SYNTHESIS ANDCHARACTERIZATIONOF NEWBINDERSFOR EMULSION COATING APPLICATIONCONTAININGIN WATER BASED METHACRYLIC HYBRID RESINS

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ABSTRACT

Binder is an important ingredient in pigment coating as it is used to impart adhesion, gloss and flexibility to the dried film as well as binding the pigment particles together. Series of emulsion methacrylic copolymers having different composition ratios of methylacrylicacid (MAA) with butylacrylate (BuA), methylmethacrylate (MMA), styrene, poly vinyl alcohol (P.V.A) were prepared and characterized. The preparation was carried out in industrial scale in batch reactor at pH 7, using potassium persulphate(KPS) and Sodium metabisulfate ($Na_2S_2O_5$) as an initiators, Dodecyl Benzene Sulphonic acid SDBA as an emulsifier,and sodium dodecyl sulfonic acid SDBAS as co-emulsifier in presence of tri metylchlorosilane(TMCS) at 70^oC for 4 hours. The chemical structures of the prepared binders were characterized by FTIR and ^{1}HNMRspectra. The various physic-chemical properties ofemulsion methacrylic copolymers including density, viscosity, chemical resistance and volatile matter were studied. The resultsshow thatemulsion acrylic copolymers are readily soluble in aprotic polar solvents such as (Toluene, Acetone, Benzene, xylene, DMF, DMSO, Methanol, and ethanol) without being in need for heating.The obtained emulsion copolymers had high solid content and were used in emulsion paints as binder. The experimental results show that these polymers supply very useful properties such as high anticorrosive. The binder film are evaluated by measuring their chemical resistance. Thermal analysis of emulsion copolymers are conducted by using thermo Gravimetric analysis (TGA) and thermal differential calorimeter (DSC) techniques, which reveals that theemulsion acrylic polymers possess thermal stability.

KEYWORDS: *Binder, Coating, Emulsion Polymerization, Methylacrylicacid, Surfactants*

INTRODUCTION

Acrylic resins, which have an important commercial application in paint industry, are prepared through the polymerization of acrylic and methacrylic acids or their corresponding esters. The key attribute of acrylic coatings is their resistance to hydrolysis during extended exterior exposure (weathering), high block resistance, hardness, gloss and high alkali and oxidation resistance [1]. Coating mixture consists primarily of pigments dispersed in water, plus binders, co-binders and other additives [2-4]. Binder is added to coating to bind pigment particles to each other and to fill voids between pigment particles so that the coating layer will not be removed during the operation [5]. Binders are desired to meet various requirements such as good binding power, mixed and dissolved easily in water, good chemical and

mechanical properties and harmless to health [6]. There is no synthetic binder which could meet all requirements of good binder so it is often need co-binder to adjust the rheology and water retention to the required level [7]. Acrylic binders have found significant uses in the field of coating for clear grease-resistant coating, excellent mixture quality, resistance to oil and solvent and permanent flexibility. Additionally, acrylate dispersions have an excellent brightness and ageing resistance and are less odorous [8]. Emulsion polymerization is an important industrial method, because it produces high molecular weight polymers, and because there is no or negligible content of volatile organic compounds (VOC). In a normal emulsion polymerization technique, the oil is emulsified in water with a conventional surfactant using a mechanical shearing device, to produce droplets of 1 to 10 min diameter. The polymerization is achieved with the assistance of a water or oil soluble initiator or catalystThese emulsions are generally opaque, milky, and viscous; but they can also be translucent emulsions with particle sizes ranging from about 8 to 80 m, when a very high surfactant concentration is employed [9].In order to ensure an adequate reaction rate it is common to introduce an initiator to the reaction system. The surfactant not only influences the nucleation of polymer particles, but the particle size distribution and the colloidal stability of the latex as well as the film properties are also affected by this component[10].the film formation process is arbitrary divided in three stages: 1) evaporation of water resulting in packing of latex particles, 2) their deformation, and 3) coalescence by inter diffusion of polymer chains between adjacent particles. The first stage is crucial because the structure achieved by the particles will remain in the film affecting its properties [11]. The permeability and the water uptake of the latex film affect its performance because they can promote the film degradation and/or the damage of the substrate. When in contact with water, the coating tends to absorb water, swells and often the adhesion is lost or decreased [9]. Besides, small hydrophilic molecules, as surfactants employed in the polymerization reaction, pigments or water soluble oligomers, can be extracted from the film by water that increases the loss of film properties [12]. Also the correlation between latex film morphology, void content and film surface characteristics is relevant in coating performance [13]. This work aimed to prepare emulsion acrylic polymers based on styrene (St), poly vinyl alcohol (P.V.A), butyl acrylate (BuA) and carboxylic acid monomers represented as meth acrylic acid (MAA) to be produced in industrial scale for industrial applications. High solid content, low coagulation, the rheological properties as well as the physical properties of the prepared emulsion acrylic polymers. The prepared emulsion acrylic polymers were characterized by using FTIR, ^{1}HNMR TGA, and DSC.

EXPERIMENTAL

Materials

Methyl Acrylic acid (MAA), Methyl Methacrylate (MMA), Butylacrylate (BuA), Polyvinyl Alcohol (PVA), Styrene, Epoxy, Dodecyl Benzene Sulphonic acid SDBA, Sodium Dodecyl Sulfonic acid SDBAS, trimetylchlorosilane (TMCS), EPOXY, Dimethyl Sulphoxide (DMSO) Dimethylformaid (DMF), Chlorophorm, Dichloro methane, Benzene, Sulfuric acid, Acetone, Hydrochloric acid, Ethylenetriamine, Potassium persulfate, sodium metabisulfate, NaCl.

Instruments

FTIR TENSOR 27, Fourier transform infrared spectroscope, BRUKER, Germany. (Oven, Trivp International Crop. Italy),(Hot plate stir, BibbyStrlintd.UK) (Measurement of 1 HNMR Spectra : recorded NMR spectra using a type of Bruker, Ultra shield 300 Mhz, Switzerl and using (DMSO-d6) as a solvent at the university's Educational teacher-Tehran Iran), (Thermogravimetry analysis (TGA) were performed on a polymer laboratories co England, Model pL-TG at Iran polymer & petrochemical institute, using a heating rate of 10ºC/min in Argon atmosphere within the temperature range of

25-800ºC) (differential thermal analysis (DSC) measurement using apparatus (DSC) type (DSC 131 Evo, SETARAM) is the origin (France) in the Department of Chemical Engineering / Faculty of Engineering / University of Qadisiyah), (viscosity device The use of viscosity measurement device for measuring the viscosity of the alkyd resin models record in the Department of Chemistry / Faculty of Education / University of Qadisiyah / by a device from a company (Brookfield) type (RVDV- II + P 8500), (230 V~) and frequency (50/60 Hz) and strongly (30 VA). The machine is manufactured in (U.S.A).

Synthesis ofEmulsion Methacrylic Copolymers

Methacrylic resin was synthesized by emulsion polymerization using batch process. Emulsion polymerization processes consist of two parts: (i) preemulsion, and (ii) reactor charge .Preemulsion was prepared with two different solutions. For solution (1) water (25.gm.), (3 gm.) of dodecyl Benzene Sulphonic acid SDBA with (1 gm.) Sodium Dodecyl Sulfonic acid SDBAS were mixed in a 100 mL beaker. For solution (2), (MAA, BuA, MMA, styrene, Epoxy, and P.V.A)with different ratios as show in table (1)and TMCS (0.5g.) were put in a separate 100 mL beaker and mixed for 5 minutes after the addition of each substance. Then, the two separate solutions were mixed and stirred for 40 minutes. After obtaining a homogeneous preemulsion, the second part-reactor charge, was started. The reaction was performed in a 250 ml three-neck glass flask. Apparatus consisted of mechanical stirrer, condenser, thermometer, a feed inlet and another inlet of nitrogen gas. The reactor was heated in an water bath. (0.45gm of KSP in 30ml distilled water) and (0.23 Sodium met bisulfate in 20ml distilled water) were fed to the reactor at (2min.) at 70oC. After the completion of the addition process, the temperature was 70°C in about 30 minutes and held at 70°C for about 4 hours to complete polymerization. After obtaining the polymer, triethylamine was added to neutralize the carboxylic groups and the mixture was stirred for another 30 minutes while maintaining the temperature at 50°C.

Table 1: Show the Percentage of Monomers

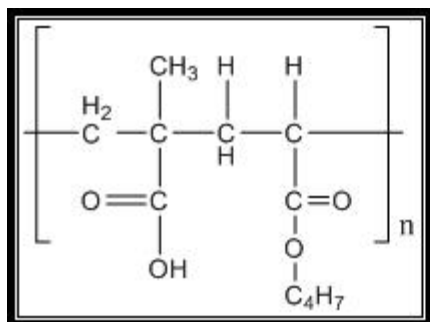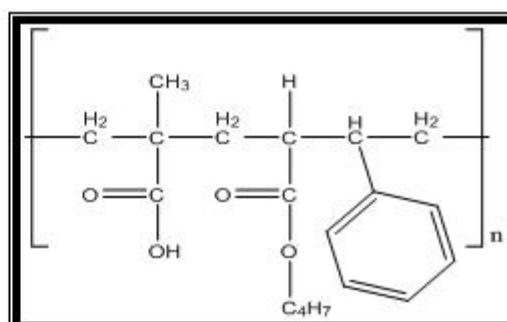| Emulsion Polymers		Monomer Percentage				
Di monomer	PMAA1	MAA			BuA	
		%80			%20	
		%50			%50	
		%20			%80	
Tri monomer	PMA2	MAA		BuA		STYRENE
		%20		%30		%50
Tetra monomer	PMA3	MAA		BuA	MMA	Epoxy
		%10		%50	%20	%20
Penta monomer	PMA4	MAA	BuA	MMA	Styrene	PVA

Figure 1: Structure of PMA1
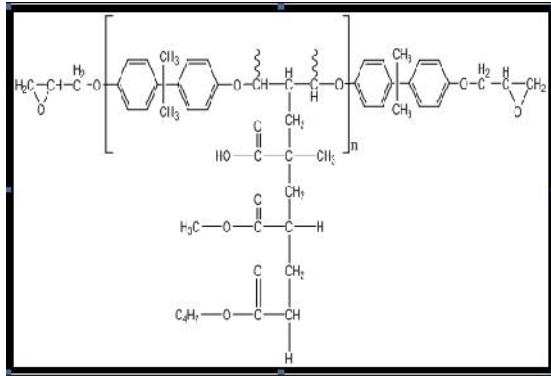

Figure 2: Structure of PMA2
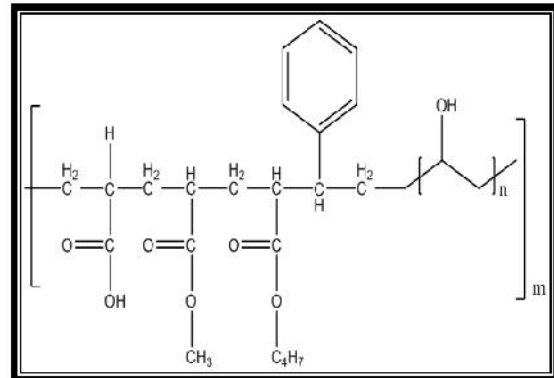
Figure 3: of Structure PMA3   **Figure 4: Structure of PMA4**

Physico – Chemical Tests

Drying Test

Aluminum plates were cleaned by ethanol to make sure that there are no contaminants present to affect the result.

A hand coater with different fixed thickness was used to evenly coat the resin on the surface of the testing plates [14].

Density Test

The density was determined according to NF EN 1097-6 using analytical scale and pycnometer S9611826, (100 ccs) [15].

Viscosity Test

Brookfield rotary Viscometer Ku-2 model RVDV-II+ P8500 was used to measure the viscosity at 25 ℃, and using different spindle and speed [16].

Volatile Matter Test

Three specimens were placed in the oven within (30) min after preparation of methacrylic emulsion copolymers in previously weighed watch glass and heated for (2 h) at (135-140) ℃. The Nonvolatile matter was calculated from the difference in initial and final weights of the watch glass. The mean value of the three results was reported as the percentage nonvolatile matter.

Corrosion Resistance Test

Salt spray test (ASTM D 1654) was performed to study the corrosion resistance of emulsion acrylic copolymers on coatings. 5% NaCl salt water solution was used as corrosive environment; test was performed in a period of 144 hours. Coated panels were examined periodically after (24 hours=one day, 72 hours =3day, 144 hours =6day) for blistering or sign of corrosion [17].

Abrasion Resistance Test

This test was performed to measure the resistance of coating films against abrasion caused by an abrasive falling from a specified height through a guide tube onto a coated metal (ASTM D968). Silica sand was used as the abrasive agent. It was poured onto the coated metal until some scratching was detected. The volume of sand which changes the

thickness of the film by certain extent determines the abrasion resistance. The abrasion is given in terms of ,, per micrometer".

RESULTS AND DISCUSSIONS

Synthesis and Characterization of Polymers Prepared

Synthesis and Characterization of (PMA1)

This polymer was synthesized by the emulsion polymerization of MAA with BA in the presence of Dodecyl Benzene Sulphonic acid SDBA as an emulsifier, sodium dodecyl sulfonic acid SDBAS as co-emulsifier and trimetylchlorosilane (TMCS). At (70°C) for (4 hours) according to the equation in the reaction scheme (1).

Scheme (1) Synthesis of PMA1
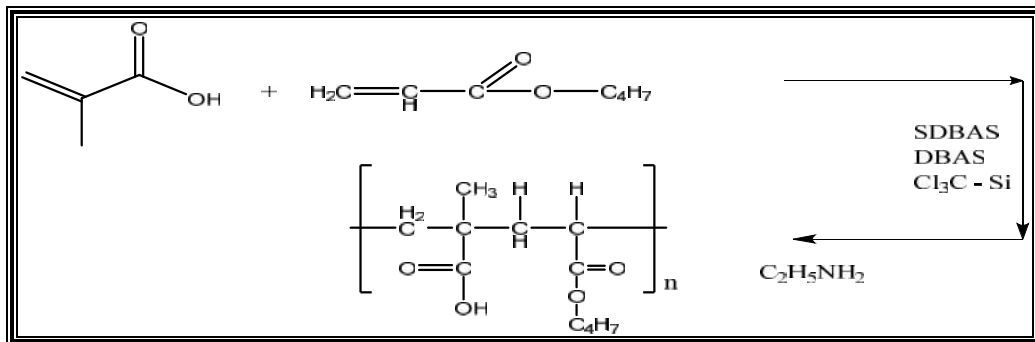
Characterization of (PMA1)

FTIR Spectra

The FTIR spectra of (PMA1) shows in Figure (5) which indicated absorption band of (OH Carboxylic) at (3400 cm^{-1}), (C = O ester) at (1730 cm^{-1}), (CH$_3$)at (1375, 1450cm^{-1}), (C=O carboxylic) at (1725 cm^{-1}), (C-O ester) at (1100cm-1), (C-Haliphatic) at (2895 cm^{-1}).
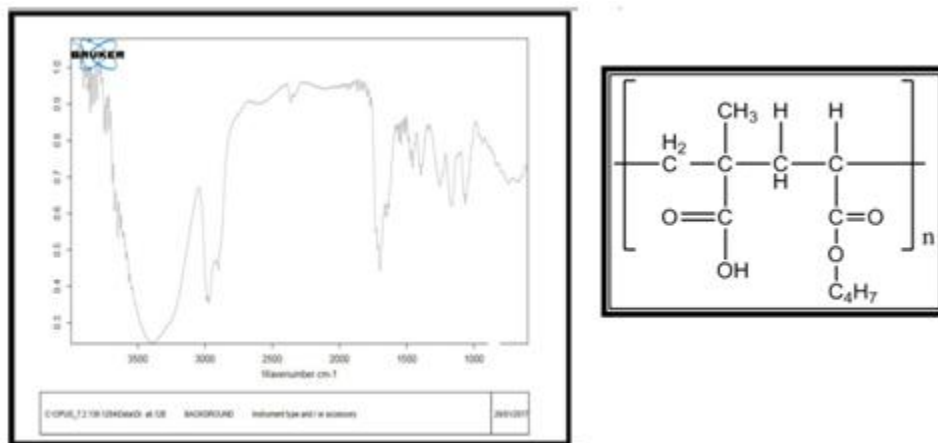

Figure 5: FTIR of PMA1

^{1}HNMR Spectra

Figure (6) showed signals at (=0.778-1.004 ppm) for (CH$_3$), as well as signals at (= 1.135-1.823) ppm) for (CH$_2$). The appearance of several signals at the (=3.25-3.068ppm) returns to the (OCH$_2$) protons. A single at (=2.468ppm) to the DMSO. A signal at (= 12,224 ppm) for H in carboxylic group (OH).
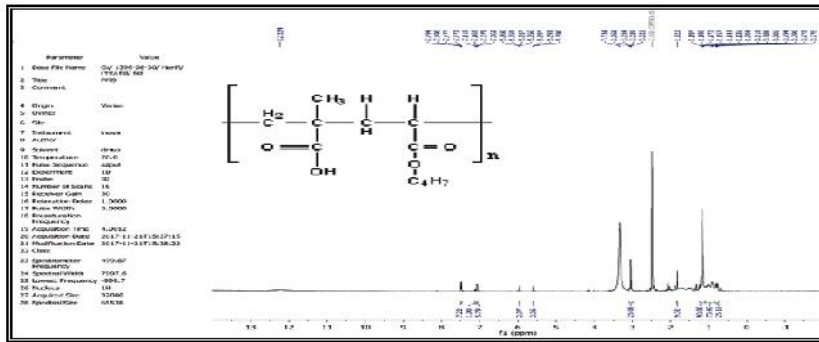
Figure 6: ^{1}HNMR of PMA1

Synthesis and Characterization of (PMA2)

This polymer was synthesized by the emulsion polymerization of MAA with BA and styrene in the presence of Dodecyl Benzene Sulphonic acid SDBA as an emulsifier , sodium dodecyl sulfonic acid SDBAS as co-emulsifier and trimetylchlorosilane (TMCS). at (70 ^{O}C) for (4 hours) according to the equation in the reaction scheme (2).
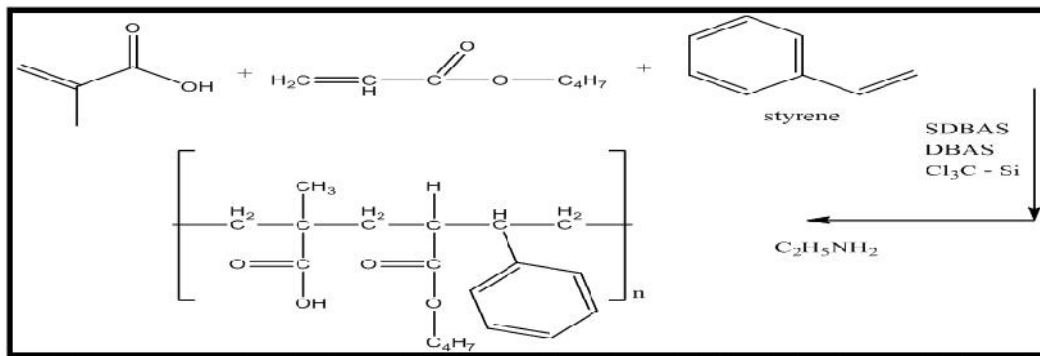
Scheme (2) synthesis of PMA2

Characterization of (PMA2)
FTIR Spectra

The FTIR spectra of (PMA2) shows in Figure (7) which indicated absorptions band of (OH Carboxylic) for (3400 cm^{-1})**,** (C = O ester)for1725cm^{-1}), (1375, 1450 cm^{-1}) for (CH$_3$), (C=O Carboxyl) for 1700 cm^{-1}), 1090 cm^{-1}) for (C-O ester), (2890 cm-1) for (C-H) aliphatic, (C-H aromatic) at (3020 cm^{-1}), (1615 cm^{-1}) for aromatic (C=C).
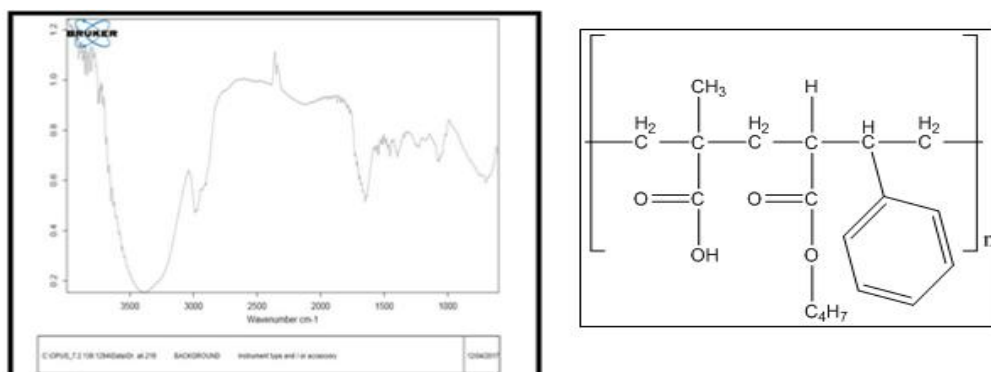

Figure 7: FTIR of PMA2

^{1}HNMR Spectra

Figure (8) showed signals at (= 0.6723-0.9015ppm) to (CH_3), as well as signals at (= 1.0110-1.0896ppm) to (CH_2). Showed signals at (= 1.4482-1.5461 ppm) to (CH), The appearance of several signals at (=2.5070-3.0512ppm) returns to the (OCH_2) protons to (ester). A single show at (=2.5 ppm) to the DMSO. A signal at (= 10.12ppm) for Hin carboxylic group (OH). A Signal show at (=7.4939-7.5101ppm) to proton of aromatic ring.
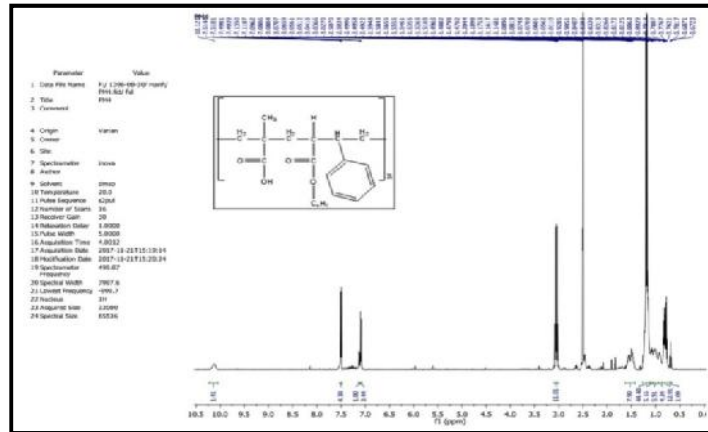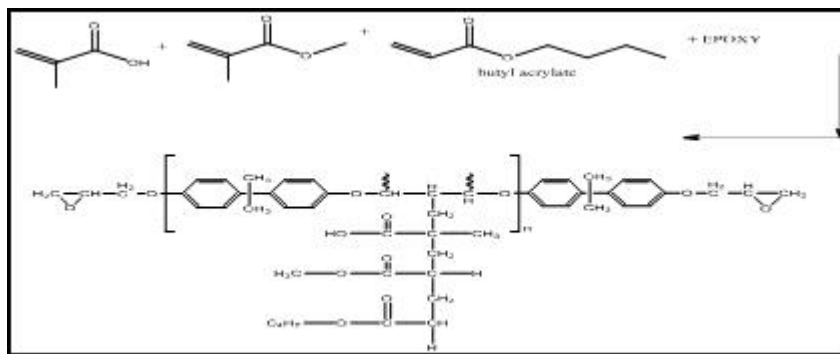

Figure8:^{1}HNMR of PMA2

Synthesis and Characterization of (PMA3)

This polymer was synthesized by the emulsion polymerization of MAA with BA and MMA, and epoxy in the presence of Dodecyl Benzene Sulphonic acid SDBA as an emulsifier, sodium dodecyl sulfonic acid SDBAS as co-emulsifier and trimetylchlorosilane (TMCS). At (70 ^{O}C) for (4 hours) according to the equation in the reaction in the scheme (3).

Scheme (3) Synthesis of PMA3

Characterization of (PMA3)

FTIR Spectra

The FTIR spectra of (PMA3) shows in Figure (9) which indicated absorption band of (OH carboxylic) at (3400 cm-1), (C = O ester) at(1770cm^{-1}), (CH_3) for (1350, 1420 cm^{-1}), (C=O carboxylic) at (1725 cm^{-1}),(C-O)ester at(1110 cm^{-1}), (CH aromatic) at (3010 cm^{-1}), aromatic (C = C) at (1650 cm $^{-1}$), (C-H) aliphatic at (2900 cm^{-1}).
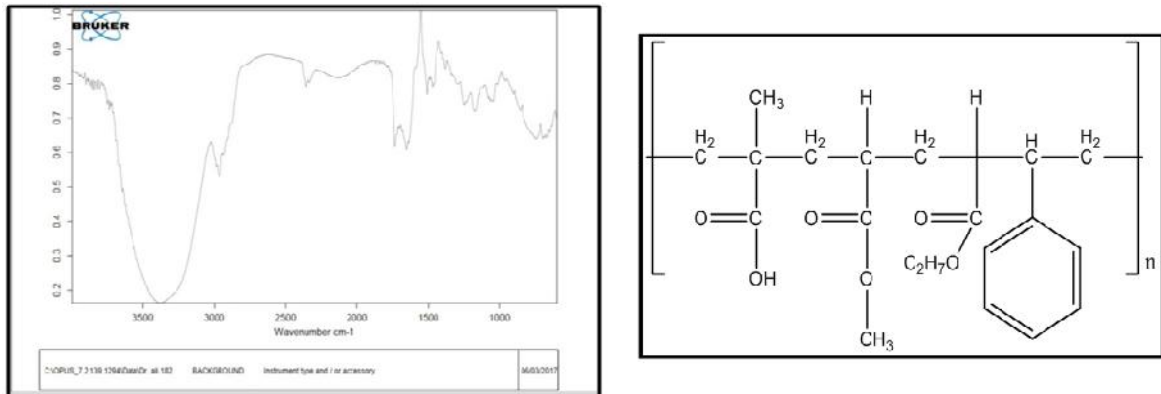
Figure 9: FTIR of PMA3

Synthesis and Characterization of (PMA4)

This polymer was synthesized by the emulsion polymerization of MAA with BA, MMA, P.V.A and styrene in the presence of Dodecyl Benzene Sulphonic acid SDBA as an emulsifier, sodium dodecyl sulfonic acid SDBAS as co-emulsifier and trimetylchlorosilane(TMCS). at (70 °C) for (4 hours) according to the equation in the reaction in scheme (4)
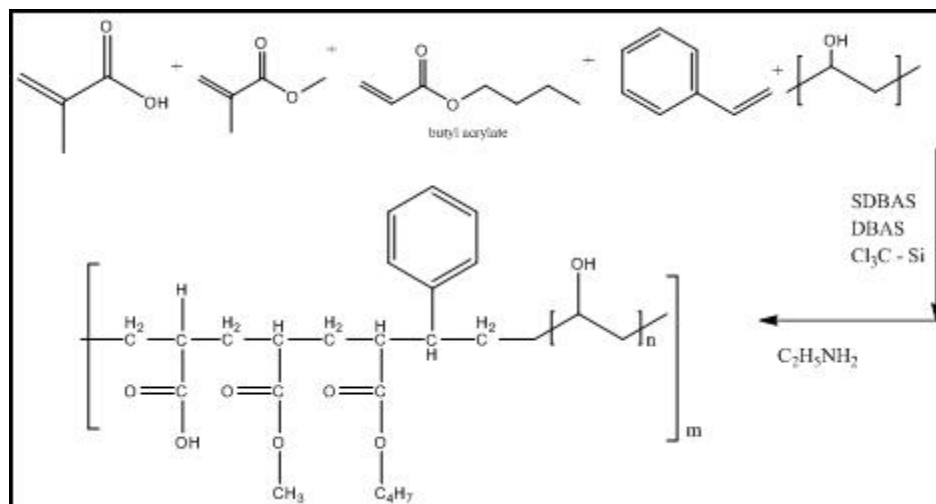
Scheme (4) Synthesis of PMA4

Characterization of (PMA4)
FTIR Spectra

The FTIR spectra of (PMA4) shows in Figure (11) which indicated absorption band of (OH carboxylic) at (3390 cm^{-1}), (C = O) carboxylic at (1745cm^{-1}), (C=O) ester at (1730cm^{-1}), (C-H) aliphatic at (1370, 1420 cm^{-1}), (C-O) ester at (1100cm- 1), (C-H) for (CH$_3$) at (2899 cm^{-1}), aromatic (C-H)at (3010 cm^{-1}), aromatic (C = C) at (1600 cm^{-1}).
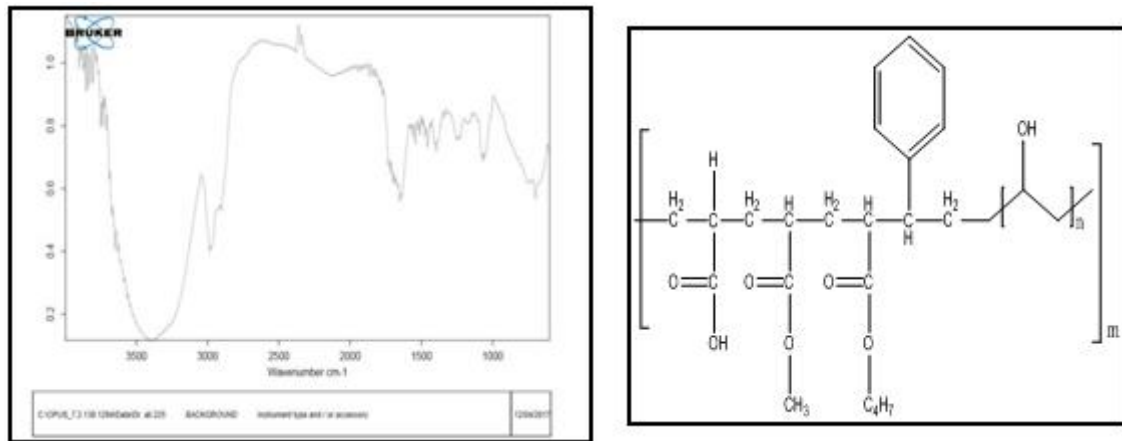
Figure 10: FTIR of PMA4

^{1}HNMR Spectra

Figure (12) showed signals at (= 0.77-0.84) ppm) to (CH_3), as well as signals at (= 1.06-1.15) ppm) to (CH_2). Showed signals at (= 1.12-1.56) ppm) to (CH), the appearance of several signals at (=2.5002-3.0343) ppm) returns to the (OCH_2) protons for (ester). A single at (=2.49) ppm) to the DMSO. Signal at (=7.5140-7.0802) ppm) to proton of aromatic ring, Signal at (=3.99 ppm) ppm) to (OH).
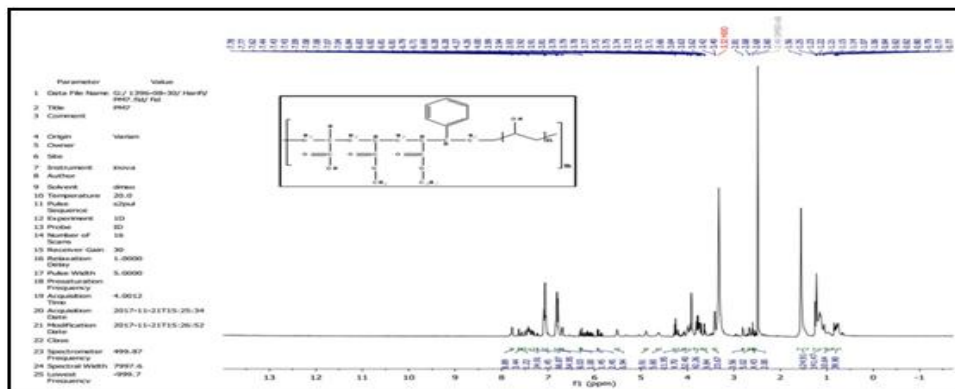
Figure11: ^{1}HNMR of PMA4

Physico - Chemical Test

Density Test

A substance density and the volumetric mass density is its mass per unit volume. Mostly used symbol for density is . and depends on temperature and pressure. The results were observed for the emulsion copolymers prepared in the (table 2), The density of emulsion methacrylic copolymers (PMA1PMA2, PMA3, PMA4) increases, when the percentage of butyl acrylate increasing.

Table2: Density of Polymer

Emulsion copolymers	Sample 1	Sample2	Sample3
PMA1	0.9830g/cm^3	1.1003 g/cm^3	1.0883 g/cm^3
PMA2		1.0348 g/cm^3	
PMA3		0.9867 g/cm^3	
PMA4		1.0659 g/cm^3	

Viscosity Test

The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress. For liquids, it corresponds to the informal concept of "thickness". The viscosity of the solution is an important tool for characterization polymers are a measure of molecular weight of polymer as the viscosity of the solution is a measure of the size. The factors affecting viscosity:

- **Pressure:** Pressure viscosity little importance but viscosity effect appears when the pressure increases (68 bar).
- **Temperature:** When temperatures decrease viscosity because at high temperature of liquid increase distances between molecules less friction and therefore less viscous. The rheology of various types of the prepared binders represented in table (3) show a decrease in viscosity as the shear rate was increased. Accordingly, it was found that all the prepared binders are thinning polymers (a thixotropic material) which become more fluid with increasing time of applied force or increasing the shear rate. A regular decrease in commercial polymer viscosity as the shear rate increased, was found where MAA:BuA:, MAA:BuA: styrene, MAA:BuA:MMA: epoxy, MAA: BuA: MMA: styrene:PVA, binders respectively, have the least thinning effect comparing with this type commercial binder. This means that a high network structure is created within the polymer molecules. Table (3) also shows that polymers MAA: BuA:, MAA: BA: MMA: styrene, MAA: BA: MMA: styrene :PVA respectively, have a high increase in viscosity as the shear rate decreased compared with MAA: BuA : styrene.

Table 3: Viscosity Measurement

Emulsion copolymers	Sample 1	Sample2	Sample	Spindle
PMA1	-	412CP	640CP	6
PMA2		160CP		6
PMA3		540CP		6
PMA4		830CP		6

Drying Test

Denser layers (120 µm) are in need of much more time to dry in comparison to thinner layers (30 µm). The thicker films drying mechanism necessitates a great deal to form cross-link between chains. The thicker films emulsion copolymers drying time can radically increase with increasing of styrene (11). It was founded that the ability of emulsion copolymers to dry by air is according to the hydrophobicity of monomer: When the monomer is the hydrophilic the drying is slow, because the loss of water becomes slower. While when the monomer was hydrophobic the drying will be faster and there is increase in drying because the loss of water become faster. Table (4) shows the drying in emulsion copolymers.

Table4: Measurement of Drying

Emulsion copolymers	Sample 1	Sample2	Sample
PMA1	03:25	03:35	03:35
PMA2		03:15	
PMA3		03.05	
PMA4		01:50	

Volatility Matter Test

It was noted by the results shown in (table 5), there is a difference in the value of the volatility between each emulsion copolymers prepared. The (PMA4) shows least value of volatility due to the presence of P.V.A., because this

monomeris hydrophilic while (PMA3) shows high value of volatility due to length chain of copolymer container in its structure on hydrophobic monomers therefore the volatility increased.

Table 5: Volatility Measurements

Emulsion (D)	Sample 1	Sample2	Sample
PMA1	11.3 %	13.01%	13.08%
PMA2		12.06%	
PMA3		17.67%	
PMA4		9.32%	

Chemical Resistance Test

The resistance of the emulsion acrylic copolymers were determined in two media, distilled water, HCl, H_2SO_4 and NaOH solution (Table 9), described that there was no effect on emulsion copolymers film after immersion in distilled water for 18 hours, was sufficient time to examine the water resistance. When the emulsion copolymer film was immersed in strong alkali solution and acid solution, (3N NaOH) (3N HCl) and($3NH_2SO_4$), the film got whitening after immersion time for 8 hours, blistering after immersion for 16 hours and removal after immersion time of 24 hours. So the result shows that have emulsion copolymers high chemical resistance.

Table6: Chemical Resistant for Emulsion Copolymers

	PMA1	PMA2	PMA3	PMA4
H_2O	+	+	+	+
NaOH	+	+	+	+
HCl	+	+	+	+
H_2SO_4	+	+	+	+

(+) chemical resistant for polymer (no soluble)

(-) chemical resistant for polymer (soluble)

Solubility Test

Emulsion methacrylic polymers showed high solubility in different type of solvents. (table 10) described solubility of samples, was measured by taking the solubility (0.01 g) of the sample prepared resin and melted in (2 ml) of the solvent, The solvents used include (DMF, Acetone,) (Polar aprotic) non-polar solvents such as (Benzene, $CHCl_3$) and other solvents such as (HCl, H_2SO_4). The solvent molecules increase with the distance between the molecular chains of the resin. The spaces between long chains with pendant side group of resin are invaded by solvent molecules as they fill the space made available by chain movements. When movements bring two chains close to proximity, short range attractive forces are therefore established resulting in restricted chain movement and thus the formation of a viscous system (12, 13). Solvent are added to deal with the problem of high viscous polymers which is an obstacle in substrates wet ability.

Table7: Solubility of Emulsions

Solvent	Acetone	Benzene	CH_2Cl_2	DMSO	DMF	THF	$CHCl_3$	H_2SO_4	HCl
PMA1	+	-	-	+	+	-	-	+	+
PMA2	-	-	-+	+	+	-+	-+	+	+
PMA3	-	+-	+-	+	+	+	+	+	+
PMA4	+	+-	+-	+	+	-+	+-	+	+

Corrosion Test

Salt spray tests are probably the most common tests applicable to corrosion resistance and the most controversial. It is well established that salts such as sodium chloride can cause rapid corrosion of ferrous substrates, and it is useful to have information on the behavior of a particular system in protecting such substrate from corrosion both with intact and damaged coating films. However, they are well established, and despite the problem of reproducibility, are quite useful guides to performance in the absence of longer term corrosion data. They are this unlikely to be discarded. They are considered to be unrealistic by some workers because of the degree of acceleration of the corrosion process that they achieve and the variability of the extent of damage that is inflicted in some of the tests. From the results, given in table (7), it can be seen that incorporation of (trichloromethylsilane) in the backbone of acrylic polymers has helped to develop a coating with improved humidity and salt spray resistance. The resistance properties of prepared polymers increases with the increase of the monomers shows that the coating quality increases and is less corroded because it gives the binder more strength to resist weather conditions such as moisture and thus increase the durability of the binder to protect the surface from damage caused by corrosion to hybrid polymers. The study shows the corrosion behavior of hybrid binders with increasing percentage of epoxy resin.

Table 8: Show the Corrosion of Emulsion Copolymers

Emulsion	Sample
PMA1	After 3 days corrosion
PMA2	After 3days corrosion
PMA3	After 6 days no corrosion
PMA4	After 6 days no corrosion

Abrasion Test

The abrasion resistance is also a measure of the coating's toughness, hardness and impact resistance. The test results are given in terms of the amount of sand required to remove a certain thickness from coating. Abrasion resistance test results are given in terms of amount of sand required to remove 1 µm thickness from coating material. The measured results are given in Table (8). The abrasion resistance increases with the increase of hardness of resins; PMA7 has the highest abrasion resistance.

Table 9: Show the Abrasion Resistance of Emulsion Copolymers

Emulsion	Sample
PMA1	350
PMA3	650
PMA5	1600
PMA7	1750

Thermo Gravimetric Analysis (TGA) Study

Thermo gravimetric analysis (TGA) involves determining changes in mass as a function of temperature. It is commonly used to search degradation temperatures, absorbed content of materials, levels of inorganic and organic parts contained in a material and analysis solvent residues. It employs a sensitive electronic balance from which the samples suspended in a furnace controlled by a temperature programmer [18]. The thermal properties of two samples of these emulsion acrylic copolymers were investigated by means of thermo gravimetric analysis (TGA) in Argon atmosphere at heating rate of 10 ºC/min. The results such as Ti, Top, Tf, T50%, % Residue at 700 ºC, and char yields at 600 ºC are

summarized in (Table 11). The temperatures of 50% weight loss of (PMA1PMA2,PMA3,PMA4)as a standard indication for thermal stability of polymers were all from 700 ºC, The char yields of (PMA1),52%, (PMA2),46% ,(PMA3), 42% and (PMA4) 52% at 600 ºC in Argon atmosphere, which indicate they could meet temperature resistant requirements, which can be used in surface coating application. Weight residue of (PMA1) are 68%, (PMA2), 56%,(PMA3), 58% and (PMA4) 61% at 700 ºC[19].

Table10: TGA Measurement

Alkyd Resin	DT/°C				$T_{50\%}$	Residueat ºC700	Char % at 600°C
	T_i	T_{op1}	T_{op2}	T_f			
PMA1	120	200	400	>700	>600	68	52
PMA2	200	400	550	>700	>600	56	46
PMA3	100	210	420	>700	>600	58	45
PMA4	260	370	450	>700	>600	61	52

DT: Decomposition temperature.
T_i: Initial decomposition temperature.
T_{op}: Optimum decomposition temperature.
T_f: Final decomposition temperature.
$T_{50\%}$: Temperature of 50% weight loss, obtained from TGA
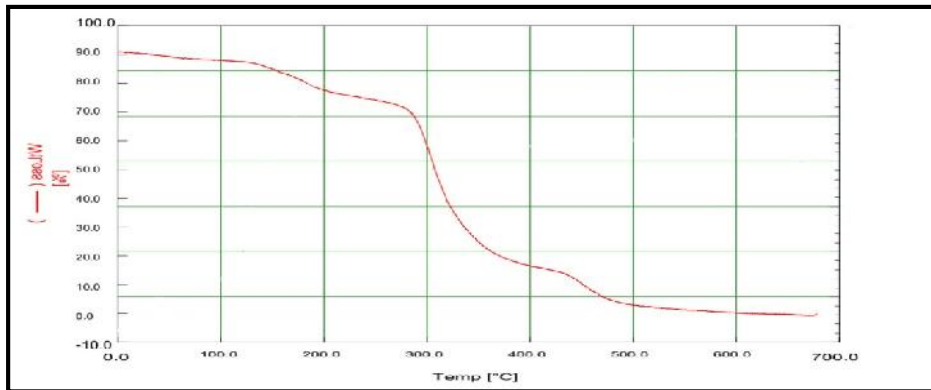**Char% at 200°C: Residual weight percentage at 200°C in Argon by TGA.**
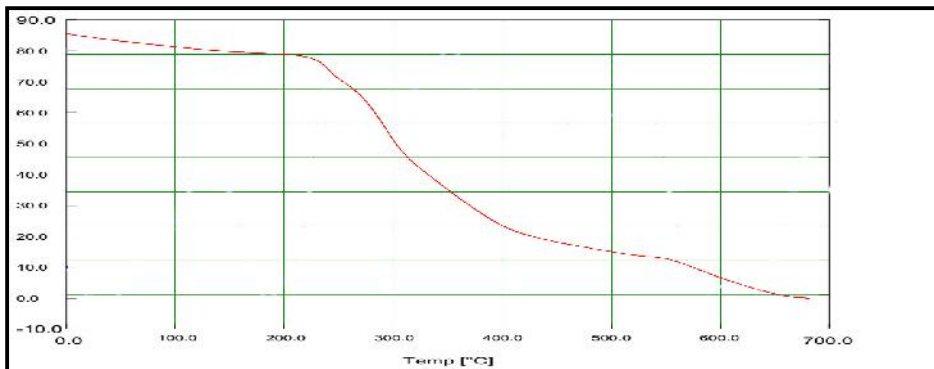

Figure 12: TGA of PMA1

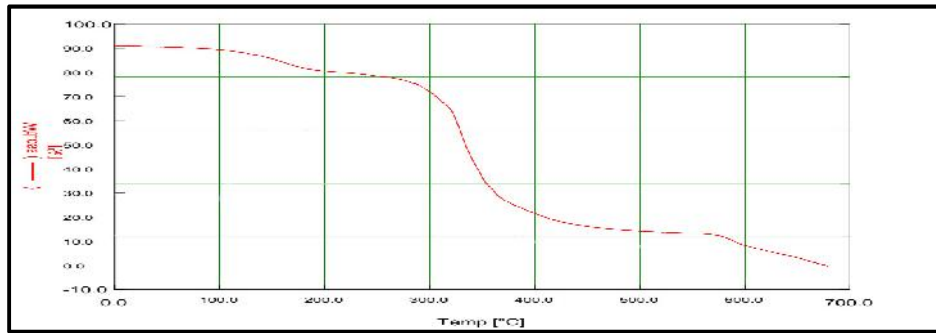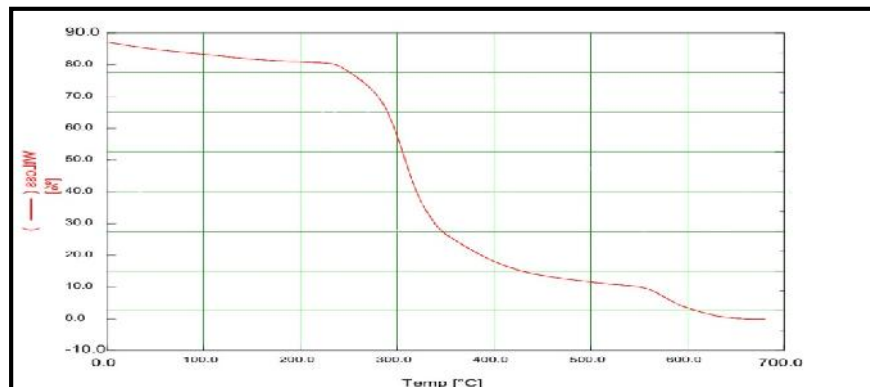**Figure 13: TGA of PMA2**

Figure 14: TGA of PMA3

Figure 15: TGA of PMA4

Differential Scanning Calorimeter Analysis (DSC) Study

Differential Scanning Calorimetry, is a technique of thermal analysis that investigates how material's heat capacity (Cp) is transformed by temperature. A known mass sample is heated or cooled and the variations in its heat capacity are observed as alterations in the heat flow. This allows to reveal transitions such as melts glass transitions (Tg), and the melting point (Tm) the degree of crystallization (Tc) (20). The results of (PMA1) polymer showed in figure (17) the value of the glass transition (Tg) of the mixture (250 ° C) indicating that the flow of temperature and then increase the rate of absorption of the sample to reach the melting point (Tm) at (510 ° C)) Is completely dissolved and then the rate of absorption of the sample to the heat and through the curve was set the degree of crystallization (Tc) of the mixture (390 °C).The results of (PMA2) polymer showed in figure (18) the value of the glass transition (Tg) of the mixture (60 ° C), indicating an increase in the flow of temperature and then increase the rate of absorption of the sample to the temperature until it reaches the melting point (Tm) at (480 ° C). In the curve, the crystallization rate (Tc) was determined for the mixture (315 ° C). The results of (PMA3) polymer showed in figure (19) the value of the glass transition (Tg) of the mixture (50 ° C), indicating an increase in the flow of temperature and then increase the rate of absorption of the sample to the temperature until the melting point (Tm) at (540 ° C) if completely melted and then the rate of absorption of the sample to heat and by the curve was set the crystallization rate (Tc) of the mixture (360 ° C). The results of (PMA4) polymer showed in figure (20) the value of the glass transition (Tg) of the mixture (100 ° C), indicating an increase in the flow of temperature and after that the rate of absorption of the sample to the temperature until it reaches the melting point (Tm) at (460 ° C) and then the rate of absorption of the sample to heat and by the curve of the formation of (Tc) of the mixture (340°C)[22].

Table 11: Shows the Degree of Glass Transition, Melting Point and theDegree of Crystallization in the Differential Thermal Analysis

Samples	Tg (cº)	TM (cº)	TC (cº)
PMA1	250	510	390
PMA2	60	480	395
PMA3	50	540	360
PMA4	105	460	340

Tg: Degree Glass Transition

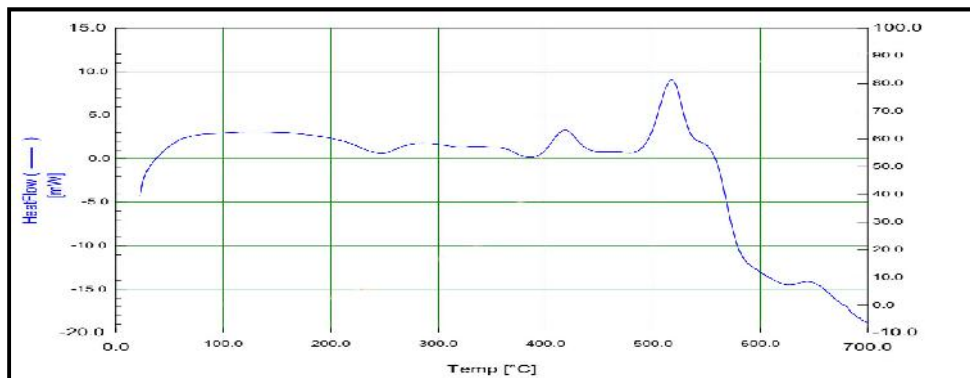**Tm: Melting Point**

Tc : Degree of Crystallization
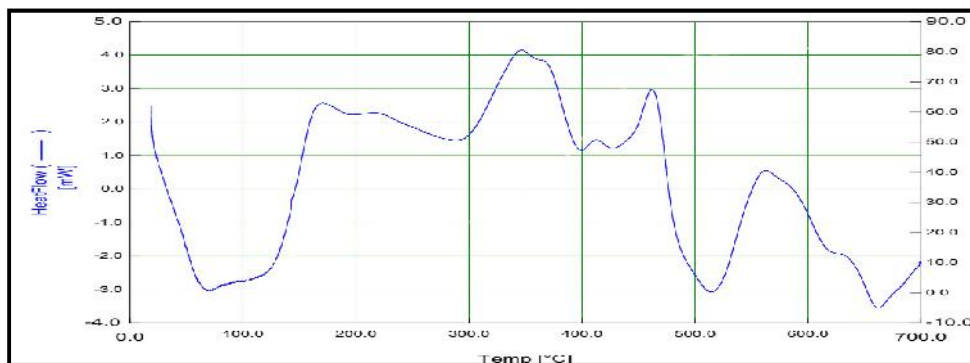

Figure 16: DSC of PMA1
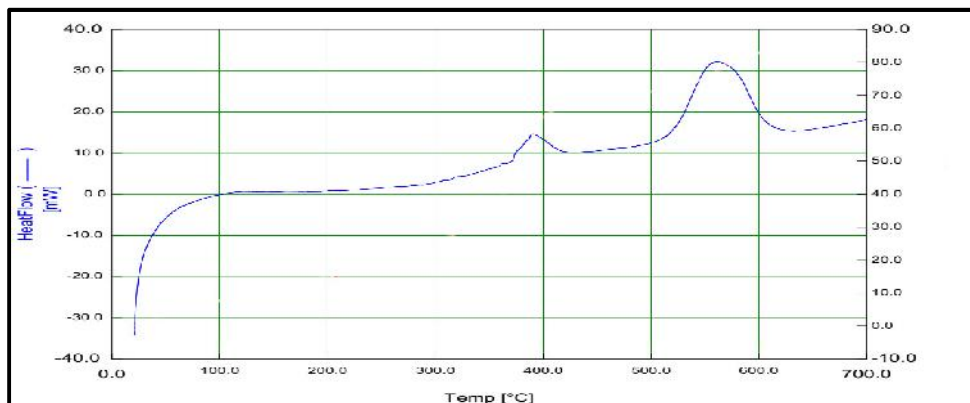

Figure 17: DSC of PMA2
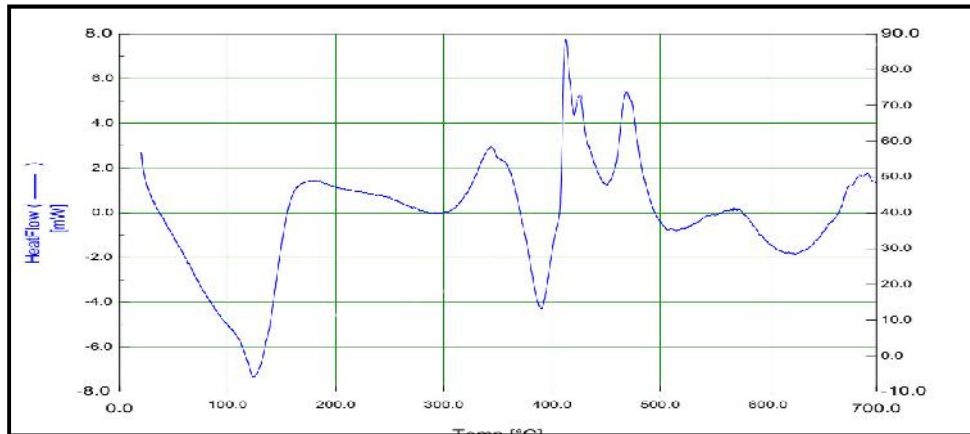

Figure 18: DSC of PMA3

Figure 19: DSC of PMA4

CONCLUSIONS

We can conclude from the data that all the prepared emulsion acrylic copolymers had non-New to nianpseudoplastic character. The methacrylic acid gave high shear rat, high viscosity and high compliance. The polymer having (MAA) monomer in its composition was of high thermal stability. Salt spray analysis confirms the improvement in corrosion resistance of hybrid binders with increasing resin content. The physical properties are subjected to the adjustment of the thermal treatment temperature due to the chemical reaction via the reactive groups incorporated for polymer and its main chain. The higher the thermal treatment temperature, the betterphysical properties for copolymers are achieved. Hybrid resin of acrylic by emulsion polymerization, leading to lower VOC as compared to conventional systems. It proofs that in a hybrid system we can improve the properties of the system by adding two component and good properties increases as the content of one component increases and other properties are not affected. So these resins can be used in coatings where corrosion resistant paints are required because of good.corrosion resistance, abrasion resistance, and resistance to various chemicals.

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