Studies on Nano science of (PVC/DEHP) composites as coating materials and printing inks

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Abstract: Nano form of (PVC/DEHP) composites showing newer and high productivity printing inks, because of its nature "oil-based "which have maximum ability to avoid screen blocking and because as its particle size "Nano-size" which minimize the ink build up, this thesis is showing the productivity of oil-based inks increased about 10 times than common water –based inks and the productivity of Nano form oil based inks increased about 3times than same inks in bulk form. Different ratios showing different viscosities which can be adjusted to applicable viscosity before Nano milling by addition of Nano form silicon resin. Nano milling of PVC/DEHP composite using wet-roll mill technology showing an increase in color depth while showing a decrease in both glossy and whiteness.
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Key Words: PVC (poly vinyl chloride) , DEHP(di ethyl hexyl phthalate), (phr) parts of plasticizer per hundred parts of resin , (KU) Krebs units which are unique to Stormer viscometers, (CP) is a centipoise and it is one one-hundredth of poise and (g) is the gravitational acceleration.

1.Introduction:

When emulsion polyvinyl chloride and plasticizer are mixed a paste is typically formed which dries upon heating at temperatures above 160° C. to form a film. As the temperature is increased the polyvinyl chloride grains in the PVC composition begin to swell eventually forming a solid composition (dry film).

This is known as the gelation temperature of the polyvinyl chloride composition and is typically in the range of 70° to 110° C. Fusion is the term that is used to describe the moment when the dry layer has developed its full mechanical or physical strength to form an integral article. The fusion temperature is typically in the range of 160° to 190° C. [(1)]

The gel Theory considers the plasticized polymer to be neither solid nor liquid but an intermediate state, loosely held together by a three-dimensional network of weak secondary bonding forces. These bonding forces acting between plasticizer and polymer are easily overcome by applied external stresses allowing the plasticized polymer to flex, elongate, or compress.

Free Volume is a measure of the internal space available within a polymer. As free volume is increased, more space or free volume is provided for molecular or polymer chain movement. [(2, 3)]

In this study a formula of PVC/DEHP in Nano form was investigated to be suitable as textile coating and printing inks which achieve newer and so specific characters, such factors as productivity, glossy, particle size and printability were studied.

2. Experimental

1-Chemicals and materials

1-1-PVC used in a wide range of applications. Paste PVC finds its principal end use in the home, where it is used to make flooring and wall coverings .The other half is spread among consumer goods, artificial leather, industrial and automotive applications, coated fabrics, gloves, sealants, conveyor belts and foams, medium molecular weight. Supplied by INEOS ChlorVinyls, Sweden *www.ineos.com*

1-2- DEHP the main plasticizer for EPVC to improve flexibility of PVC resin, Supplied by LG Chem, Ltd. Korea *www.lgchem.com*

1-3- **ESO** Refined Soybean Oil can be used for making Plasticizers and Epoxidized Oils, to maintain the plasticity of PVC and as a stabilizer for increasing the stability in PVC and Pesticides, used in Surface Coating Industries such as Paints, Varnishes, Printing Ink and related products, Supplied by Gujart ambuja exports limited. India *www.ambujgroup.com*

1-9- **Pigment** (black F, Sunbrite Red 481, 234-3955) supplied by sun chemicals co.USA. *www.sunchemichals.com*

2- Substrates

2-1 -100% knit red cotton fabric 150gm/m^2
2-2-100% knit white cotton fabric 145gm/m^2

Red cotton samples were scoured; half bleached and dyed with reactive vinyl sulfonyl dyestuff at 60C^o, washed and dried, white cotton samples were scoured; on bath bleached, washed and dried, poly ester red samples scoured and dyed with red disperse dyestuff, washed and dried.

(All fabrics supplied by Martex clothing company, Egypt)

3-Tools and equipments

3-1- Low speed mixer

www.anatol.com

3-2 -Laboratory high-speed disperser SAII-3

www.sowerchina.com

3-3- Wet Nano Milling machine

www.millgroup.co

3-4-Manul printing machine

6-colors printing machine

www.lancergroup.com

3-5- Flash-cure digital infra-red unit:

Anatol Infrared Panel Flash is an affordable and simple solution that is especially a great option for a startup textile printing shop.

www.anatol.com

3-5- Convert-belt infra-red digital dryer

The Solutions series dryers are perfect for textile printers looking for an efficient and affordable complement to their output demands. www.anatol.com

4- Measuring instruments

4-1- viscometer:

Measuring according to ASTM –D562 and GB9269-88 Standard Practices for Basic Calibration of Master Viscometers and Viscosity Oil Standards [(4)]

4-2- Glossy meter:

Measuring according to ASTM D4400 - 99(2012) Standard Test Method for Sag Resistance of Paints Using a Multinotch Applicator [(5)]

4-4- Nano meter:

(6)

www.lancergroup.com

4-5- Rubbing tester

Measuring according to ASTM D3702 - 94(2009) Standard Test Method for Wear Rate and Coefficient of Friction of Materials in Self Lubricated Rubbing Contact. [(7)]

4-6- Color reader:

Measuring according to ASTM D1729 - 96(2009) Standard Practice for Visual Appraisal of Colors and Color Differences of Diffusely Illuminated Opaque Materials. [(8)]

www.vernier.com

4-9- Infra-red digital thermometer:

Infra-red thermometer allows to easily determining the surface temperature of difficult to reach targets, or objects that are moving or fragile.

www.professionalequipment.com

4-10- Digital microscope:

A digital microscope is a variation of a traditional optical microscope that uses optics and a charge-coupled device (CCD) camera to output a digital image to a monitor.

www.dino-lite.com

5- Methodology

5-1-Mixing process

Suggested recipes from PVC, plasticizer and additives were mixed with low speed hand mixer for 5 minutes, then dispersed with t high speed disperser for about1minute, the temperature during mixing and dispersing process must be below 60C^{o}, all samples were kept for 1 hour before testing or further processing.

5-2-Milling process

The dispersed samples were subjected to wet nano mill two times under cooling condition to keep the temperature below 60 C^{o}; the milled samples were kept for about 1hour before testing or subjected to further processing.

5-3-Printing and coating

The printable pastes were printed or coated upon the substrates which described as mention through screen with mesh count 61/cm using square shape 70Duorometer squeegee using manual screen printing machine, two layers were applied ,flash for 2 seconds in between two layers to dry 1st layer using infra-red flash cure unit.

5-4-Curing and fixation

All coated or printed fabrics were flashed for 2seconds after printing or finishing process was finished then fixed at 150C^{o}for 1minute using infra-red convert belt dryer.

5-6-Measuring and testing

All finished fabrics were subjected to a suitable instrument for measuring and testing according to standard international test method for each test; all instruments were calibrated before testing.

5-7-preparing and testing laboratory

All samples were prepared and tested at SPI production and QC laboratory while productivity study was done at Garo-print shop.

www.spi-eg.com

6-Practical procedures

1-Viscosity study (clear PVC/DEHP composite)

Seven samples were prepared with different ratios between PVC and DEHP plasticizer as follow: DEHP plasticizer: PVC (90:10, 80:20, 70:30 ,60:40 ,50:50 , 40:60 and 30:70) . The samples were mixed with low speed hand mixer for 5 minutes, and then at high speed disperser for about1minute, the temperature must be below 60C^o, the samples were kept for one hour then the viscosity was measured for each ratio, results were reported in table1 and figure1.

2-Thickening study (clear PVC/DEHP composite)

To achieve applicable viscosity which enable to study either affecting factors, Nano form silicon resin was applied in a percentages of 1%, 2%, 3%and 4% for each recipe reported in table 1, 28 results were obtained, 7 considerable viscosity results were reported in table2and figure 2

3-Particle size study of (clear PVC/DEHP composite)

six ratios which achieve acceptable viscosity (2, 3, 4, 5, 6, and 7) were milled two times using wet-Nano mill as mention, the particle size for each composite were measured before and after milling ,results were reported in table3 and figure 3.

4-Glosssy study of (clear PVC/DEHP composite)

4-1 Effect on Nano-milling on glossy of PVC/DEHP composite.

Both bulk and Nano composite of the 6 successful ratios (2, 3, 4, 5, 6, and 7) were applied upon red cotton fabrics with the description method as mention, the glossy of printed or coated films were measured for bulk and Nano-composite, results reported in table 4 and figure 4.

4-2 Effect of high gloss additive on (Nano composite of PVC/DEHP)

High gloss additive were added to Nano-composite ratios (2, 3, 4, 5, 6, and 7) in percentage of 2%, 4%, and 6 %. all the prepared Nano-composite were applied upon red cotton fabrics with the description method as mention, the glossy of printed or coated films were measured, results reported in table 5 and figure 5.

5- Softness study (clear PVC/DEHP composite)

Both bulk and Nano composite of the 6 successful ratios (2, 3, 4, 5, 6, and 7) were applied upon red cotton fabrics with the description method as mention, the Softness of printed or coated films were observed for bulk and Nano-composite.

6-Microscopic study (clear PVC/DEHP composite)

Both bulk and Nano composite of the 6 successful ratios (2, 3, 4, 5, 6, and 7) were applied upon red cotton fabrics with the description method as mention, 12 microscopic photos for printed or coated films were studied for bulk and Nano-composite.

7-Washing fastness (clear PVC/DEHP composite)

Both bulk and Nano composite of the 6 successful ratios (2, 3, 4, 5, 6, and 7) were applied upon red cotton fabrics with the description method as mention, 12 samples were washed at standard conditions 60C^{o}for 20miniutes, samples were dried at room temperature, samples were subjected to color reader for testing.

8-Rubbing fastness (clear PVC/DEHP composite)

Both bulk and Nano composite of the 6 successful ratios (2, 3, 4, 5, 6, and 7) were applied upon red cotton fabrics with the description method as mention, the 12 samples were subjected to Crocker instrument for standard wet and dry rubbing test ,24 results were obtained for clear PVC/DEHP composite system.

9-Coloring of PVC/DEHP composite

1% of red organic pigment powder was added to the 6 successful ratios (2, 3, 4, 5, 6, and 7) the pastes were mixed dispersed and milled as mention, both bulk and Nano-composite were applied upon 100% white cotton fabric with the methodology as mention, the printed or coated samples were subjected to several measurements.

9-1 Effect of Nano-milling on Particle size of (colored PVC/DEHP composite)

The 6 red color pastes with ratios (2, 3, 4, 5, 6, and 7) which prepared in step 7 were measured by nanometer before and after milling, 12 results were reported in table 6 and figure 6.

9-2 Effect of Nano-milling on color depth of (colored PVC/DEHP composite)

The color depth of the printed or coated cotton fabrics which prepared in step 7 with ratios (2, 3, 4, 5, 6, and 7) was measured for both bulk and Nano-composite; 12 results were reported in table 7and figure 7.

3. Results and Discussion

Plasticizing of PVC with DEHP

Structure and formula of DEHP (C_6 H_4 (COO-$C_8H_{17})_2$

The use of phthalate esters as plasticizers, or softeners, in PVC resins has been a feature of PVC technology since the 1930. A family of esters of phthalic anhydride (like benzoic acid) but with a second acid group in the ortho position relative to the first) is used. The alcohol portions of these esters range from the C_4 to the C_{13} entities has been used, although the vast majority of products used are in the C_8 to C_{10} range. In terms of chemistry they are relatively simple esters, made by the reaction of the relevant alcohol (two molecules) with the anhydride (1 molecule) and removing the water that is also produced in the reaction. [9, 10]

1-Viscosity study (clear PVC/DEHP composite)

Viscosity is one of the most important physical phenomena which affect other physical properties as film nature, rubber hardness, softness, printability and appearance.

Table 1 show the applicable ratio which achieves accepted viscosity was ratio no.7 which has 70% PVC: 30% DEHP .the other ratios achieve low viscosity so it was inapplicable.

Thickening agent must be added to the low viscosity ratios until reach the applicable viscosity ,to achieve applicable viscosity which enable to study either affecting factors, Nano form silicon resin was added in a percentages which suitable for each ratio. Not: silicon resin is inert compound that was not affecting any other characteristics except viscosity as shown in table 2.

An increase in the viscosity was noticed as the PVC percentage was increased due to the nature of PVC which is in powder form as showing in table 1 and figure 1, the ratios1was out of application as it shows very low viscosity even with 4% of silicon resin.

Although ratio 7 which was 70% PVC and 30% DEHP shows good viscosity without adding silicon resin it cannot applied as printing inks due to its sticky effect , ratio 6 shows good viscosity with adding 1% silicon resin but it is not preferred as printing inks because of higher percentage of PVC which casing sticky and build up when applied as printing inks, ratio 5, 4 shows good viscosity with adding 1% and 2% silicon resin respectively, ratio 3 shows good viscosity with adding 3% silicon resin while ratio 2 shows good viscosity with adding 4% silicon resin. The applicable viscosity and best ratios which enable studying other factors as coating material and printing inks were in range between 1990 CP to 2500 CP as showing in figure 2 which were achieved with ratios 2, 3,4 and 5 with addition of silicon resin 4%, 3% ,2% ,2% and 1% respectively.

Table 1 Relation between (PVC/DEHP) ratios and viscosity at 33C^O

Ratios	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**
PVC%	**0**	**10**	**20**	**30**	**40**	**50**	**60**	**70**
DEHP %	**100**	**90**	**80**	**70**	**60**	**50**	**40**	**30**
KU	82.9	84.4	87	88.5	93.4	107	115	N/A
CP	887	971	1009	1340	2090	2294	2330	N/A
g	207	230	240	237	445	447	476	N/A
appearance	liquor	Liquor	liquor	liquor	Low viscosity paste	Low viscosity past	Low viscosity past	Past

Relation between (PVC& DEHP) ratios and viscosity"KU, CP, g" at 33C^O

2-Thickening study (clear PVC/DEHP composite)

Table 2 Effect of adding suitable percentage of silicon resin on the viscosity of (Clear PVC/DEHP composite)

Ratio	1	2	3	4	5	6	7
PVC%	10	20	30	40	50	60	70
DEHP %	90	80	70	60	50	40	30
Silicon %	4%	4%	3%	2%	1%	1%	-
KU	88.2	108	112	114	118	135	N/A
CP	1064	2010	1990	2300	2500	4030	N/A
g	243	420	380	453	577	890	N/A
Appearance	liquor	past	past	past	past	past	Past

Table 3 Effect of Nano milling on the particle size of PVC/DEHP composite

Ratio 5	PVC%	DEHP%	Silicon %resin	Pvc powder	Size before milling	Size after milling
parameters	50	50	2	0.7um	600nm	92nm

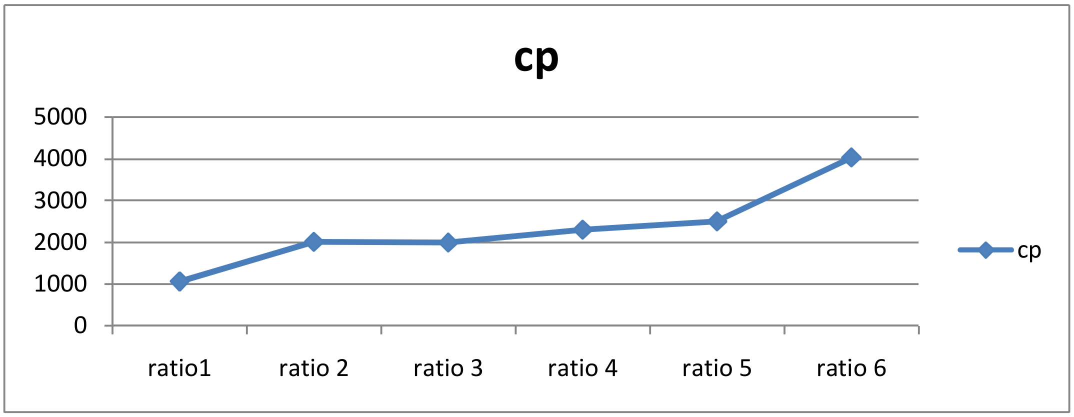
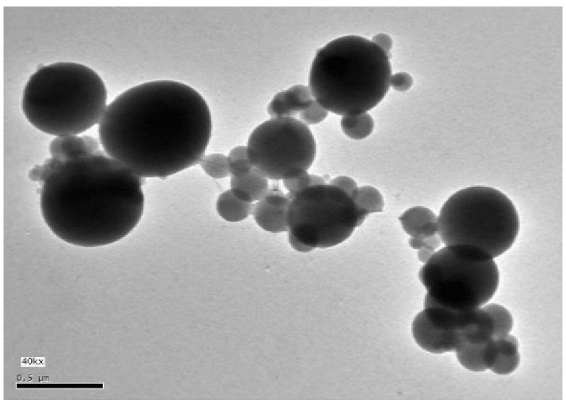
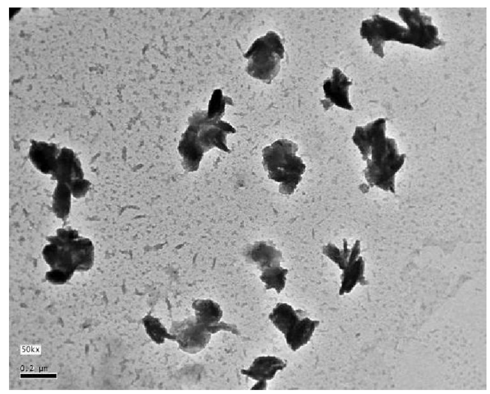


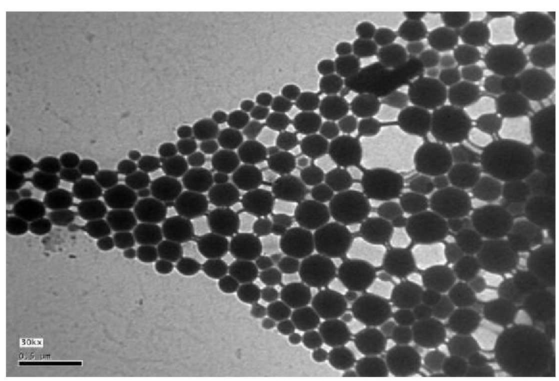
Figure 2 Effect of adding silicon resin on the viscosity of (clear PVC/DEHP composite)



PVC powder



Clear PVC/DEHP before milling



Clear PVC/DEHP after milling

Figure 3 Effect of Nano milling on the particle size of clear PVC/DEHP composite

3-Particle size study of (clear PVC/DEHP composite)

Nanometer particles (NPs) were synthesized via a chemical route. The particle size estimated by x-ray diffractometry and transmission electron microscopy the excitation peak of NPs due to the charge-transfer band shifted toward the high-energy side as compared with that of MPs. According to x-ray diffractometry, the lattice distortion and the lattice constant were larger for NPs than for MPs, showing the restructure at the near surface and the increase in iconicity particles bond with decreasing particle size. [9]

In order to change the prepared paste from bulk form which has some disadvantages into Nano form which achieve a lot of perfect and newer properties milling the successful recipes were done, changes in particle size clearly noticed after milling as showed in table 3 and figure 3.

Figure 3 showing that the particle size of clear (DEHP/PVC) composite was about 600nm with non-homogenous form before milling while the particle size was about 92nm with homogenous form after milling.

4-Glosssy study (clear PVC/DEHP composite)

Glossy is phenomena that deals with the shiny of coating and printing film which in some cases described as advantage of the coated substrates , in the other side glossy is a disadvantage of coating materials if matt film or semi glossy film was needed, so studying this phenomena is an important for application

According to plasticizing theory if the plasticizer diffuse in the amorphous region of PVC polymer ,if the percentage of plasticizer is much higher it will affect the crystalline region of PVC polymer ,the amount of destroyed crystalline region of PVC polymer depend on the amount of plasticizer ,as the crystalline region decreased the glossy of coating and printing film decreased ,when drying the coating film, the plasticizer migrate into the outer layer of printing film . [10]

The measured properties involved specular gloss, color, contact angle, and critical surface energy. Regardless of the substrates, WPI-coated films possessed excellent gloss and no color, as well as good adhesion between the coating and the substrate when an appropriate plasticizer was added to the coating formulations. [11]

Plasticizers used in the formation of PVC polymers tend to migrate into and through adjacent layers as the plastic film ages. Migration of the plasticizers into the pressure sensitive adhesive layer can lead to reduction in the adhesive bond. Similarly, migration of the plasticizers into the clear coat layer can lead to delaminating or loss of surface gloss. Finally, PVC paint films lack the high gloss "paint-like" appearance that is desirable in the automobile industry. [12]

Glossy inversely proportional to the amount of plasticizer and directly proportional to the percentage of PVC, so the decrease in glossy was in direction from ratios 7 to 2 due to two main reasons the 1st is The decrease in PVC percentage which negatively affects the amount of scattered light beams, second is the higher percentage of plasticizer which destroy some of crystalline region of PVC particles.

The glossy is inversely proportional to the plasticizer percentage that due to the migration of plasticizer into the surface layer of coating or printing film, Nano milling has negative effect on glossy as the particle size of PVC resin was decreased, for high glossy with milling 2% of high gloss additive must applied. Ratio 5 clear past showing the ideal glossy , the printed film with this recipe need more curing time to achieve transparency due to high PVC percentage.

After Nano milling table4 and figure 3 shows that glossy of all prepared ratios were decreased after milling that due to the smaller size of PVC which negatively affect the scattered beams of light, milling facilitates the plasticizer to diffuse into the crystalline region of PVC destroying some PVC particles, when the particle size is too much smaller less than 200nm the glossy is inversely proportional to the particle size.

Ratio 2shows the same glossy result after and before milling, that due to much plasticizer which was 80% so no further effect after milling.

In order to achieve high glossy film with Nano milling, gloss additive or glossy paper is recommended. Table 5 and figure 5 shows that 2% was the best percentage for all recipes ,the best glossy was achieved by ratio5 with 4% gloss additive that may be due to that the main and secondary plasticizer were enough to fill the amorphous region without affecting the crystalline region of PVC resin so maximum glossy was achieved. , also noticed this sample also over com pilling Problem when printed on textile cotton fabric, the glossy decreased in all ratios with 4% gloss additive except ratio 2 that due to the gloss additive is as secondary plasticizer so it can help in destroying some PVC crystalline region if the concentration is much higher than PVC polymer .ratio 2 shows an increase in glossy with the addition of gloss additive from 2% to 6% that due to that the plasticizer is already much higher in this recipe so no farther destroying occurred to PVC resin.

Before Nano milling table4 shows the highest value of glossy achieved with ratio 7 which can only apply as textile coating material as it is not suitable as printing inks due to higher viscosity, ratio 3 shows the suitable glossy result as printing inks when the glossy effect was needed as metallic inks, ratio 5 shows the semi glossy result which suitable for printing inks in general.

Before Nano milling Table 4 and figure 4 showing that the glossy increased as the PVC percentage increased so ratio 7 shows highest glossy value while ratio 2 shows the lowest glossy value. That due to the higher percentage of PVC which scatters much beam of light so higher glossy values was observed.

4-1 Effect on Nano-milling on glossy of PVC/DEHP composite.

Table 4 Effect on Nano-milling on glossy of PVC/DEHP composite

Ratio	2	3	4	5	6	7
PVC%	20	30	40	50	60	70
DEHP %	80	70	60	50	40	30
Silicon %resin	4	3	2	2	1	-
Glossy before milling	**0.7**	**1**	**1.1**	**1.8**	**2.5**	**4**
Glossy after milling	**0.7**	**0.9**	**0.9**	**1.3**	**2.1**	**3.4**

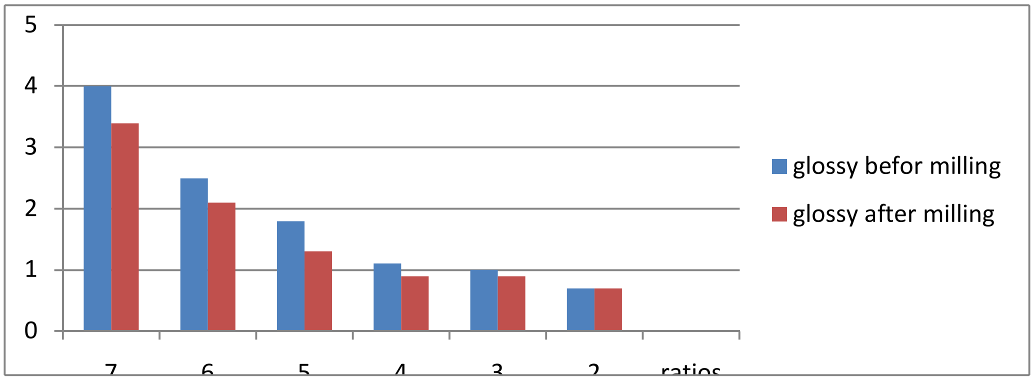


Figure 4 Effect on Nano-milling on glossy of PVC/DEHP composite

4-2 Effect of high gloss additive on (Nano composite of PVC/DEHP)

Table5 Effect of high gloss additive on (Nano composite of PVC/DEHP)

Ratio	2	3	4	5	6
PVC%	20	30	40	50	60
DEHP %	80	70	60	50	40
Silicon %resin	4	3	2	2	1
0% gloss additiv	**0.7**	**1**	**1.1**	**1.8**	**2.5**
2% gloss additive	**0.9**	**1.8**	**2**	**2.1**	**2.8**
4% gloss additive.	**1.1**	**1.6**	**1.2**	**2**	**2.8**
6% gloss additive	**1.4**	**1.4**	**1.1**	**3**	**3.1**

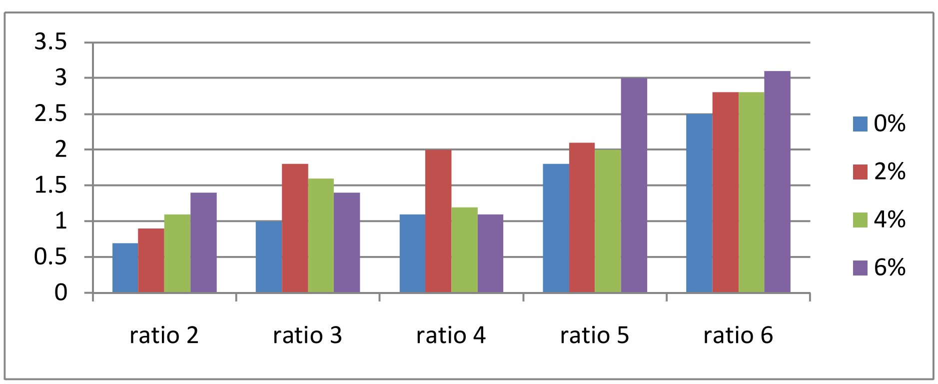


Figure 5 Effect of high gloss additive on (Nano composite PVC/DEHP)

5- Softness study (clear PVC/DEHP composite)

Phthalate are required to give Softness for PVC resin as it diffuse in amorphous region of polymer making it more flexible and softening that was meet further application. Suitable plasticizers and its percentage required for each application that must keep polymer from destroying.

If the C_8 ester was replaced by a C_9 ester, 52.5 parts (an extra 5%) was required to impart the same softness. If a C_{10} ester was used, an extra 5 PHR or

10% of plasticizer was needed, this is related to the overall number of active >C=O sites decreasing and hence the overall reduction in the stretching frequency is also reduced.

The film formation of ratios (2, 3, 4, 5, 6, and 7) shows that ratio 7 shows hard film due to the percentage of PVC which is 70%, the softness increased as the percentage of PVC was decreased. Generally the softness and leveling much improved after Nano application which makes the size of the particles smaller so it arranged by homogenous way lead to softening the coated film. Also applying of silicon coated paper on the coated film using heat pressing machine at certain condition shows maximum softness.

Finally softness of coating film using PVC/DEHP was increased by increasing the plasticizer percentage at which no further destroying to crystalline region of PVC ,also Nano-composite achieve too much softness than that of bulk form. [11, 13]

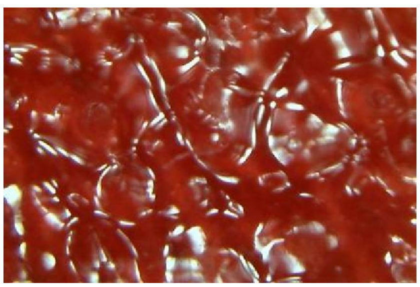
6-Microscopic study (clear PVC/DEHP composite)

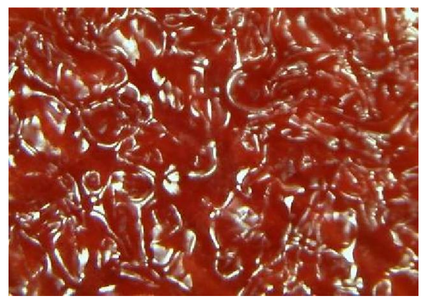
The illustrated microscopic captures of clear PVC/DEHP composite showing that the leveling and transparency of printing and coated film was clearly improved after milling due to the homogenous distribution of plasticizer onto the PVC polymer

The shiny of coated and printing films were increased as the percentage of PVC was increased; after milling the particle size was decreased clearly at ratios with higher PVC percentage while not noticed clearly at ratios with higher plasticizer percentages. Not: red color is the background.

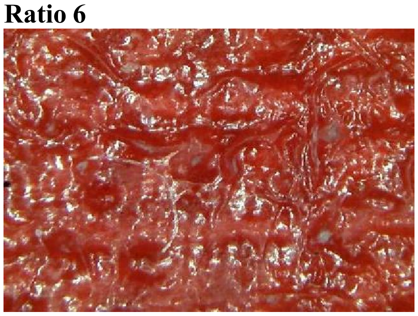
Before Nano milling **After Nano milling**

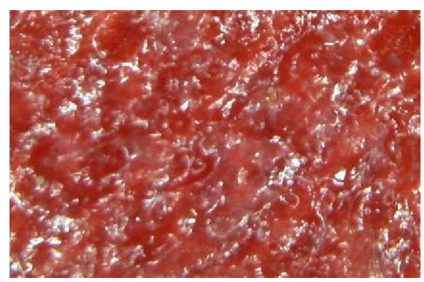
Ratio 7



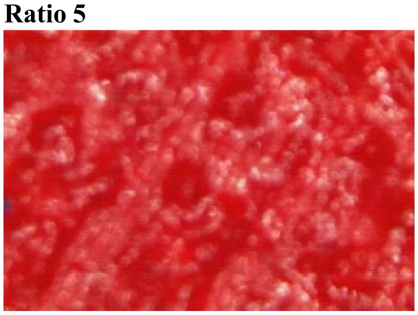


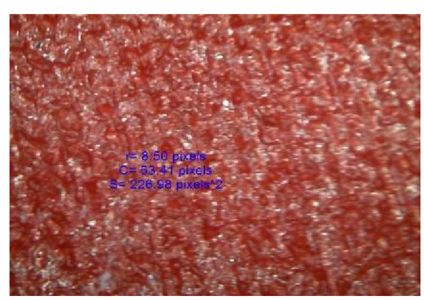
Ratio 6





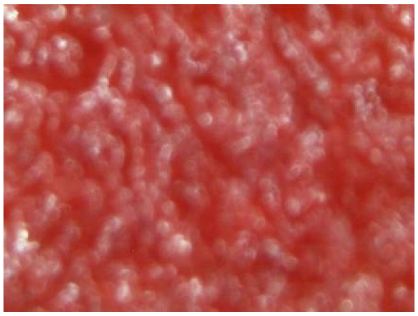
Ratio 5





Before Nano milling **After Nano milling**

Ratio 4



Ratio 3

Ratio 2

7-Washing fastness of (clear PVC/DEHP composite)

Both bulk and Nano composite of ratios (2, 3, 4, 5, 6, and 7) showing very good washing results meaning that 20%PVC resin was enough percentage to achieve good washing result as showed in ratio 2 while higher PVC percentages as in other ratios 3, 4,5,6,7 has further effect on film characteristics as elongation, transferring power glossy, drying and adhesion power. The color reader dos not detect any color change after washing so no results were reported.

8- Rubbing fastness of (clear PVC/DEHP composite)

Both bulk and Nano composite of ratios (2, 3, 4, 5, 6, and 7) showing very good dry and wet rubbing results meaning that 20%PVC resin was enough to achieve good rubbing fastness ,either dry or wet printed film not affected by crock-meter so no results were reported ,actually clear films showing good rubbing fastness than pigmented films.

9-Coloring of PVC/DEHP composite with pigments

Pigments

Pigments are finely divided, organic or inorganic, crystalline solids, they are insoluble in the system in which they are used as paints, inks, surface coatings, plastics and artificial fibers and must be dispersed in them depending on mechanical energy, the pigments not only dispersed as isolated primary particles but also as aggregates and agglomerates. [19]

Primary particles these are inorganic or organic structures held together by atomic or molecular bonding. They are the “fundamental” particles; they cannot be separated into smaller particles except by the application of ultrahigh energy. In any sample they are usually present at only a fraction of a percent.

The parameters involved in dispersion are the particle size, the method of dispersing (equipments used), the physical and chemical nature of the solvent and polymers in which the pigments have to be incorporated, their mutual interaction affects the size of the particles dispersed in the medium and thus the application properties of the system.

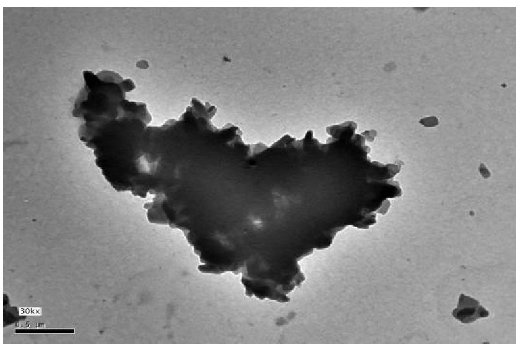
The coloring properties of pigments system are decided by the chemical and crystallographic structure of the pigments themselves; also depend on the particle size and distribution of pigments in the medium which they are applied. [14]

As PVC/DEHP was a solvent-base composite it has the ability for coloring with organic pigments powder which dissolve easily into the composite system achieving certain color, in this study red color organic pigment was successfully applied.

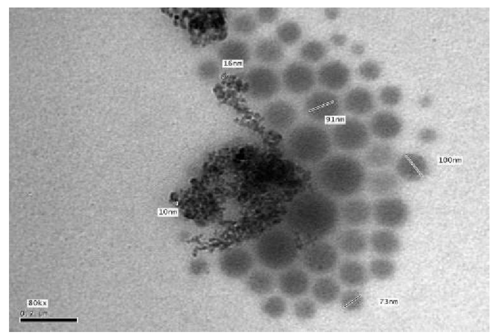
9-1 Effect of Nano-milling on Particle size of (pigmented PVC/DEHP) composite

Table 6 Effect of Nano milling on particle size of colored (PVC/DEHP) composite with 1% red organic

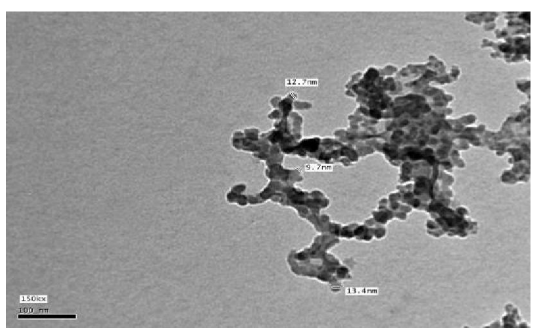
Ratio5	PVC%	DEHP %	Silicon %resin	Size of powder	Size before milling	Size after milling
Parameters	50	50	2	2microns	100nm	12nm



Red pigment powder



Red of (DEHP/PVC) composite before milling



Red of (DEHP/PVC) composite after milling

Figure 6 Effect of Nano milling on particle size of colored (PVC/DEHP composite with 1% organic pigment red color.

The illustrated figure showing that : the particle size of pigment powder was about 2microns while the particle size of dispersed red pigment was about 100nm and the milled red pigment was about 12nm,the milled composite showing a homogenous form more than that before nano-milling.

9-2 Effect of Nano-milling on color depth of (colored PVC/DEHP composite)

Milling affect the color strength by two opposite actions, first is the increasing of the total surface area of printing and coating film which positively affect the color strength, second is the decreasing of molecules particle size which is negatively affect the color strength if the particle size was below its critical size, the total color strength result is the summation of both two effects.

Maximum scattering occurs when the particle size is around 0.2micron when size gets smaller; it will lose opacity and get transparent, color is generated by both scattering and absorption, absorption will increases as the size increase.

Transparent oxides Particle size: 100 nm in length, 10 - 20 nm in width while transparent TiO2 Particle size: 10 - 60 nm, Nano pigment with Small primary particle size and large surface area has high surface energy for more severe aggregation and reactivity.

Both color strength and opacity depend on pigment particle size. Scattering increases with the pigment particle size increase, until the wavelength of incident light is reached.

At higher pigment particle size, the opacity decreases again. Thus, the opacity of an ink pigment is maximum around 350-500 nm as showmen in illustrated figure.

If scattering is so intense that no light passes through the material, the ink is opaque, the smaller the particles in the ink, the more transparent the ink. (15-18).

Table 7 shows that the color strength of ratios 2, 3, 4 and 5 were highly increased after milling that due to the increase of the surface area of coated or printed film which was occurred because of decreasing the size of pigment molecules and increasing its numbers lead to reflect much beams of light which was noticed as much color depth ,while ratios 6 and 7 showing slightly increase in color strength after Nano milling that because of these ratios not contain a sufficient percentages of plasticizer which reduce the pigment diffusion into the composite.

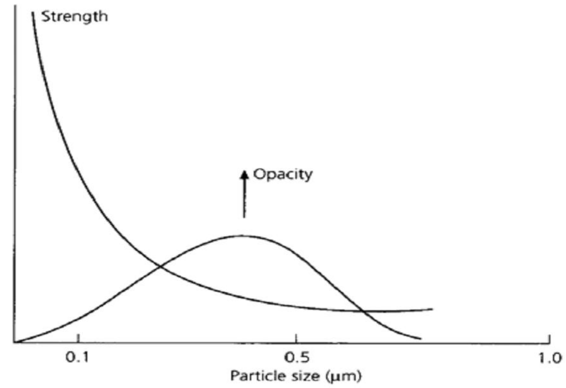


Figure 7 Dependence of Color Strength and Opacity of Pigments on Particle size [19]

Figure 8 shows that the ΔE (Total color difference between bulk and nano composite) was increased in the direction from ratio 2 to ratio 5that may be due to the increase of PVC percentage while ΔE was decreased at ratios 6 and 7 due to the low percentage of plasticizers which reduce the diffusion of pigment molecule into the composites.

Table 7 Effect of Nano milling on color strength of colored (PVC/DEHP) composite with 1% organic pigment red color

Ratio	2	3	4	5	6	7
PVC%	20	30	40	50	60	70
DEHP%	80	70	60	50	40	30
Silicon %resin	4	3	2	2	1	-
Color strength before milling	351.3	346.3	346.8	345.3	349.4	357.8
Color strength after milling	358.8	358.7	357.7	359	359.1	359.5
ΔE	9.8	11	11.6	13.7	6.3	4.8

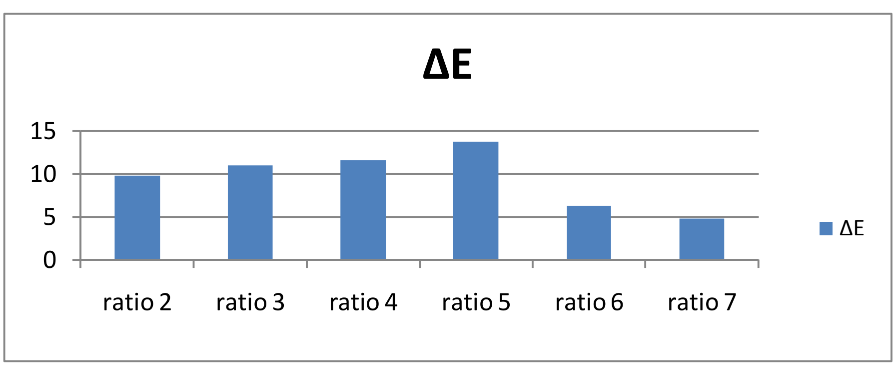


Figure 8 Effect of Nano milling on color strength of colored (PVC/DEHP) composite with 1% organic pigment red color

9-3 Glossy study of colored PVC/DEHP

As the glossy of coating film increased by decreasing the particle size due to the larger surface area, theoretically the glossy of nano-milled composites will achieve a higher value of glossy than those which exist in bulk form, practically table 8 and figure 9 showing that the glossy of coated film was decreased after milling that due to the particle size of composites including PVC and pigments was decreased under the value of 200nm which achieve the maximum light scattering and so maximum glossy.

Table 8 and figure 9 showing a decrease in glossy as plasticizer ratio increased that typically due to the decrease of PVC ratio with scattered light and achieve glossy ,much plasticizer destroy some of crystalline region of PVC macromolecule which negatively affect glossy as showmen in ratio 2

The applied wet-milling process affects the particle size of the composite including pigments to reach such value at which the glossy of coated film was decreased.

As milling of composite improve many characteristics as softness and film homogenous and color strength, it has a negative effect on glossy, the decrease in glossy value can be avoided by addition of glossy additive, table 9 and figure 10 showing that 2% for all ratios achieve acceptable glossy value while ratio5 achieve the maximum glossy value with addition of 4% high gloss additive. Finally the glossy not affected only by pigments particle size but there are many parameters that affecting the glossy, particle size is one of these parameters also the composite components as plasticizer ratio and type, PVC ratio and type ,milling process also has a great effect as it can control both size and shape.

Table 8 Effect of Nano-milling on glossy of (colored PVC/DEHP composite)

Ratio	2	3	4	5	6	7
PVC%	20	30	40	50	60	70
DEHP%	80	70	60	50	40	30
Silicon %resin	4	3	2	2	1	-
Glossy before	0.8	1	1.2	1.3	1.5	1.9
Glossy after	0.8	0.8	0.8	1	1	1.5

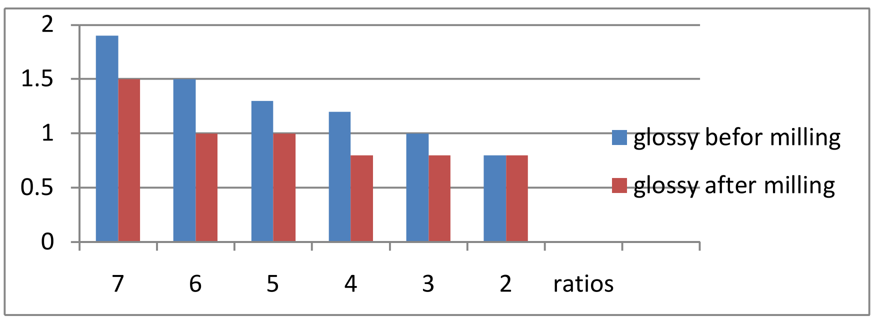


Figure 9 Effect of Nano-milling on glossy of (colored PVC/DEHP composite)

There is a clear relations between color strength and glossy as in most cases the ratios which achieve high color strength reflect highest glossy values ,practically pigmented composite system achieve the maximum color strength and glossy at particle size about 350-200 nm .

Plasticizer has no direct effect on glossy of pigments particle itself as it considered as a solvent for pigment but it has indirect effect on glossy of pigmented composite film by affecting other components as PVC macromolecules by changing its morphology [15, 16, 25, 26]

Table 9 -Effect of high gloss additive on (colored Nano composite of PVC/DEHP)

Ratio	2	3	4	5	6	7
PVC%	20	30	40	50	60	70
DEHP %	80	70	60	50	40	30
Silicon %resin	4	3	2	2	1	-
0% gloss additive	0.8	0.8	0.8	1	1	1.5
2% gloss additive	1	1.4	1.6	3.8	1.3	1.8
4% gloss additive	0.9	1.3	1.1	4.4	0.8	1.1
6%gloss additive	0.8	1	1	1.6	0.8	1.1

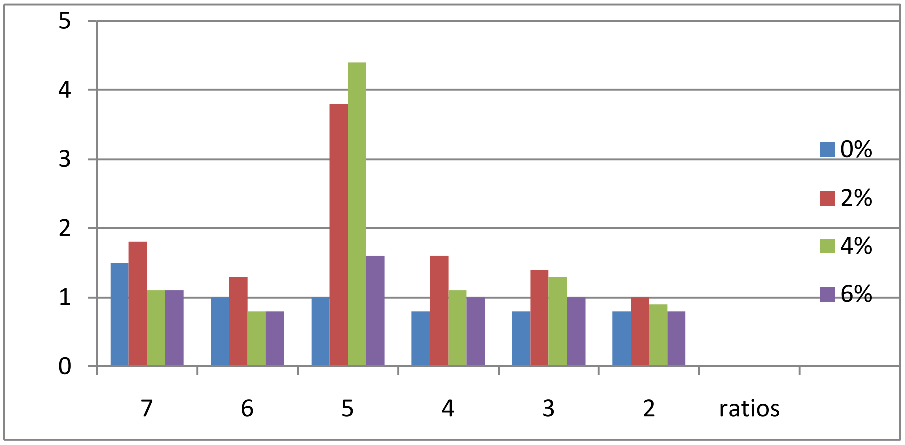


Figure 10 Effect of high gloss additive on (colored Nano composite of PVC/DEHP)

Conclusion

Nano-milling increase the number of particles per unit area so the total surface area was increased, theoretically the color depth and glossy will increase as the surface area increased ,practically the surface area not only the factor that affect the scattered light as the particle size has a specified action on scattered light ,actually the smaller particle size scatter much light until reach critical point , below this point the ability of particles to reflect light at visible area was decreased so the color depth and glossy values were decreased , if the particles reach a very small size it may lose its color.

A specified particle size applied for such purpose, as the particle size which reflect much light suitable as colorants or glossers while the size at which the particles has no ability to scattered light at visible area has a very useful application as finishing substance.

The particle size of such materials which achieve maximum scattered light can be calculated using MIE theory which depending on the reflective index of the particles and the reflective index of the medium and the wavelength of light.

Maximum scattered light depends on reflective index of the particle (n_p), reflective index of the medium (n_m), particle diameter (D) and wavelength of light (λ), according to MIE- theory it can be calculated by the equation:

$D = \lambda / 2.1 (n_p - n_m) * (n_m)$ .So the particle size which reflect maximum color strength can be estimated by this equation.

The color depth depending on the concentration of colorants, its particle size, the dispersion of the colorant into the medium and the medium itself as each medium has specific reflection index.

Finally we can come to the conclusion that: nano-form printing inks and coating materials either colored or clear were successfully investigated with specified applications according to the composite characteristics.

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