramic slurry viscosity: Under the conditions of 85 °C polymerization temperature and 90 min polymerization time, acquired proportion of $n(\text{GAA}):n(\text{SMADS})$ are equal to 60:20 mole ratios and 0.3 % admixture quantity ratio of dispersant, catalyst quantity 8 % ($n(\text{NaPS}):n(\text{NaHP}) = 2:6$ %) of total monomer mass, Fig. 5 shows change tendency of ceramic slurry viscosities varies with $n(\text{MA})$ mole ratios. An increase in dosage of maleic acid, the slurry viscosity decreases to an inversion point and overloading of $n(\text{MA})$ slowly regains the viscosity in the ceramic slurry (Fig. 5). In this experiment, the dosages were increased slowly from 5 to 25 mol % of $n(\text{MA})$. Upto 20 mol of $n(\text{MA})$ dosage, the ceramic slurry exhibited a down trend of flow time and goes to the least flow time at 20 % and further increment of dosage upto 30 %, again proved to be increasing viscosity and increasing flow time. During the dosage increment, $-\text{COOH}$ groups starts to absorb on the surface of clay particles and this absorption causes the electric potential on the particles. This phenomenon creates a reverse effect of flocculation and causes particulate repulsion and hence easy flow of particles. Dosage above the inversion point proves to be reversed the effect caused by overdose of carboxylic groups and long polymeric chains.

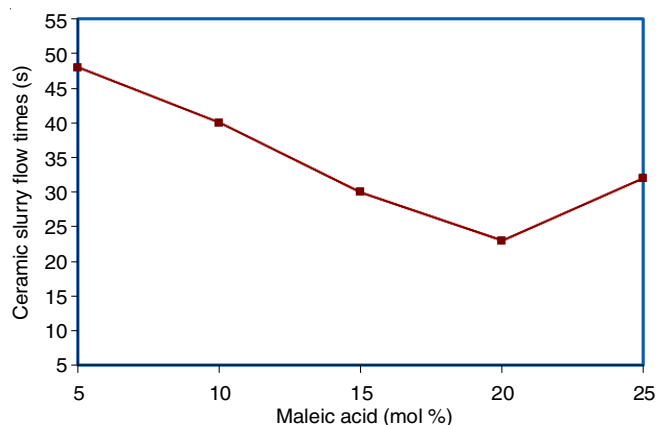


Fig. 5. Tendency of ceramic slurry viscosity varies with maleic acid mole fractions

Effect of sodium methallylsulfonate (SMAS) on ceramic slurry viscosity: It is observed that $n(\text{SMAS})$ increased the dosages effects on ceramic slurry viscosity (Fig. 6). Initially, a reduction of flow time with increase in dosage of $n(\text{SMAS})$ is observed but after inflection point, the flow time increases. With increase in $n(\text{SMAS})$, sulfonic ($-\text{SO}_3\text{H}$) functional groups are increased in the dispersant polymer and creates an electrical repulsion forces. These forces show to be insufficient initially which has slowly reduced with increase in dosage. Further increase in $n(\text{SMAS})$ after 20 mol % would reduce the effect of carboxylic functional groups and hence reduces the particular absorption phenomenon on the ceramic clay particles. This further increases the flow time as $-\text{SO}_3\text{H}$ groups cannot compensate the reduced carboxylic groups.

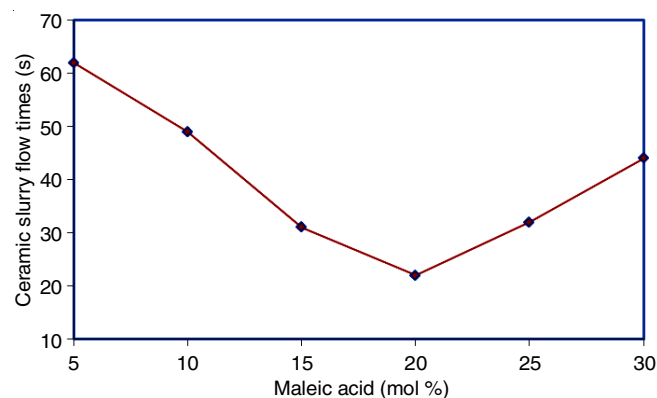


Fig. 6. Tendency of ceramic slurry viscosity varies with SMAS mole fractions

Effect of molecular weight on ceramic slurry viscosity: Fig. 7 shows the effect of molecular weight on the ceramic slurry. In this context, the molecular weight of 4900 Daltons proven to be the best flow time producer as the optimum electrostatic repulsion forces in the ceramic slurry. This increase in molecular weight from 2000 to 4500 Daltons enhances the absorption of carboxylic and sulfonic groups onto the clay particles and hence reducing the flow time of slurry. If the molecular weight exceed beyond 4900 Daltons, the polymeric effect hinders the flow time of ceramic slurry due to long chains. However, once the molecular weight exceed 5500 Daltons, the positive effect of absorption becomes lower than the negative effect of polymeric chain flow hindrance and henceforth, the flow time increases again.

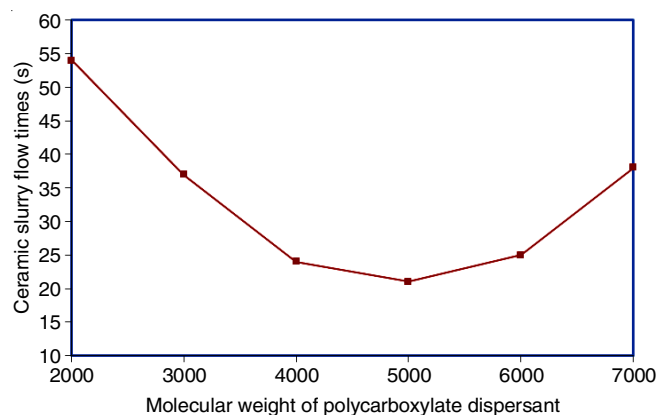


Fig. 7. Tendency of ceramic slurry viscosity varies with molecular weight of the polymer

Terpolymer of GAA-MA-SMAS polycarboxylate performance evaluation and comparison with industrial dispersant grades: Fig. 8 shows the tendency of ceramic slurry viscosity was reduced with increasing dosage of different dispersants which include Flosperse 40152, PC 67 super-plastizers commercial dispersants and GAA-MA-SMAS polycarboxylate. Viscosities of three dispersants initially reduce to a point and after that slurry viscosities increase with increasing dosages. Flosperse 40152 and PC67 super-plasticizer showed similar performance and its least viscosity of 85 and 90 mPa.s at 0.3 % dosage, which further increased with increase in dosage. Further GAA-MA-SMAS dispersant polymer recorded their least viscosities at 69 mPa.s. Fig. 8 indicated that GAA-MA-SMAS polymer found to be giving a good results in terms of low viscosity and as well as flow time with same combination of clays. The linear GAA-MA-SMAS polycarboxylate has prevented the flocculation aggregation of ceramic body slurry particles by forming a strong steric layer. At the same time polycarboxylate anionic molecules are easily absorbed onto the surface of slurry particles, when the particles comes close to each other, the electric double bond layer intercepts/overlaps with each other and does not allow the particles to aggregate easily, hence the slurry particles of ceramic body shall efficiently disperse without any sedimentation [9,29,30].

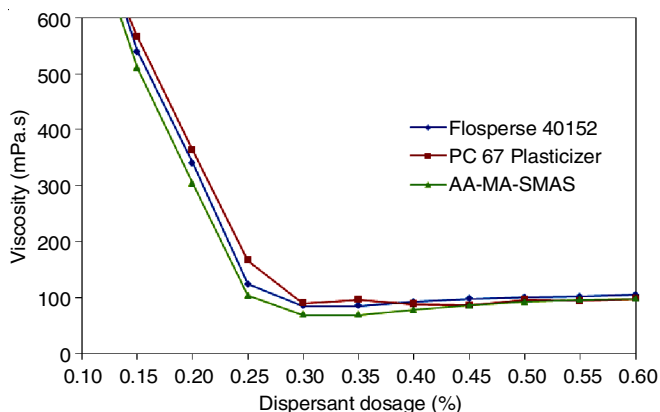


Fig. 8. Tendency of ceramic slurry viscosity varies with different dispersants

Conclusion

In this work, a linear low molecular weight GAA-MA-SMAS dispersant polymer is synthesized by using free radical initiation system consisting of sodium hypophosphite and sodium persulfate through aqueous solution free radical polymerization. The structural characterizations were done through FTIR and NMR techniques. The molecular weight of dispersant polymer was analyzed using GPC and residual monomer levels in final product were measured with HPLC. When the initiation system of $\text{Na}_2\text{S}_2\text{O}_8$: NaH_2PO_2 ratio is 2:6 %, n(GAA):n(MA):n(SMAS) = 60:20:20 mole ratios, polymerization temperature and time are 85 °C and 2 h, respectively, the optimized polycarboxylate dispersant ratio 0.30 % (absolutely dry based) and with this amount of dispersant, the effectiveness proves to be optimum and with slurry viscosity 69 mPa.S only.

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