EXPLORING TERPOLYMERS NANOPARTICLES: THEIR PREPARATION, CHARACTERIZATION, AND ROLE AS OVER PRINT VARNISHES FOR OFFSET INKS

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ABSTRACT

New over print varnishes based on ethyl acrylate, 2-ethyl hexyl acrylate and methyl methacrylate (MMA) terpolymersnano emulsions were prepared. They give stable properties for a timeframe (half year strong) and low coagulum of ethyl acrylate ,2-ethyl hexyl acrylate and methylmethacrylate (MMA) terpolymer. Two surfactant systems were used as well as changing the monomers ratio in the presence of constant percent of initiator. The prepared polymers were investigated and confirmed IR spectroscopy, TGA, GPC molecular weight and TEM for particle size (nm), also by testing: solid content %, wet coagulum 100mesh, (g/l), viscosity (cP),pH, hardness, adhesion. The prepared emulsions terpolymerspolymer were conducted to incorporate instandardformulationof water base overprint varnish and compared with trade mark emulsion polymer Johncryl 90. The prepared water base overprint varnish examined by viscosity, gloss, tackiness, adhesion to metal, adhesion to plastics and chemical resistance.

Keywords: *Acrylate terpolymers , nanoemulsion,water base overprint varnish,tackiness.*

I. INTRODUCTION

Emulsion polymerization processes are widely used for the industrial production of different commercial polymer emulsions, or latexes, such as synthetic elastomers (SBR, NBR), plastics (ABS, PVC) and water-borne coatings (vinyl and acrylic paints, paper coatings, vinyl adhesives) [1]. Polymer latexes with high solid con- tents (above 55 vol% of polymer relative to the continuous aqueous phase) exhibit several advantages such as lower costs of transport and storage[2], and shorter drying and film formation times.In general,the increase of solids content causes an increase in the macroscopic viscosity of the emulsion. In more straight forward polymerization, alkenes, which are relatively stable due to σ bonding between carbon atoms form polymers through relatively simple radical reactions; in contrast, more complex reactions such as those that involve substitution at the carbonyl group require more complex synthesis due to the way in which reacting molecules polymerize [3].Most commercial latexes are copolymers designed by the simultaneous copolymerization of two or more monomers. The eventual latex properties are determined the copolymer composition, molecular weight distribution and particle morphology. To control these properties, many operative variables can be used (temperature, initiator, and co monomer (s)types and concentration. In view of that, acrylic acid was added to modify styrene acrylate copolymer during latex synthesis. [4].semi continuous emulsion polymerization, hetero- Phase polymerization with reactive surfactants or by non-seeded semi-batch emulsion polymerization were carried out with different applications like as a binder for flexographic printing ink for this type of copolymers [5].Coated papers have an excessive impact on the appearance and utility of printed materials with respect to the increase in mechanical strength, print gloss and print density. Styrene–butyl acrylate copolymers were synthesized utilizing different emulsifer systems and modified with acrylamide[6].Hydrophobically alkali-soluble emulsion HASE was prepared by using semi batch emulsion polymerization technique and evaluated as a binder for water based printing inks. HASEwas prepared by using vinyl acetate and methyl methacrylate as hydrophobic monomers in addition to meth acrylic acid as a hydrophilic monomer. Besides, anionic and nonionic emulsifiers are used and sodium per sulfate as initiator[7].Overprint varnishes (OPVs) are coatings applied to an already printed sheet or web. The primary reasons for applying an OPV are gloss enhancement; stain resistance; edge fusion resistance; burnish or scuff resistance; and resistance to discoloration from absorption of impurities in the environment.

Overprint varnishes formulation Consists of the following:emulsions / resins,waxes,additives and defoamers.[8]It is unusually unnecessary to blend more than two emulsions .The majority of emulsions used in aqueous coatings are modified acrylic polymers[9], which can be divided into two types : (1- non-solubilising) which characterized by High solids , medium viscosity polymers which are relatively unaffected by changes in alkaline pH , thereby offering very good press stability , They exhibit high gloss and generally good resistance properties. (2-solubilising)[10]which characterized by Supplied as very low viscosity , high solids emulsions.

II. EXPERIMENTAL

2.1 Materials

Ethyl acrylate ,2-ethyl hexyl acrylate,and methylmethacrylate (MMA) were supplied by Sigma-Aldrich and distilled with reduced pressure before use and stored at -20ºC.- Potassium persulphate (KPS), Sodium acetate, acrylic acid (AA),Sodium laurylsulphat (SLS),Acrylamide (AAM), NP30 Anon ionic surfactants, were supplied from Sigma chemicals and distilled water was used. All chemicals were fine chemicals.- Anti Fungi (VINYZENE™ IT-4000 DIDP),Dipropylene glycol methyl ether (Dowanol DPM) were supplied from Dow Chemical Company, JONCRYL90, JONCRYL® 682 was importedfrom BASF Chemical Company and Wetting Agent(Surfynol 104) was importedfrom Muzing Company.

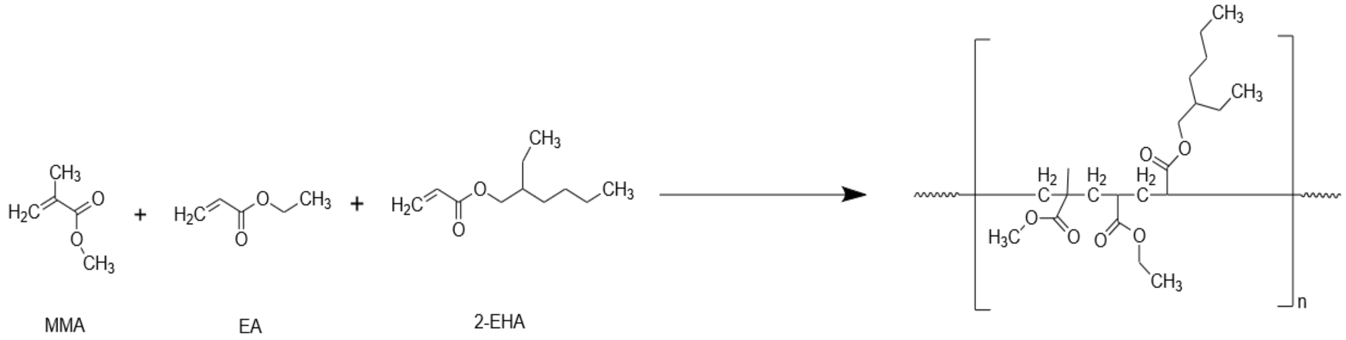
2.2 Procedures:

2.2.1. Pre-emulsion

Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate (MMA) as terpolymer were mixed (in three time portions) into the flask equipped with high speed homogenizer for 30 min).The acid monomer acrylic acid (AA) is added to both co- polymer and terpolymer during continuous homogenizing.

2.2.2. Emulsion polymerization of Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate (MMA)

The emulsion polymerization of Ethyl acrylate, 2-ethyl hexyl acrylate and methyl methacrylate (MMA) take placed in three necked round flask fitted with a condenser , a stirrer and nitrogen gas inlet system. For at least 30 minutes purging nitrogen through the mixture for removed the oxygen. Then in 88 ml distilled water adding 2.2 g of Sodium lauryl sulphate (SLS) & (NP30) as anono ionic surfactants and 0.4 g' as nonionic surfactants and followed by adding 0.1gm potassium per sulfate (KPS) as initiator, the mixture was stirred under nitrogen atmosphere at 80ºC in water bath. Then different ratio of Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate (MMA) monomers were mixed under vigorous stirring at room temperature for 30 min. The 10% of obtained pre-emulsion was charged into the reactor for 30 min as seeding stage, then after 30 min, the 0.1 g KPS dissolved in 17 ml distilled water used as initiator was gradually dropped into the reaction mixture. The (2%AA and 0.4 NP30) were mixed with 90% of lasting pre-emulsion by the homogenizer, was charged into the reactor within 3h. The reaction was allowed to proceed under continuous stirring at 80 rpm, then the temperature raise to 83 ºC. At the end of the pre-emulsion addition, the temperature was raised from 83 to 85ºC for 1h to complete the polymerization reaction. The emulsion mixture was cooled till 40ºC and the pH adjusting using aqueous solution of ammonia till pH 8 as represented in scheme 1 and table 1.



Scheme1. Chemical structure of the prepared ter-polymer methyl methacrylate , ethylacrylate and 2ethyl hexyl acrylate nanoemulsion terpolymer

2.3. Latex formulation strategies:

By changing the types and ratio of monomers Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate (MMA) at fixed ratio of anionic emulsifier(SLS) and non ionic emulsifier (NP30) ratio, the recipe for the synthesis is given in Table (1)[11-15].

Table (1): Recipe for different ratios of Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate (MMA) Terpolymer containing of SLS as anionic surfactant, NP30 as non ionic surfactant

	Group (I)		
Component*	**A**	**B**	**C**
Ethyl acrylate	**43.5**	**42**	**40.75**
Methyl methacrylate	**3.5**	**5**	**6.25**
2-ethyl hexyl acrylate	**3**	**3**	**3**
Sodium lauryl sulphate (SLS)	**2.2**	**2.2**	**2.2**
NP30	**0.4**	**0.4**	**0.4**
Dest.H_2O	**48**	**48**	**48**

***All ingredients weighted in grams.**
The above recipe contains pot.persulphate as free radical initiator (0.2 g), acrylamide monomer (0.1) and Acrylic Acid (2 g). Temp 80°C, pH 8.5 .

2.4.Preparation of Over Print Varnish for Offset Inks

Over Print Varnish used in the samples were made according to standard procedures in the ink art. The over Print Varnish vehicle was prepared with the composition of 62.5% of terpolymers of different types of polymer (A, B and C), 25% JONCRYL® 682 ,1.5 % water , 0.5 antifoam , 5% polyethylene wax emulsion , 3 % wetting agent and 2.5 % Dowanol DPM as shown in table (2) . After stirring until a good dispersion was obtained pH value was (8 - 9.5) . The prepared water base overprint varnish examined by (viscosity, gloss, tackiness, adhesion to metal, adhesion to plastics and chemical resistance).

Table (2):Recipes for different ratios of over print varnish containing Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate Terpolymer containing (SLS) and NP30 group (I) as following:

Ingredients*	**Group (I)**		
	A	**B**	**C**
Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate	**62.5**	**62.5**	**62.5**
JONCRYL® 682	**25.0**	**25.0**	**25.0**
Defoamer (gm)	**0.5**	**0.5**	**0.5**
Wetting agent(gm)	**3.0**	**3.0**	**3.0**
PE wax emulsion(gm)	**5.0**	**5.0**	**5.0**

Dowanol DPM(gm)	**2.5**	**2.5**	**2.5**
Dest. H_2O(gm)	**1.5**	**1.5**	**1.5**

***All ingredients weighted in grams**.

2.5 Characterization

a. Transmission electron microscopy (TEM)

The morphology of the copolymer particles was examined using transmission electron microscopy(TEM). In TEM the dry sample has transferred into ultra-high vacuum and is illuminated by a high energy Beam of electrons (100 keV).In an ideal case, a lateral resolution of around 1nm is achievable. To perform TEM analysis, the latex was diluted with distilled water, a drop of the diluted latex was placed on a carbon – coated grid and dried in a dissector, then, 1 – 2 drops of a 0.8 wt. % aqueous solution of phosphor tungstic acid (PTA) was used to stain the particles. The shape and particle size distribution of the nanoparticles were determined by using transmission electron microscope JEOL-JEM-1011, 30KV Japan.

b. Gel permeation chromatography (GPC).

The weight-average (Mw), and number-average (Mn) molecular weights, were determined using Agilent 1100 series gel permeation chromatography (GPC), Germany, equipped with G1362A refractive index detector with 100-104-105 A° ultra styragel columns. Polystyrene was used as a standard. THF was used as an eluent with a flow rate of 1ml min^{-1}.

c. Coagulum

Coagulum of the polymer are generally done on a 100-g lot, and are a simple gravimetric determination of that percent retained on a 100-mesh .This can be put in a ring stand and the latex sample poured through quickly.Dilution with water will speed up the process for viscous latexes, provided the dilution doesn't cause coagulation. The screen is preweighted (dry). And the coagulum collected, ASTM D4828.

d. Density

A pyknometer having a volume of 50 cm is utilized to decide the thickness of latex, whenever required, at 20 or 25°C. Thickness of polymer is more noteworthy than 1 g/cm like all the water-based latex. Exceptional hydrometers are likewise utilized for fast assurance of latex thickness. Thickness esteem is essential for the vehicle and shipment of the fabricated latex; it has less logical disadvantages.

e. Thermo gravimetric analysis (TGA).

Thermo gravimetric analysis(TGA) analysis was performed using Shimadzu TGA – 50 thermo gravimetric analyzer, Columbia, EUA, in a nitrogen atmosphere at a heating rate of 10 ˚C /min in the range between room temperature and 600˚C.

f. Fourier transform infrared (FTIR)

The copolymer composition of dried samples was proved by FTIR spectra using JASCO FTIR 6100 in the range of 4000 – 400 cm^{-1} using KBr pellets. FTIR was also used to examine the functional group of the prepared samples.

g. Viscosity

Consistency of Over Print Varnishwas assessed by utilizing Ford Viscosity Cup No. 4 at 25ºC. All estimations with the Ford consistency glasses might be made at 77°F (25°C) or a temperature settled upon amongst maker and client. The Ford thickness container is filled level full with the fluid under test, and the ideal opportunity for the material to course through one of the standard openings is estimated.

h. Gloss

Gloss of Overprint varnish was evaluated. The degree of gloss a coated film may be directly measured using a gloss meter. Gloss meter contain a light source set at a specific incident angle to the coated sample; a photoelectric cell, which is a set at the same angle as the angle of incidence, measures the reflected light"

i. Coffee stain (60-second)

This test method can be defined when an adequate amount of press varnish has been applied then Pour a few drops of coffee on varnished .Leave for 60 seconds, then see if it wipes away cleanly. It should all come off.

III. RESULTS AND DISCUSSION

This work aims to prepare high solid content of (50% emulsion for industrial applications in water based over print varnish). Many trials were carried out to get the optimum formulations for preparingethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate (MMA) terpolymer emulsion with stable properties for a period of time (six month solid) and low coagulum of ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate (MMA) terpolymer and accelerating test. The prepared terpolymers were investigated by testing: solid content %, wet coagulum 100mesh, (g/l), particle size (nm), viscosity (cP), molecular weight, hardness, adhesion, pH, TEM, TGA and IR spectroscopy analysis. Two surfactant systems were used as well as changing the monomers ratio in the presence of constant ratio of initiator. The following Tables (1-2) represent the two groups of surfactant systems and different concentration of monomers.

3.1 Characteristics of the prepared emulsion terpolymers of (Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate (MMA)), and (SLS , NP30)surfactant system [group (I)]

The physical, chemical as well as mechanical properties of the prepared Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate (MMA) terpolymer containing Sodium lauryl sulphate (SLS) as anionic surfactant, NP30 as non ionic surfactant [group (I)] were examined according to international standard. Also, pencil hardness test, bending test of the film and adhesion to different substrate were examined to dried film and recorded as shown in Table (3) **.**

Table (3): Characterization of the prepared Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate Terpolymer [group (I)]

Properties	**Standard**	**Group (I)**		
	ASTM	**A**	**B**	**C**
Coagulum(%)		**0.5**	**0.44**	**0.36**
Solid Content (%)	**D2369**	**50.5**	**50.1**	**49**
Particle size (nm)	**TEM**	**110**	**90**	**100**
Brookfield Viscosity RVT #50 rpm, (cps)	**D 2196**	**2000**	**2400**	**3000**
Molecular weight	**Mn*10^4(g/mole)**	**4.1**	**4.3**	**4.7**
	Mw*10^5(g/mole)	**1.99**	**2.2**	**2.3**

3.1.1. Effect of methyl methacrylate on viscosity of the prepared terpolymer

Fig. 1 shows the relation between viscosity of the prepared Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate (MMA) terpolymer and changing methyl methacrylate concentrations . The viscosity of the prepared terpolymers increased as the concentration of methyl methacrylate was increased .

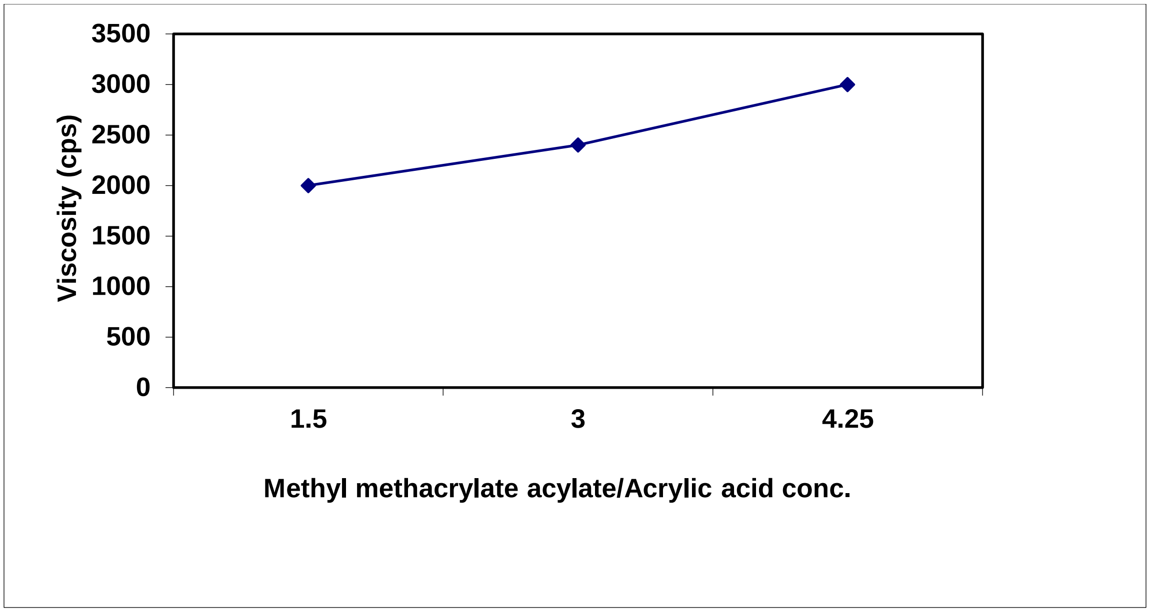


Figure (1): Effect of methyl methacrylate concentration on viscosity of Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate terpolymers (group(I))

3.1.2. Effect of (SLS, NP30) surfactant system on Molecular weight and Molecular Weight Distribution Group (I).

As mentioned previously, Molecular weight is the important factor affecting all the polymer characteristics. The MWT of the prepared polymers have a direct relationship with particle size. The Molecular Weight “Mw” is (1.99) $\times 10^5$ for sample(A) ,(2.3) $\times 10^5$ for sample(C) and (2.2)$\times$ 10^5 for sample (B)**.** The Molecular Weight distribution “Mn” is (4.1) $\times$ 10^4 for sample (A) , (4.3)$\times$ 10^5 for sample (B) and (4.7)$\times$ 10^5 for sample (C)**.**

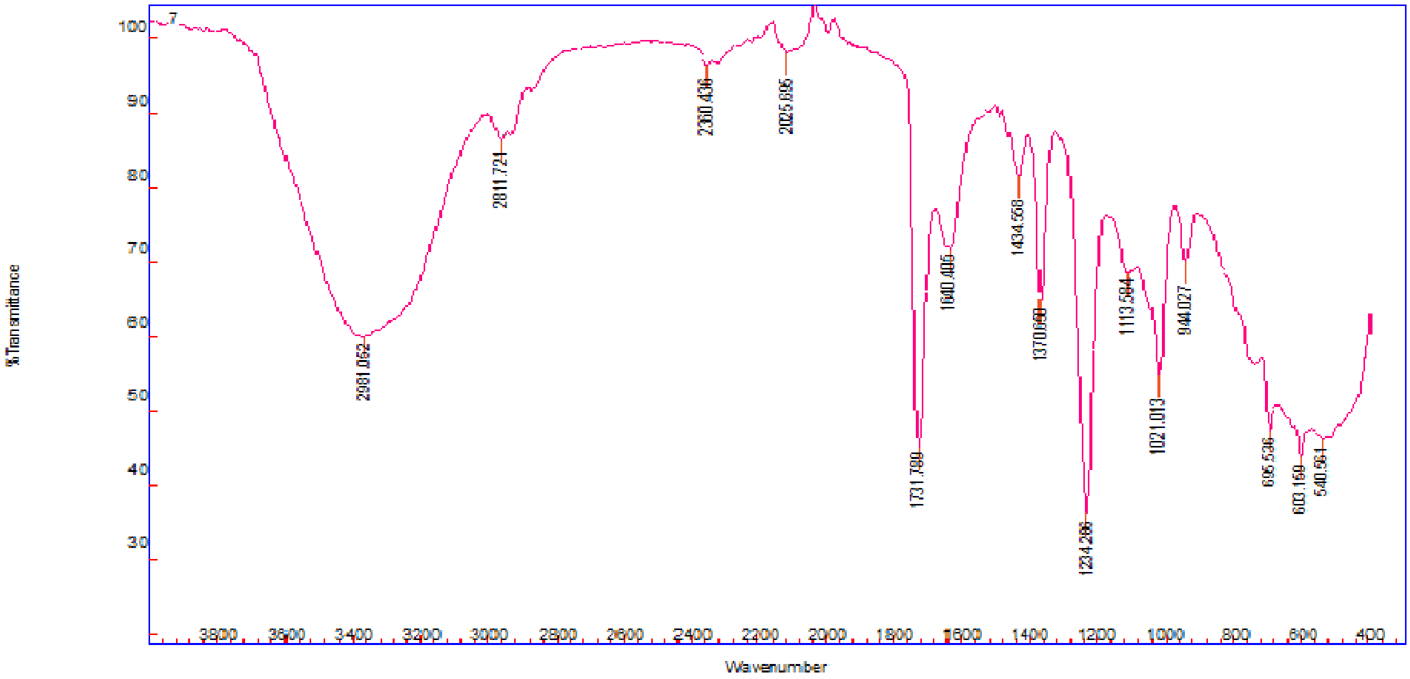
3.1.3. FTIR spectroscopy of the prepared terpolymer [group (I)]

FTIR spectra shown in Fig. 2 sample A group (I) illustrate the following groups: The carbonyl group C=O double bonds appear in the region of 1731.8 cm^{-1} of saturated acrylate ester, the band at 2981.5 cm^{-1} is specific of aliphatic methylene groups of acrylate group.

FTIR spectra shown in Fig. 2 sample B group (I) illustrates the following groups: The carbonyl group C=O double bonds appear in the region of 1731.8 cm^{-1} of saturated acrylate ester, the band at 2987.7 cm^{-1} is specific of aliphatic methylene groups of acrylate group.

FTIR spectrum of latex showed that vinyl Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylatetook part in the polymerization reaction and terpolymerization latex was prepared.

Sample (A)


%Transmittance
100
90
80
70
60
50
40
30
7
2981.052
2811.721
2360.436
2025.695
1731.789
1640.405
1434.568
1370.690
1234.286
1113.584
1021.013
944.027
695.536
603.169
540.961
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
Wavenumber

Sample (B)

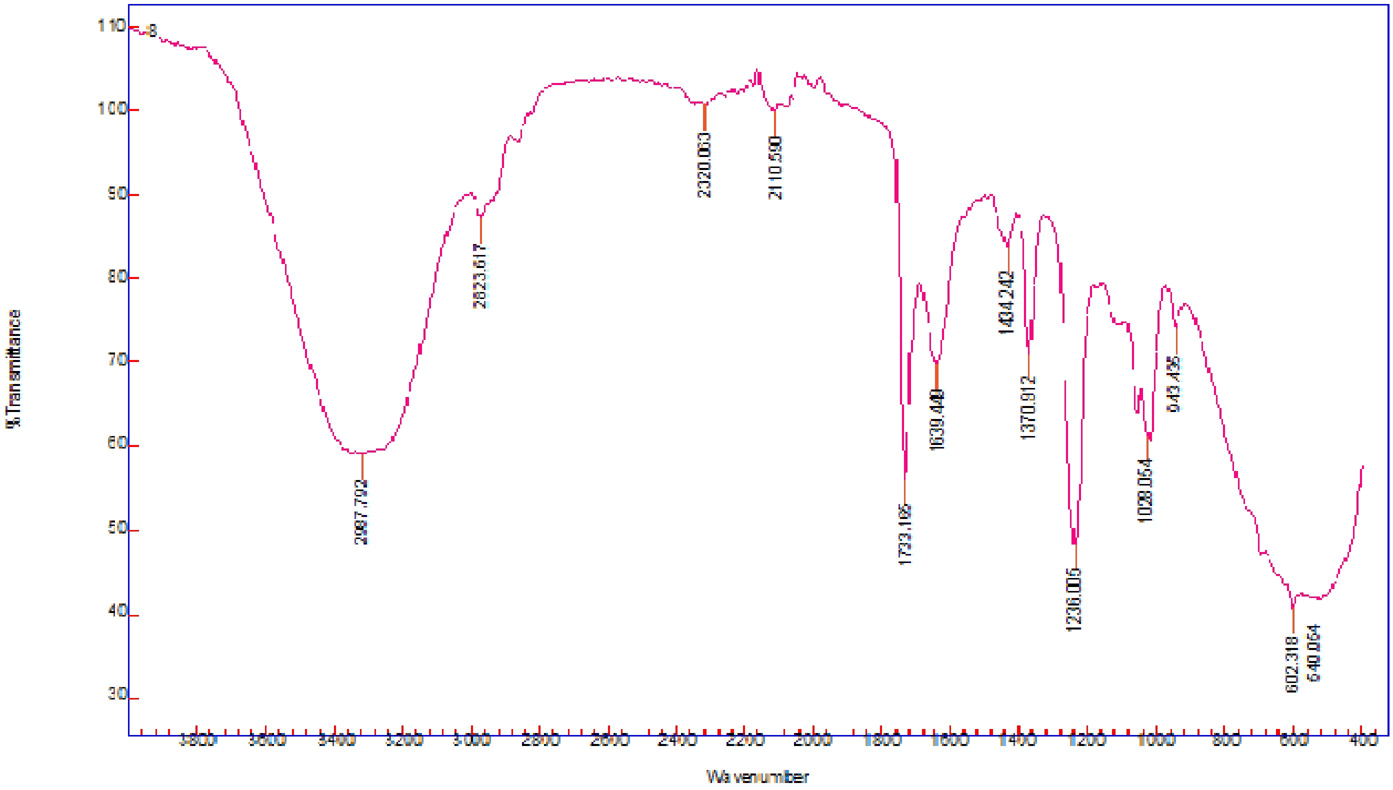
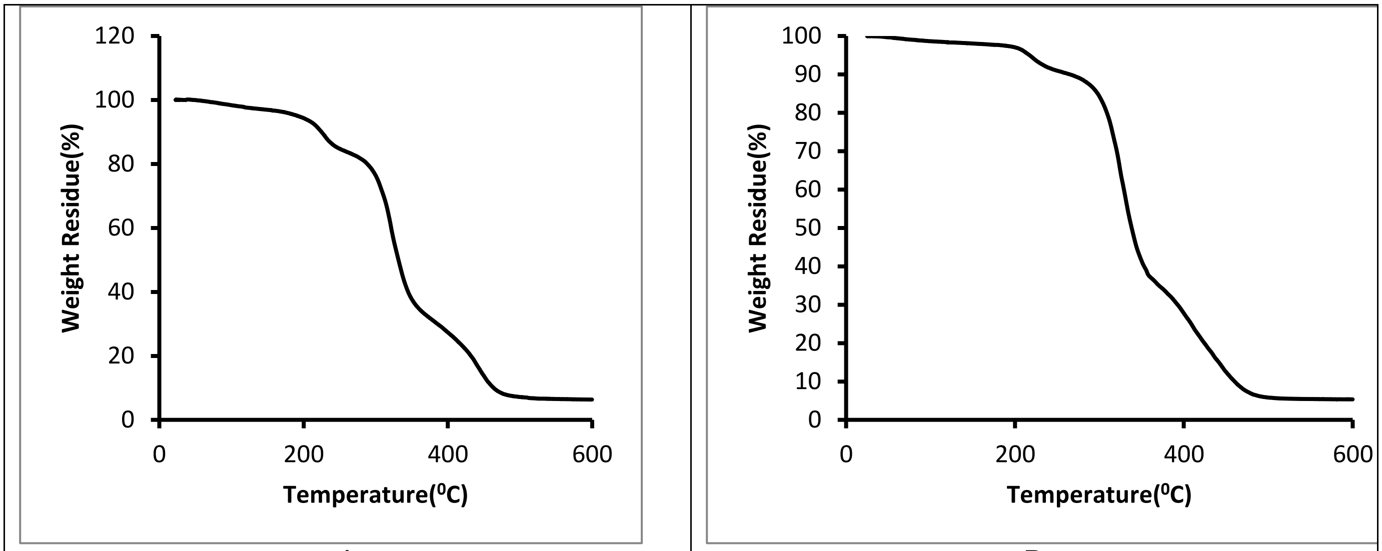


Figure (2): FTIR spectra of Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate Terpolymer Group (I) sample (A) and sample (B).

3.1.4. Thermo gravimetric analysis (TGA)

The TGA curves of the Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate nanoemulsion terpolymer shown in Fig.3 sample A showed that, the initial decomposition temperature is 200 °C, while it starts to complete or final decomposition at 401 °C and it completely decomposed at 510.1 °C with a total mass loss of 94 % wt while, and the decomposition temperature range is 310 to 470 °C

The TGA curve in Fig.3 sample B showed that, the initial decomposition temperature is 200 °C, while it starts to complete or final decomposition at 412 °C and it completely decomposed at 503.1 °C with a total loss of 88.32 % wt while, and decomposition temperature range is 302 to 455°C

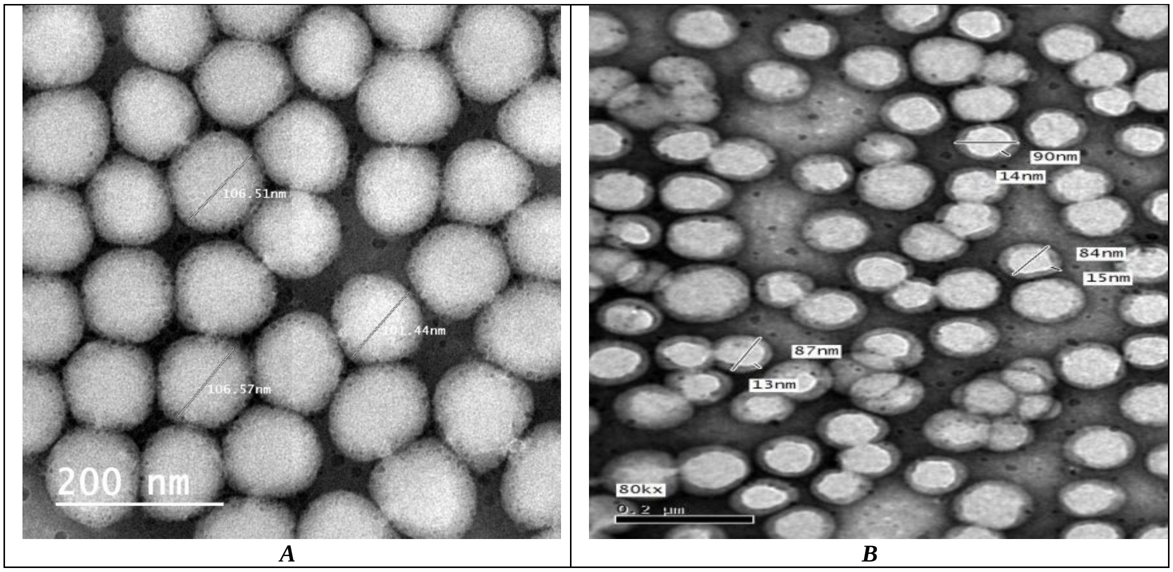


A B

Figure (3) : TGA curve for sample (A) and sample (B) Weight loss versus temperature range for clarity the curve have been plotted (0-100) °C.

3.1.5. Transmission electron microscopy (TEM) of the prepared terpolymers (group I)

Transimition electron microscopy image showed that the diameters of most particles of (A),(B) and (C) were between (90 - 110) nm as shown in Figure (4) with narrow distribution which prepared from Ethyl acrylate , 2-ethyl hexyl acrylate and methyl methacrylate terpolymer in presence of acrylic acid and acrylamide monomer. It is clear from the images that the particles were spherical shape without any deformation for samples (A), (B) and (C).



A *B*

Figure (4): Transmission electron microsope of the prepared emulsion terpolymer sample (A) Group (I) (avg.110nm) and (B) Group (I) (avg.90nm).

3.2 Preparation and evaluation of Over Print Varnish for Offset Inks formulation based on the prepared Terpolymers.

3.2.1. Over Print Varnish(Water base)

3.3. Viscosity, Gloss and Tackiness of the prepared Over Print Varnish based on the nanoterpolymers as over print varnish.

Overprint varnishes (OPVs) are coatings applied to an already printed sheet or web. The primary reasons for applying an OPV are gloss enhancement; stain resistance; edge fusion resistance; burnish or scuff resistance; and resistance to discoloration from absorption of impurities in the environment.

The prepared emulsion terpolymers were conducted to incorporate in standard formulation of water base overprint varnish and compared with the commercial polymer (Johncryl 90) in standard formulation to study the difference between the prepared and the trade mark emulsion polymer. The prepared water base overprint varnish examined by viscosity, gloss, tackiness, adhesion to metal, adhesion to plastics and chemical resistance.

3.3.1. Viscosity

Based on the results which tabulated in table (4), it is clear that the viscosity of the prepared terpolymers in group (II) had slightly low viscosity in compare to the trade mark co-polymer (Joncryl). This low viscosity may be reduce the film thickness of the Over Print varnish and may be decrease the spreading of the varnish on the surface of offset ink.The viscosity also may be improve the film thickness of the overprint varnish and may be increase the spreading of the varnish on the surface.

Table (4): Mechanical, physical characteristics obtained of Over Print Varnish using group (I).

	standard formulation	**Group (i)**		
		A	**b**	**c**
Viscosity (Sec) Ford. Cup No.4 at 25˚C	**60**	**40**	**42**	**50**
Tackiness	**12**	**14**	**15**	**13**
Gloss at 60º	**55**	**44**	**45**	**51**
Coffee stain (60-second)	**Pass**	**Pass**	**Pass**	**Pass**
Linseed oil test (60-second)	**Pass**	**Pass**	**Pass**	**Pass**

3.3.2. Gloss

Over print varnish comes in a variety of finish gloss levels, which correspond to different levels of specular reflection some common names for levels of gloss include: flat, matte, eggshell, satin, silk, semi-gloss, high gloss. These terms are not standardized and not all manufacturers use all these terms. Gloss level and sheen level are terms that are often used interchangeably.

The gloss level of over print varnish can also affect its apparent color. Gloss level can be characterized by the angular distribution of light scattered from a surface, measured with a gloss-meter. Manufacturer measures gloss as percentages (at an unspecified angle) and gives:

Flat (1–9% gloss)
Low Sheen (10–25% gloss)
Eggshell (26–40% gloss)
Semi Gloss (41–69% gloss)
Gloss (70–89% gloss).

As a gloss finish will reveal surface imperfections such as sanding marks, surfaces must generally be prepared more thoroughly for gloss finishes. Gloss-finish varnishes are generally more resistant to damage than flat varnish, more resistant to staining, and easier to clean.
It is clear from table (4) that the prepared Terpolymers in group (i) had lower gloss in compare to the trade mark (Joncryl 90) except sample No C. This may be reducing resistant to staining, and easier to clean.

3.3.3. Tackiness

Most overprint varnishes used to laminate varnish have a tack numbering in between 13 – 20. Lower numbers means less tack. Newer presses, which have fewer varnish rollers to soften the varnish than older models, require less tacky varnishes. Improper tack may results poor trapping. High tack results (poor varnish transfer, picking, piling and may rupture the paper).

From Table (4) we can conclude that the prepared Terpolymers in group (I) had higher tackiness in compare to the trade mark co-polymer (Joncryl 90) except sample

No C. This may be resulting (poor varnish transfer, picking, piling and may rupture the paper). But these results were not stained the over print varnish with coffee and linseed oil.

IV. CONCLUSIONS

- Increasing the binder ratio enhanced the gloss values.
- Emulsion polymerization is a flexible process by which a wide range of practical materials can be made, and in each case, the process is tailored to optimize the performance properties of the final product.
- Change some of the specifications of the polymer so two surfactant systems were used in this work.
- High viscosity may be improve the film thickness of the overprint varnish and may be increase the spreading of the varnish on the surface especially sample no. (C).
- High gloss may be improving resistant to staining, and easier to clean.
- Low tackiness may be improving varnish transfer, picking, and piling . These results show good stained properties of the over print varnish with coffee and linseed oil.
- Nano acrylate polymer gave promising results as a binder for water base over print varnish with respect to print quality

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