

The Role of Carboxylic Acid on the Characterization and Evaluation Seed Emulsion of Styrene/ Butyl Acrylate Copolymers Lattices as Paint

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Abstract: Series of emulsion lattices having different composition ratios of styrene/butyl acrylate (St/BuA) as base monomers in conjunction with acrylic acid (AA) and/or methacrylic (MAA) were prepared and characterized. The preparation was carried out in industrial scale in semi batch reactor at pH range of 3-5 using potassium persulphate (KPS) as an initiator, sodium lauryl sulphate (SLS) as an emulsifier and nonyl phenol ethoxylated (NP9) as co-emulsifier at 80°C for 4 hours. The prepared lattices were characterized using XRD, TGA, DSC, TEM and rheological properties. The obtained lattices was examined and evaluated as binder in standard paint formulation using pencil hardness test, adhesion to metal and washability. The data showed that all the prepared emulsion lattices had non-Newtonian pseudoplastic character. Moreover, the dynamic oscillation for all examined lattices samples clarified that the elastic modules (storage modules) governed by the variation of the monomer composition ratios. The polymer having (AA) monomer in its composition was of lower thermal stability than that having the same composition content of (MAA). [Nature and Science 2010;8(8):94-103]. (ISSN: 1545-0740).

Keywords: Emulsion, styrene, butyl acrylate, acrylic, methacrylic, characterization, rheological, morphological, TGA, DSC.

1. Introduction

Many authors proved that dispersion particles are used as binders in different fields such as paints, adhesives and in paper coatings⁽¹⁻⁴⁾. These uses are due to the dispersion particles have the behavior of non linear shear conditions⁽⁵⁾. So, the control of flow characteristics or rheology of suspension or emulsion is essential for industrial systems. It is well known that studying rheological properties of fluids and gels are critically important^(6,7). Since, it is the key for design processing operations that depend on the way that the product flows, for example, flow through a pipe, stirring in a mixer, and packaging into containers. Many of the sensory attributes of emulsions lattices are directly related to their rheological properties, for example, creaminess, thickness, smoothness, spreadability, pourability, flowability, brittleness, and hardness⁽⁸⁾.

Most industrial dispersions are non-Newtonian since they are prepared at high volume fractions and also they contain many additives such as polymers which produce non-Newtonian flow. These systems show complex rheological behavior encountering various responses of simple liquid (viscous), plastic or elastic and mixed viscous and elastic (viscoelastic)⁽⁷⁾. Control of the morphology and viscosity of these lattices particles has been a well-practiced art within industry for some time now, given its great importance in determining the physical and mechanical properties of polymer systems⁽⁹⁾.

Usually, carboxylic acids are added to improve

the mechanical, freeze-thaw, and pigment-mixing stability of the lattices. Carboxylic acid monomers are often completely soluble in water; however, they will still distribute to vary extents into the organic phase depending on their relative hydrophobicity.

The most frequently studied acid monomers copolymerized with styrene are itaconic acid (IA), acrylic acid (AA) and methacrylic acid (MAA), listed in order of increasing hydrophobic nature. Copolymerization of (IA), (AA) and MAA with styrene in separate reactions, the copolymerization rates were found to increase with the presence of carboxylic monomers in the order (IA)<(AA)<(MAA).

The rate increased as the hydrophobicity of the monomer increased⁽¹⁰⁾. The use of AA tends to produce significant amounts of water-soluble polymer, and that portion of the acid copolymer that is in the particles is usually located near the outer surface of the lattices particles. With MAA, there is significantly less water-soluble polymer formed and the MAA copolymer in the particle is somewhat more evenly dispersed within the particle.

A part from their use as the base resin, latticeses can also be used to thicken the formulation of a given paint⁽¹¹⁾.

The most important mechanisms of thickening are: (a)-associative thickening; (b)-thickening by alkali neutralization. Even when using acrylic dispersions with low (AA/MAA) contents as 2%, the

second mechanism of thickening is quite interesting, since additionally to the increase in viscosity, the stability of the dispersion can be improved, via electrostatic repulsion between carboxylate groups present on the particles surface⁽¹²⁾.

This work aimed to prepare emulsion lattices based on styrene (St), butyl acrylate (BuA) and carboxylic acid monomers represented as acrylic acid (AA) and/or methacrylic 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 lattices were the most important properties of the prepared lattices. The prepared emulsions were characterized by using XRD, TGA, DSC, TEM and rheological properties. Also, the obtained lattices will be examined and evaluated as binder in standard paint using pencil hardness test, adhesion to metal and washability.

2 - Materials and Methods

2.1. Raw materials

Styrene (St), butyl acrylate (BuA) were supplied by Aldrich and distilled with reduced pressure before use. Potassium persulphate, nonyl phenyl ethoxylated (NP9), sodium lauryl sulphate (SLS), NaHCO₃, ammonia water, methacrylic acid (MAA), acrylic acid (AA), and other reagent were supplied from Sigma chemicals. Distilled water was used.

2.2. Pre-emulsion

Distilled water, emulsifiers, (St) and (BuA) were added into the flask equipped with high speed homogenizer for 30 min (in three time portions). The acid monomer (AA and/or MAA) is added during continuous homogenizing.

2.3. Seeded emulsion polymerization

Polymer lattices based on (St), (BuA) as well as (AA) and/or (MAA) were prepared by semi batch emulsion polymerization technique with solid content of 50%. Distilled water, residual emulsifiers, NaHCO₃, part of initiator and part of pre-emulsion were added into the four-neck flask equipped with continuous stirring under reflux. The polymerization reaction was carried out at 80 °C using thermo stated water bath for 30 min under an inert atmosphere of N₂.

The recipe used for preparation of different compositions of polymer lattices is given in Table (I). When the reaction mixtures appeared blue and no evident back flow existed in the reactor, the remaining pre emulsion and initiator were step wise

added into the reactor within 3 h.

2.4. Characterization

The morphology of the particles was examined using electron microscope is of (Zeiss type model, EM.10) Germany. It works at 60 kV, and resolution until 0.5 nm.

The Rheological characterization was measured using (Bohlin rheometer Model CS10), UK. The used tool in our experiments is measured using Cone Plate (CP 4°/40mm). The diameter of the plate was 40 mm. The gap was fixed at 0.15mm. The samples were measured at temperature of 25±0.1°C. In dynamic measurements, the sample was forced by sinusoidal shear stress and from the shear strain response and the phase shift between stress and the strain sine wave, dependences of storage (*G'*) and loss (*G''*) moduli on the frequency () characterizing elastic and viscous properties of the system were calculated.

The thermogravimetric analysis (TG) and the differential scanning calorimetric (DSC) measurements for the obtained microemulsion samples were carried out at a temperature range starting from 50°C to 700°C under nitrogen atmosphere with heating rate of 10°C/min using (Shimadzu TGA-50 and Shimadzu DSC -50), Japan

X-ray diffraction for the prepared samples was investigated by x-ray diffraction using (Philips analytical X-ray).

Polymer film was evaluated^(13,14,15,16) via pencil hardness testing, adhesion to metal; bending test and washability as recorded according to ASTM No. D 3363, D 3359, D 522 and D 3450 respectively.

3- Results and Discussion

High solid content (50%) and low coagulum were the main demand in production of styrene/butyl acrylate carboxylic acid emulsion on industrial scale for industrial applications. Many trials were carried out to get the optimum formulation to prepare styrene/butyl acrylate carboxylic acid with stable properties for a period of six month, stability at accelerating test for lattices and solid content (ASTM No. 2369) were examined.

Different surfactant systems were used as well as the initiator. The following Tables (1) represent the optimum surfactant systems and initiator concentration as well as the monomers concentration with changing the concentration of the carboxylic acid.

Table (1) : Recipe of styrene/butyl acrylate emulsion co-polymer containing different ratios of acrylic acid and/or methacrylic acid

Ingredients	Sample code								
	A	B	C	D	E	F	G	H	I
Styrene (gm)	26	26	26	26	26	26	25	26	27
Butyl (gm)	24	24	24	24	24	24	25	24	23
Acrylic acid (gm)	1.5	1.75	2	--	--	--	1	1	1
Meth acrylic acid (gm)	--	--	--	1.5	1.75	2	1	1	1
Solid Content (%)	46.5	47.8	49.1	46.9	47.9	49.8	49	49.5	48.6
Molecular weight (Mn) x 10 ⁵	2.9755	3.8692	4.1248	3.7736	4.6540	5.2700	5.3246	5.9430	5.4598

3.1. Rheological Properties

3.1.1 Flow behavior

Rheological measurements are frequently used by some scientists as an analytical tool to provide fundamental insights about the structural organization and interactions of the components within emulsions, for example, measurements of viscosity versus shear rate can be used to provide information about the strength of the colloidal interactions between droplets. The choice of shear rate to use when measuring the apparent viscosity of a non-ideal liquid is a particularly important consideration when carrying out rheological measurements that are supposed to mimic some process that occurs in a product naturally, for example, flow through a pipe, stirring, or mixing in a vessel, pouring from a bottle, creaming of an individual emulsion droplet.

The flow behavior of studied samples is shown in Figures (1 - 4). The effect of shear rate (400-1000sec⁻¹) on the shear stress of emulsion lattices samples prepared at different composition contents of acrylic or methacrylic acids (1.5, 1.75 and 2) as well as (St/BuA) contents (25/25, 26/24 & 27/23) are shown in Figures (1, 2). All samples were measured at constant high solid content of 47±0.5%. It is evident, regardless of ingredient composition contents that all samples show non-Newtonian pseudoplastic behavior where the plots are convex to the shear stress axis with different extents of yield stress. Herschel–Bulkley⁽¹⁷⁾ is the best fit model representing the flow behavior of these samples.

$$\tau = \tau_0 + k \dot{\gamma}^n \quad (1)$$

Where τ is the shear stress at the shear rate $\dot{\gamma}$, τ_0 the yield stress, k a plastic viscosity and n a parameter characterizing pseudoplasticity (power law value) of the system as it is evident that the yield stress are increased by increasing either (AA) or (MAA) contents in the composition of the lattices.

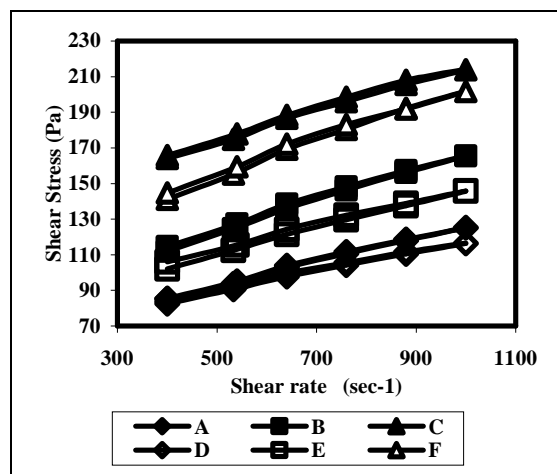


Figure (1): Effect of shear rate on (sec⁻¹) on the shear stress (Pa) of emulsion lattices prepared using varied AA and MAA content ratios.

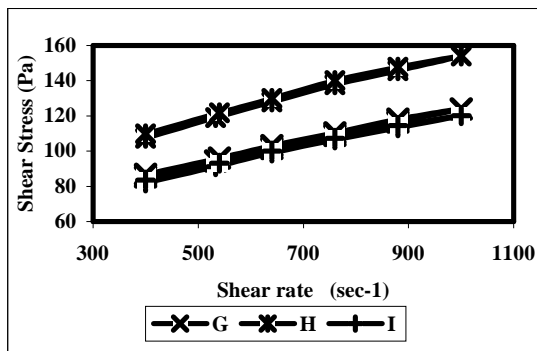


Figure (2): Effect of shear rate on (sec^{-1}) on the shear stress (Pa) of emulsion lattices prepared using varied (St/BuA) content ratios.

On the other hand, for lattices prepared at content (AA/MAA) ratio (1/1) and different (St/BuA) contents the power law and yield stress values follows the following sequence: 26/24 > 25/25 > 27/23.

The data plotted in Figures (3, 4) shows the viscosity – shear rate dependence for the previously mentioned samples. For all samples in question the apparent viscosity decreased by increasing the shear rate which manifest the pseudoplasticity of the prepared lattices samples. It is evident that the viscosity increased by increasing the contents of either (AA or MAA) contents. This result clearly shows stronger interactions between components in the sample with higher caboxylic acid contents causing a higher thickening effect. Another proper explanation state that after alkalization of the originally acidic material, electrostatic repulsion between ionized carboxylic groups attached to polymer chains of the lattices leads to particle swelling, which increases steric and electrostatic particle interactions^(18, 19).

For the lattices prepared at different (St/BuA) content ratios the observed highest value of apparent viscosity for (26/24) ratio than other two ratios can be explained due to the high miscibility of lattices ingredient at such condition of lattices preparation. Many research papers^(20, 21) demonstrated that the apparent viscosity for any composite of two components is directly proportional to its miscibility.

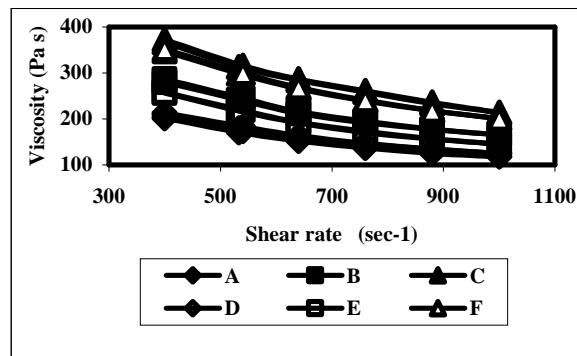


Figure (3): Effect of shear rate on (sec^{-1}) on the viscosity (Pa s) of emulsion lattices prepared using varied (AA and MAA) content ratios.

The lattices preparation under the experimental condition of different monomer ratios and emulsifiers concentrations will produce different polymeric substrate of homopolymers and copolymers. Most probably, the presence of (St/BuA) at ratio of (26/24) as well as (AA/MAA) at ratio of (1/1) create the suitable conditions for the higher miscibility with higher intermolecular interaction than other two (St/BuA) ratios.

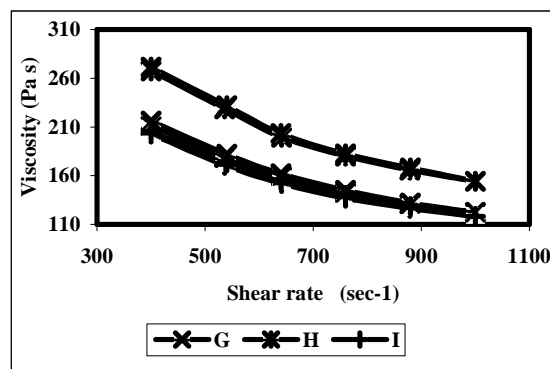


Figure (4): Effect of shear rate on (sec^{-1}) on the viscosity (Pa s) of emulsion lattices prepared using varied St/BuA content ratios.

3.1.2. Dynamic Oscillation

The viscoelastic properties of the studied samples are shown in Figures (5-7). It is evident Figure (5) that at (AA) content of 1.5 gm the loss moduli (G'') in the whole frequency range was significantly higher than the storage moduli (G'). This indicates the viscous property of the sample at all studied frequency sweep. Also, by increasing the (AA) content 1.75 gm the storage moduli considerably increased (G') so that at the highest frequency used, a crossover of (G'' and G') occurred for this sample. This means that increasing (AA) content causes higher thickening effect in the lattices samples, i.e., an elastic solid property were observed when the (AA) content increased.

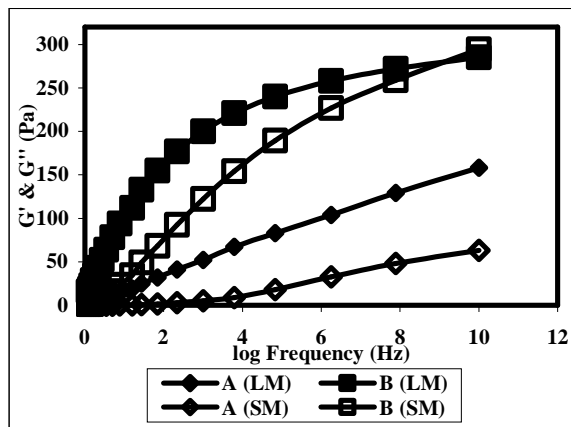


Figure (5): Dependence of storage moduli (G') and loss moduli (G'') on the Frequency () for polymer lattices prepared at different (AA) content ratios.

Different situation was mentioned when (MAA) is incorporated in the composition of the polymer lattices where a crossover of (G'' and G') occurred at (MAA) content ratios of 1.5 gm and by its increasing the storage moduli was predominating at whole studied frequency sweep Figure (5). This observation clearly demonstrates that the presence of (MAA) in the polymer lattices composition causes an elastic solid property even at its initial content ratio compared with (AA).

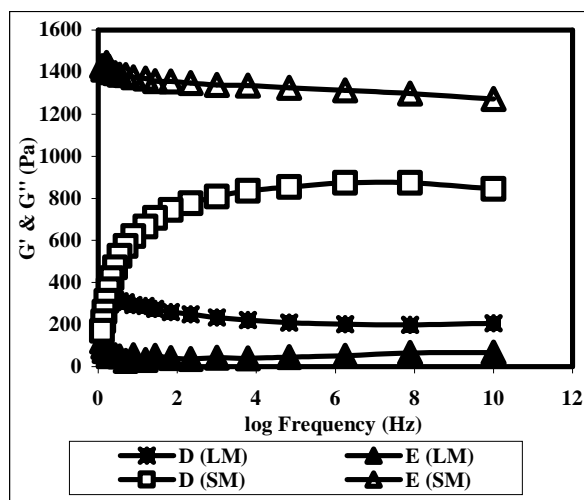


Figure (6): Dependence of storage moduli (G') and loss moduli (G'') on the frequency () for polymer lattices prepared at different (MAA) content ratios.

For polymer lattices having different (St/BuA) content ratios, increasing the styrene content bring

about considerably higher storage moduli (G') at whole studied frequency sweep. The data represented in Figure (7) shows that the loss moduli (G'') for formula No. (H) which having (St) content of 26 gm is lower than that of formula No. (G) which having (St) content of 25 gm. This makes clear that increasing (St) content is directly proportional to the increase of the stiff structures of the thickened polymer lattices with elastic properties.

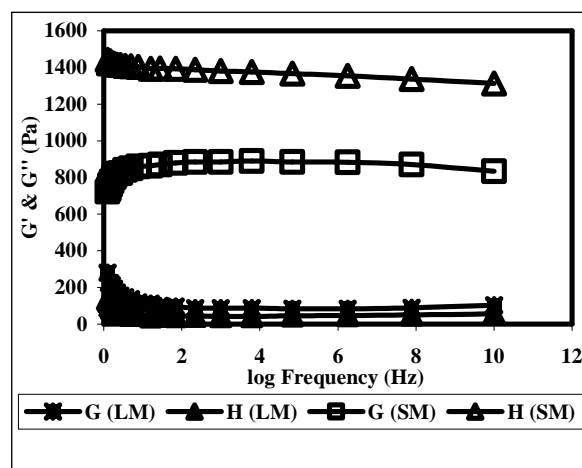


Figure (7): Dependence of storage moduli (G') and loss moduli (G'') on the frequency () for polymer lattices prepared at different (St/BuA) content ratios.

3.1.3. Creep Test

Rheological investigation for materials that exhibit viscoelastic behavior show a time-dependent strain ($\epsilon(t)$) under applied constant stress (σ_0 (Pa) as

$$\epsilon(t) = \sigma_0 J(t) \quad (2)$$

Where J (Pa^{-1}), is the material compliance. The higher the compliance, the more easily the material can be strained at a certain applied stress. Viscoelastic response at lower values of applied stress usually leads to a linear viscoelastic behavior. Under higher values of applied stresses, nonlinear viscoelastic behavior, results of viscosity, and elasticity measurements will be dependent upon test conditions and sensor parameters. Furthermore, applied stress within the linear viscoelastic range will be non-destructive for investigating viscoelastic behavior.

During this range, deformed energy can be recovered if the applied stress is released. It shows the possibility of the network to be elastically strained while the network still intact. Therefore, within the linear viscoelastic range, the compliance is independent of the applied stress. All our experiments are carried out at linear viscoelastic ranges. This is

done by carrying out creep- recovery test at different values of shear stress over range of (1 Pa) to (12 Pa). A linear viscoelastic response is observed at shear stress of (1 Pa). The creep–recovery behavior of the prepared emulsion lattices prepared at different acrylic acid concentrations (A, B & C) are shown in Figures (8). It is evident that the compliance decrease with increasing the acrylic acid concentration. For example, at time of stress of 60 s, the compliance reaches 4.5 Pa^{-1} for acrylic acid (AA) concentration of 1.5 gm, where as it drops to 0.007 Pa^{-1} for concentration of (AA) 2 gm. Moreover, the data observed demonstrate that the prepared emulsion at different acrylic acid concentrations show viscoelastic behavior with different degree of recovery.

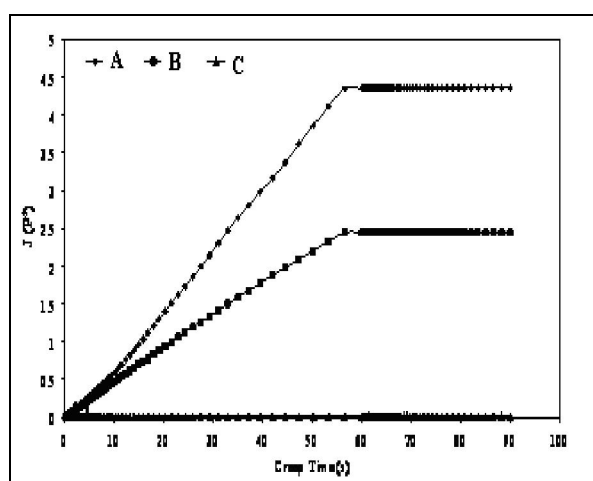


Figure (8): Compliance behavior of emulsion lattices at different(AA) content ratios.

After 60 s of applies stress in the creep mode, the applied stress is released and the recovery mode is reported over time for another 30s. It is also evident that there is a linear gradual recovery response till the end of the test period. The compliance values of the prepare emulsions lattices at 500s are nearly the same values recorded at 60s, i.e., without any value changes. The recovery (%) can be defined as

$$\text{Recovery (\%)} = (J_{60} - J_{90}) \times 100/J_{60} \quad (3)$$

The effect of the type of acid monomers on the creep- recovery behavior is shown in Figure (9). Higher compliance is observed for acrylic acid monomer formula No. (C) and lower is observed for methacrylic acid formula No. (F) and equal composition lies in between. This mean that the acrylic acid of more elasticity having higher viscous properties than methacrylic acid. This is in accordance with each of viscometry and dynamic oscillation results.

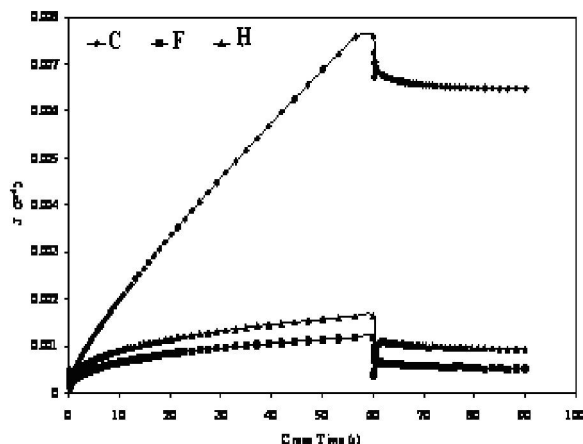


Figure (9): Compliance behavior of emulsion lattices at different carboxylic acrylic monomers formula No. (C; F, H)

Figure (10) shows the creep- recovery data for emulsion lattices prepared at different (St/BuA) composition ratios at formula No. (G, H & I). Polymer with higher BuA content ratio is of higher compliance with much viscous properties. Also, lower compliance with greater elastic properties was observed at equal composition ratio between (St and BuA).

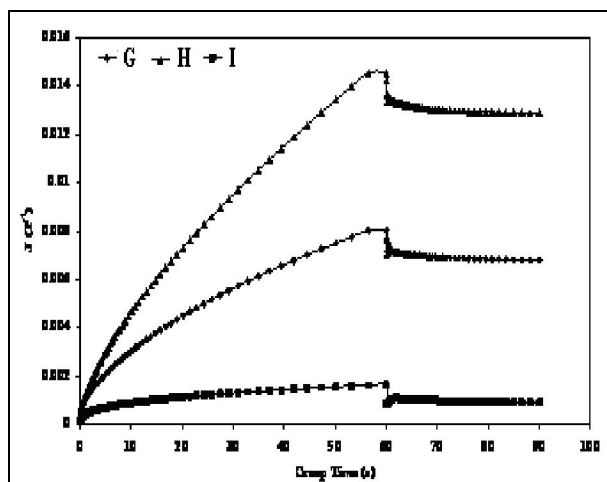


Figure (10): Compliance behavior of emulsion lattices at different (St/BuA) content ratios

3.2. Thermal characterization

3.2.1. Thermal gravimetric analysis (TG) and differential thermal gravimetric analysis (DTG)

The thermo gravimetric (TG) and differential thermo gravimetric (DTG) curves characteristic for (AA, MA, and blend) are shown in Figure (11). In these polymeric samples the (St/BuA) composition ratios were kept constant at (26/24) and the acids

monomers contents varied. It is evident that the thermal degradation process for all polymer samples proceeds in one step. For polymer sample having acrylic acid 2gm in its composition (AA) the initial, final and main degradation temperatures (T_i , T_m and T_d) were 349°, 410° & 380° C. This against values of 372°, 418° & 396° C, respectively, were recorded for (MAA) having methacrylic acid in its composition. On the other hand, T_i , T_m & T_d were 322°, 493° and 358° C for (blend) having equal composition ratios of (AA and MAA) (1:1).

This mean that the thermal stability for the examined polymers follows the following sequence: (MAA 2 gm) > (AA 2 gm) > (blend 1:1). In other meaning introducing (AA) monomer in the polymer lattices composition produces more thermally stable polymer than that having the same content of (MAA). It is also evident that (Blend) with equal amount of (AA and MAA) having the least thermal stability values. Most probably, the synergistic effect between AA/MAA in polymer back bond as well as extent of miscibility of polymer lattices plays a significant role in the stability of polymer samples.

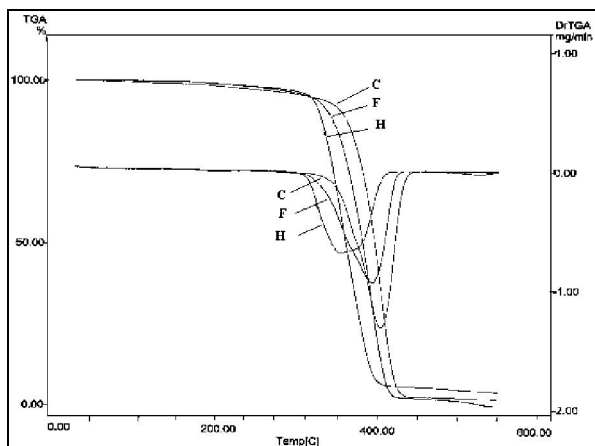


Figure (11): TGA/DrTGA thermograms of formulations No. C, F and H

3.2.2. Differential scanning calorimetry (DSC)

Figure (12) shows the DSC curve for (AA), (MA), and (blend). It is evident that all samples show similar curves with two characteristic endothermic peaks. The first peak represents the glass transition temperature (T_g) of the polymer sample which varied between 34°C to 44°C for the three polymer in question. It is well known that the (T_g) of butyl acrylate and styrene are about $-52° \pm 2°$ C and $102° \pm 2°$ C respectively, and by increasing styrene mole fractions up to 0.45 and 0.63 the (T_g) increased to $25° \pm 2°$ C and $44° \pm 2°$ C⁽²²⁻²³⁾. The second endothermic peak in the range of 122–125°C appeared for the DSC curves of the three polymers represent crystallization of polymers. An endothermic

peak around $400° \pm 20°$ C is may be due to the oxidation and polymers degradation.

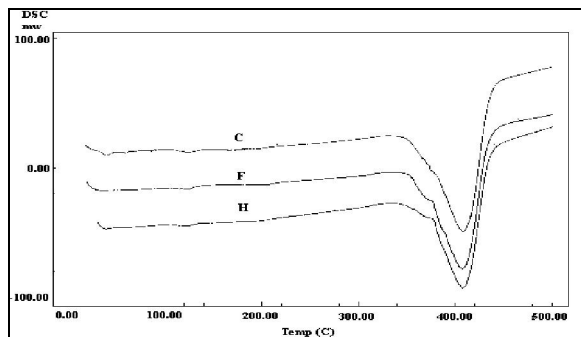


Figure (12): DSC Curves for formulations No. C, F and H.

3.3. X- ray diffraction analysis

The main physical properties of polymers (including their mechanical properties) are dependent on their molecular weight and degree of crystallinity. Typical XRD patterns for polymer samples C, F, G, G, H & I are represented in Figure (13). All samples showed the fundamental broad pattern centered at $2\theta = 18-24°$ that represent the styrene/BuA copolymer. It is evident that, at constant (AA/MAA) composition ratios (1/1), the half band width of the fundamental band decreases by increasing the styrene content in the composition, which indicates an increase in the crystallite size (an inverse relation)⁽²⁴⁾ and high molecular weight. The changes in band intensity of the fundamental band with changing the (St/BuA) content ratios were also taking in consideration through determination the change of the crystalline regions. The intensity values showed a pronounced decrease in band intensity as the (BuA) concentration increase in the polymer composition which indicates a reduction in the crystalline regions⁽²⁵⁾. By comparing between XRD patterns of polymer samples prepared in presence of (AA) and (MAA), it could be observed that the crystalline size and regions is much higher for (AA) than that observed for (MAA). This indicates the formation of more crystalline chains in the structure of polymer by using (AA) rather than using (MAA).

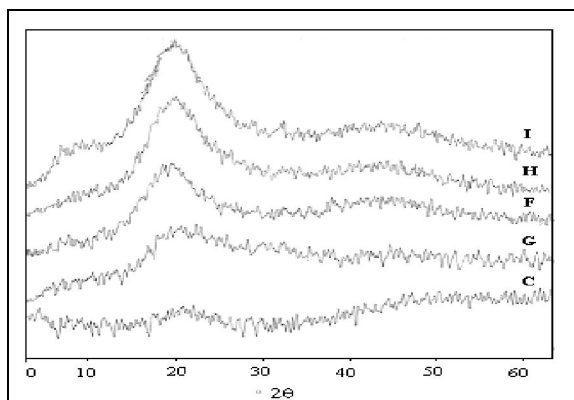
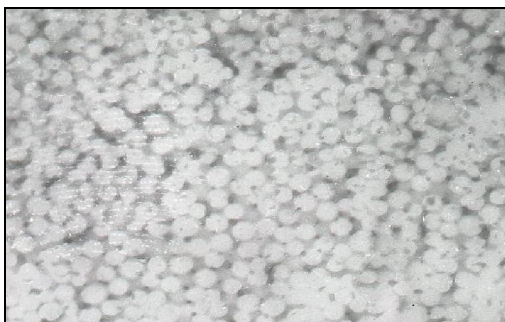


Figure (13): X-ray Diffraction of I, H, F, G and C

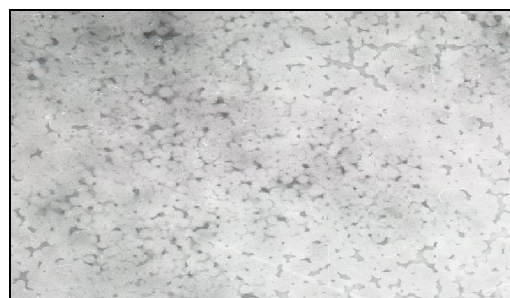
3.4. Transmission electron microscope (TEM)

Figure (14) show the effect of the type of carboxylic acid on the particle size and the shape of the prepared emulsion lattices which characterized using TEM. It was found that the prepared emulsion lattices had homo-dispersed particles with complete spheres. It is noticeable that the particle size were arranged in the order AA>blend>MAA.

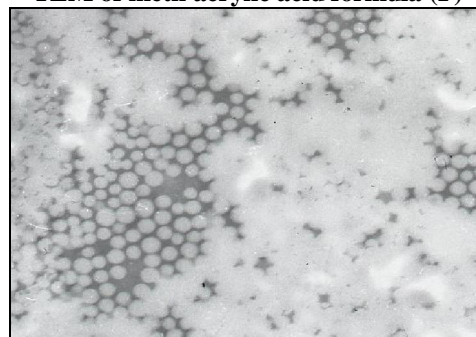
It has also been reported that the hydrophobic/hydrophilic character of the monomer(s) used in emulsion polymerization has a decisive influence on particle morphology: according to some authors, macromolecules with an increase in hydrophilicity facilitate carboxyl ionization, resulting in higher particle swelling (increase in viscosity), particles with high contents of AA and/or MAA being completely solubilized⁽²⁶⁾



TEM of acrylic acid formula (C)



TEM of meth acrylic acid formula (F)



TEM of blend formula (H)

Fig (14):Transmission electron microscope of the prepared lattices of formulations No. C, F and H

3.5. Effect of the prepared lattices as binder

The prepared lattices were conducted to incorporate in standard formulation of paint as shown in Table No. 2. Some physical and mechanical testes were carried out mechanical on each formula. It was found that the formulations containing high content of acrylic acid gave high viscosity comparing to the same concentration of the meth acrylic acid and the blend. It is noticeable that all formulation passed in the washability hardness, bending tests and adhesion to metal except formulas No. (H), and (I) which containing high content of styrene. This means that the mechanical properties of the prepared lattices were not independent on the concentration of carboxylic acid but depend on the styrene concentration where the hardness of the paint increased.

Table (2) : Effect of the prepared lattices as binder in slandered paint formulations

Ingredients	Sample code								
	A	B	C	D	E	F	G	H	I
Pencil Hardness test	HB	B	2B	HB	F	H	F	2H	3H
Bending test	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Failed	Failed
Washability (Cycle)	>5000	>5000	>5000	>5000	>5000	>5000	>5000	<5000	<5000
Adhesion to metal	Gt ₀	Gt ₀	Gt ₀	Gt ₀	Gt ₀	Gt ₀	Gt ₀	Gt ₁	Gt ₁

Binder 20%, TiO₂ 22%, filler 18%, dispersing agent 1.5%, wetting agent 1.5%, antifoam 2%, Coalescing agent 5%, thickener 3.9%, preservative 1%, water 24.1%, ammonia 1%

4. Conclusion

We can conclude from the data that all the prepared emulsion lattices had non-Newtonian pseudoplastic character. The acrylic acid gave high shear rate, high viscosity and high compliance with respect to meth acrylic acid. The dynamic oscillation for all examined lattices samples clarified that the elastic modulus (storage modulus) governed by the variation of the monomer composition ratios. The polymer having (AA) monomer in its composition was of lower thermal stability than that having the same composition content of (MAA). The paint formulations were affected by the increasing of the styrene content and the type of the carboxylic acid.

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5/5/2010