



STUDY EFFECTED GRAPHENE OXIDE SHEETS FUNCTIONALIZED WITH POLYANILINE (GOPA) ON DIELECTRIC AND CONDUCTIVITY IN BINARY SYSTEM LIQUID CRYSTALS

Osamah Adnan
Ministry of Education Iraqi

ABSTRACT

Prepared the compound (A) 4,4-bis-[4-methyl benzylidene]-phenyldiamine-(1,4) and (B) 4,4-bis-[4-bromo benzylidene]-phenylen diamine-(1,4). Then a binary system D was created with concentration (0-100%) and found less eutectic point at concentration (60%). This was taken concentration from binary system pure D and measurements of a microscopy polarized and permittivity and conductivity. After taking a mixture pure and has been doping by Graphene oxide sheets Functionalized with Polyaniline (GOPA) to the same measurements observed the increase remarkable properties of graphene oxide (GO) in LC mixtures dispersions.

KEYWORD: Liquid Crystals, Graphene Oxide, Dielectric constant, conductivity, nanoparticle.

INTRODUCTION

Characterization of Graphene oxide (GO) sheets Functionalized with Polyaniline

As already referred, GO contains a variety of reactive oxygen functional groups, which renders it a good candidate for use in a wide variety of applications through well-known chemical functionalization. The detailed structure of GO is still under discussion - since it depends on the chemical oxidation process used to its preparation.

Because of this, models for the GO structure proposed in the literature differ considerably^[1]. In figure (1) shown the structure of GO can be simplistically assumed to be a graphene sheet bonded to oxygen in the form of hydroxyl (C-OH), carbonyl species (C=O), carboxyl (COOH), epoxide (C-O-C) and various C-O and C=O containing chemical species such as lactol, peroxide, dioxolane, anhydride and ether^[2].

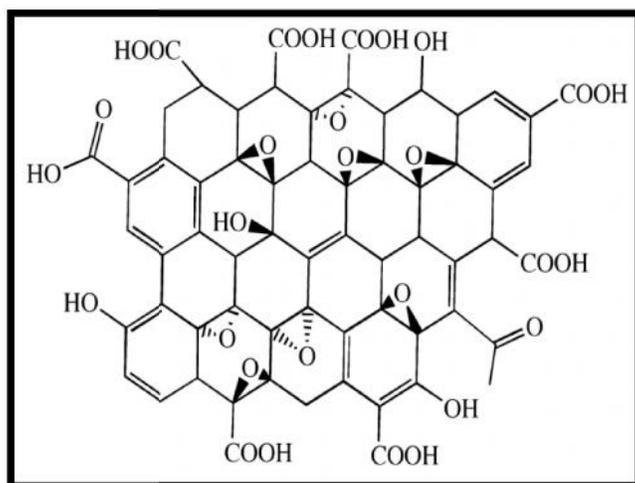


FIGURE 1: Bonding Nature Between Carbon Atoms in Graphene Oxide ^[3]

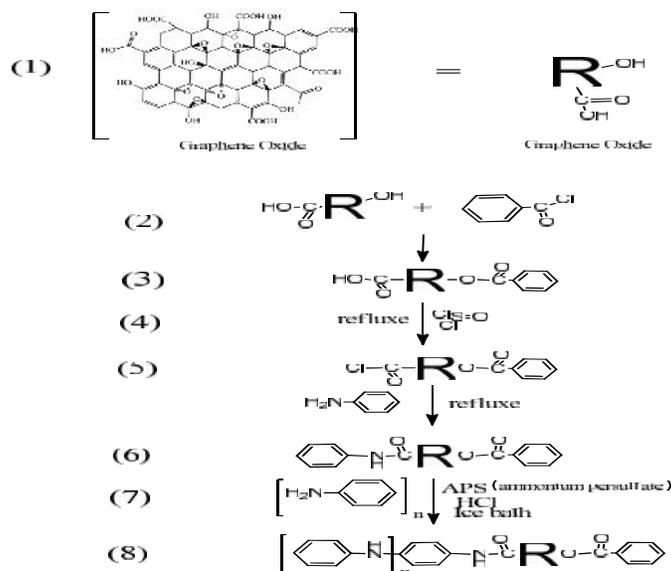
EXPERIMENTAL PART

Chemicals material

Graphite, Acetone, conc sulphuric acid, Sodium nitrate, Hydrogen peroxide, p-Bromo benzaldehyde, p-Methyl benzaldehyde, Phenline diamine, Polyaniline, ammonium

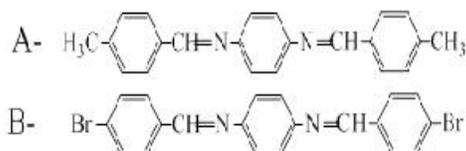
Persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$, Thionyl chloride, Ethanol (Absolute)

Procedures of the step-wise synthesis of Graphene Oxide Functionalized with Polyaniline Sheets



Preparation of binary mixtures

The binary mixtures D are composed of (A) 4,4-bis-[4-methyl benzyliden]-phenyldiamine-(1,4) and (B) 4,4-bis-[4-bromo benzyliden]-phenyldiamine-(1,4). The components have the following structural formula:



The components (A, B) taken a molar fractions and weighed in known proportions and melted together in fusion tubes. They were thoroughly mixed in their melt to obtain a homogenous mixture, after which they were cooled. The solid obtained was finally ground and used for determining transition temperatures, by using polarizing microscope fitted with a heating stage^[4]. Table (1) shows the melting points and a molar fractions with different values of the binary mixtures (D).

TABLE 1: Melting points and a molar fraction of the binary mixtures (D)

Mol % A	M.P(°C)
100	174
90	175
85	173
80	172
75	170
70	169
60	146
50	169
25	185
0	227

Preparation of Graphene oxide functionalized with polyaniline

Thionyl chloride graphene oxide (0.5g) was added to aniline (1mL); the stirred mixture by glass rod for 30 minutes. Then hydrochloric acid (HCl) (5mL) (1

concentration) was added, the mixture was kept stirring at (0°C) and ammonium per sulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$ 3ml solution (2M concentration) was added slowly to the stirred and mixture (20 minutes duration). The mixture was kept stirring at (0°C) for 2hrs. The mixture was kept at room temperature for 24hrs. Then washed with HCl solution (0.1M) and dried. The above precipitate is placed in a beaker (50 ml), and ammonium hydroxide NH_4OH solution (30 ml) (0.5M concentration) is then added with stirring for 1hr. The solution was filtrated and the precipitate is washed using 25 ml distil water and dried. HCl 10 ml (1 M concentration) was added with stirring for 30 min was filtered and dried, the product was filtered and dried, The peripatetic was washed with benzene (15 ml) for 10 min and dried^[5]. The collected peripatetic was 1.67gm.

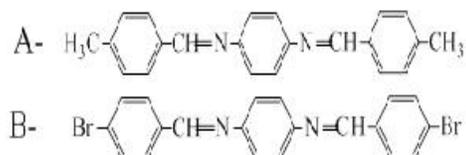
Preparation of binary and tertiary mixtures with Graphene oxide functionalized with polyaniline

Geaphene oxide functionalized with Polyaniline (0.003g) and mixture D{4,4-bis-[4-methayl benzyliden]-phenylen diamine-(1,4). [A]+4,4-bis-[4-bromo benzyliden]- pheny lendiamine-(1,4).[B]}(0.05g) was dissolved in benzene (10mL). Then mixture was taking to the Ulter- sonud device for 15minutes. Then it was left at room temperature for 24 her. Then the mixture has transferred to separator. The solvent was evaporated^[6].

RESULTS & DISCUSSION

Liquid Crystalline Properties and Characterization of mixtures Binary systems

The binary mixtures are composed of two compounds, (A) 4,4-bis-[4-methayl benzyliden]- 1,4-phenyldiamine + (B) 4,4-bis-[4-bromo benzyliden]- 1,4-phenyldiamine. The components have the following structural formula :(D)



Liquid crystalline properties of binary mixtures (D) were studied by the DSC thermo gram and hot-stage polarized microscope. The thermal behavior of this compound was shown in DSC thermo gram Figure (2) which showed two transition temperatures, the first one at 183°C belong to

the transition from crystal solid to the liquid crystal nematic phase, the second at 227.05°C liquid crystal nematic phase to the isotropic liquid phase.

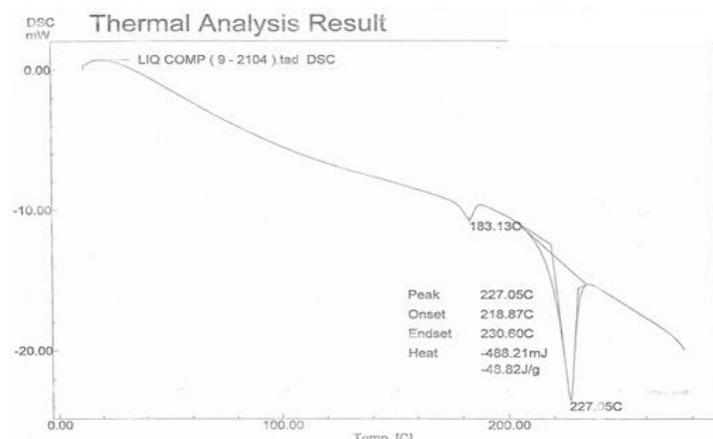


FIGURE 2: DSC thermogram of mixtures binary systems (D)

A liquid crystalline property of these mixtures binary systems (D) was studied using hot stage polarizing microscopy where taken molar fractions with different values and as necessitated cases the diagnosis.

TABLE 2: shows transition temperatures(°C) of mixtures binary system (D) phases

Mol % A	Cr	N	I
100	.	174	.
90	.	175	.
85	.	173	.
80	.	172	.
75	.	170	.
70	.	169	.
60	.	146	.
50	.	169	.
25	.	185	.
0	.	227	.

The table (2): show the binary mixture systems between (A) with methyl terminal groups and (B) with a strong polar Barium atoms as terminal groups, this show a concave down curve mesophase nematic- isotropic transition temperatures, enantiotropic nematic phase Figure (3) possessed wide concentration area (0-100% of

A).This system were show the eutectic (E) transition temperature Cr N(146 ° C) and N I transition at(268) ° C figures (4,5,6) respectively at the concentration region 60% A (mixture D).

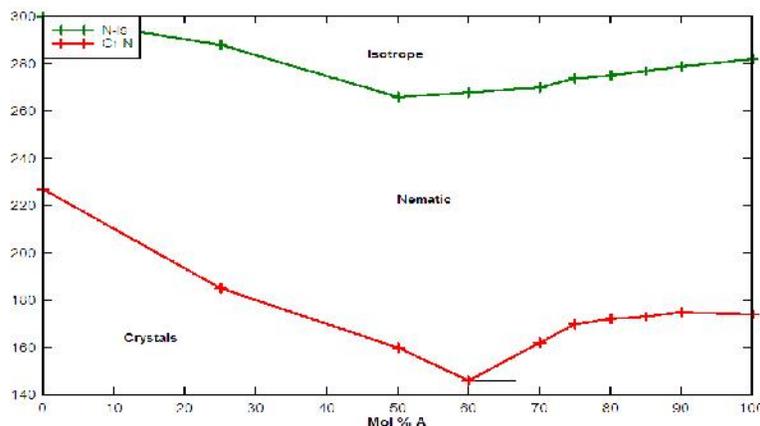


FIGURE 3: Graph of the transition temperature °C to blend the tow compounds (D)

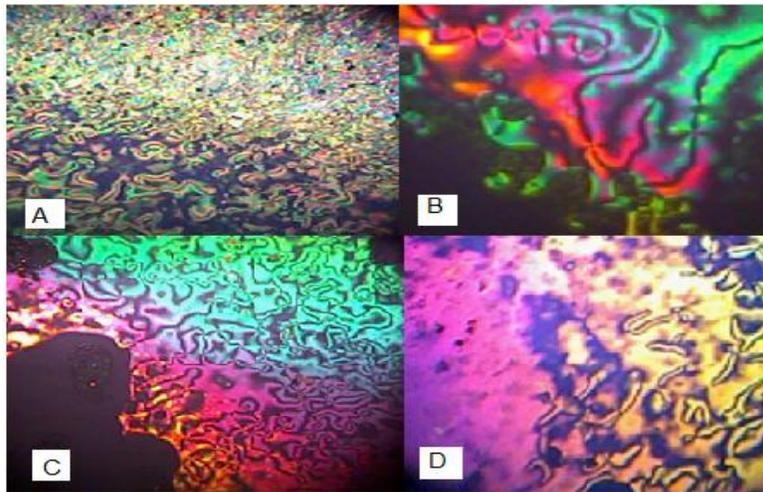


FIGURE 4: Transition phases crystal at(A) nematic thread-like texture of binary systems focus at (25)% (A) (185) °C (60X) (B) Nematic texture at isotropic of binary systems focus at (25)% (A) at (288) °C (C) Nematic schlieren texture at isotropic of binary systems focus at (50)% (A) at (266) °C (60X) (D): Nematic thread-like texture of binary systems focus at (60)% (A) (204) °C (60X)

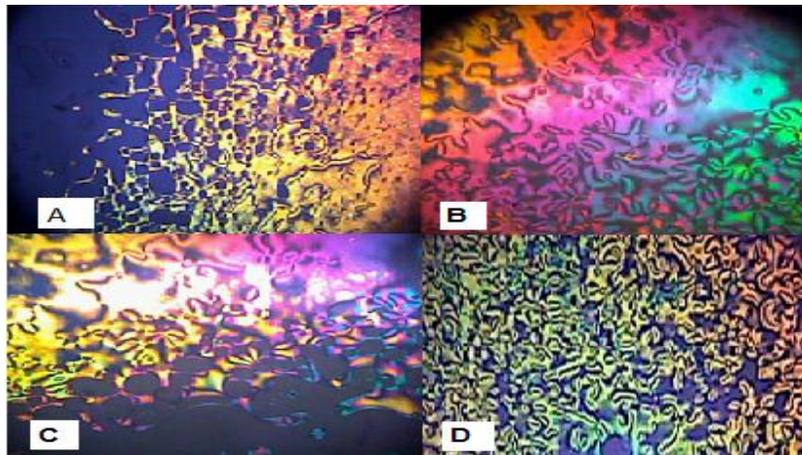


FIGURE 5: Transition phase (A) Nematic thread-like texture at isotropic of binary systems focus at (60)% (A) at (268) °C (60X) (B): Nematic schlieren texture of binary systems focus at (70)% (A) at (266) °C (60X) (C): Nematic schlieren texture at isotropic of binary systems focus at (70)% (A) at (270) °C (60X) (D): Nematic schlieren texture binary systems focus at (80)% (A) at (60X)

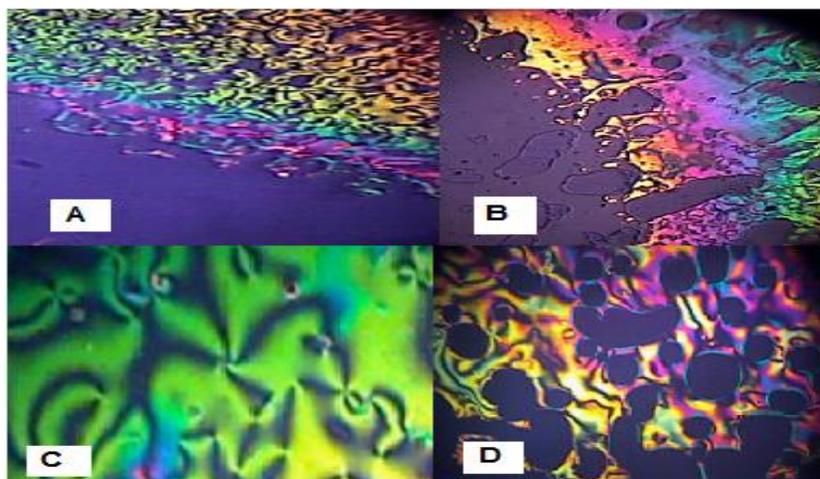


FIGURE 6:Transition phase (A) Nematic schlieren texture at isotropic binary systems focus at (80)% (A) at (275) °C (60X) (B) nematic schlieren texture at isotropic binary systems focus at (85)% (A) at (277) °C (60X)(C):Nematic schlieren texture binary systems focus at (90)% (A) at (245) °C (60X) (D) Nematic schlieren texture at isotropic binary systems focus at (90)% (A) at (297) °C (60X)

FT-IR Characterization of Graphene oxide functionalized with Polyaniline

The resultant showed typical absorption peaks at 3600, a cm⁻¹, broad band as shown in Figure (7). These bands were associated with stretching mode of benzenoid and quinoid rings as well as N–H stretching mode of benzenoid amine groups of PANI, respectively, which

suggests that the PANI had been successfully decorated on the surface of the RGO sheets. The appearance of typical absorption of C=C stretching in benzene rings was at 1608.6 and 1577.7 cm⁻¹. The carbonyl of the ester appeared at 1733.6 and 1458 cm⁻¹ while the C–O stretching of the ester appeared at 1292 and 1249.8 cm⁻¹.

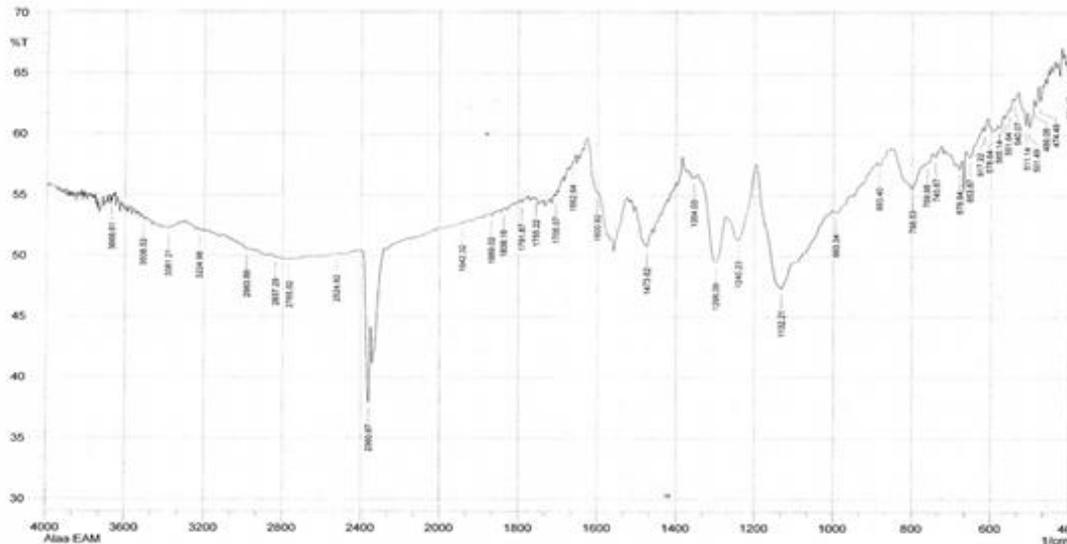


FIGURE 7: FT-IR Spectrum of Graphene oxide functionalized with polyaniline

X-Ray Diffraction of Graphene Oxide Functionalized with Polyaniline

Three new broad peaks of graphene oxide functionalized with polyaniline figure (8) centered at 2θ = 8.3° and broad intense peak at 25.6° and around 43.1° correspond to (001), (002) and (100). Crystal planes are almost the same as that of pure polyaniline as indicate by Kumar [7], which are also the characteristic Bragg diffraction peaks of the polymer. Interestingly, for the GO-functionalized with polyaniline, we observed a weak and broad peak appearing nearly at 2θ = 8.3, which is lower than that of graphene

oxide. This could imply that the interplanar spacing of the graphene oxide functionalized with polyaniline composite was broadened due to possible intercalation of polyaniline and that the graphene oxide was fully exfoliated by treatment with polyaniline. Therefore, the XRD patterns confirm also the formation of polyaniline grafting on the surfaces of the graphene oxide. These results provide further insight and clear evidence for the formation of functionalized graphene with polyaniline from graphene oxide during the process [7-10].

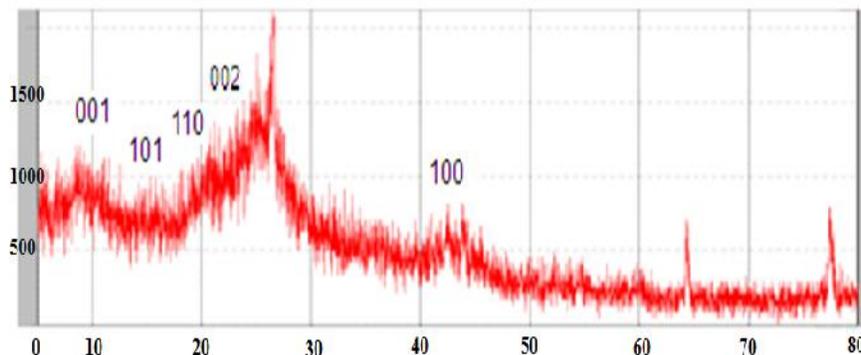


FIGURE 8: XRD of Graphene Oxide Functionalized with Polyaniline

Characterization of nanosheets with Atomic Force Microscope Technique (AFM) and scanning electron microscope (SEM)

On other hand, graphene oxide functionalized with polyaniline (9A) to (9C) show in 2D and 3D image with

the amplitude of the relief lower than 9.21nm figure (9B) and, The mean value of the maximum height of the nanosheets were lower than 9.95 nm figure (3-68), the results of the two type of the nanosheets indicated the accumulation of the nanosheets One above the other. It is

known that the synthesis of graphene materials from reduction of exfoliated GO generally yields samples which are not based on single separated graphene sheets, but rather on an interconnected network with regions of overlapped multiple layers^[11,12]. Conversely figure (9C) show the three dimensions image of the graphene oxide

functionalized with polyaniline nanosheets the relief was about 4.97nm, the accumulation of the sheet about five layers (when the thickness of single sheet about $(1.1 \pm 0.2 \text{ nm})$ ^[13,14], this due to the hydrothermal sheets synthesis method.

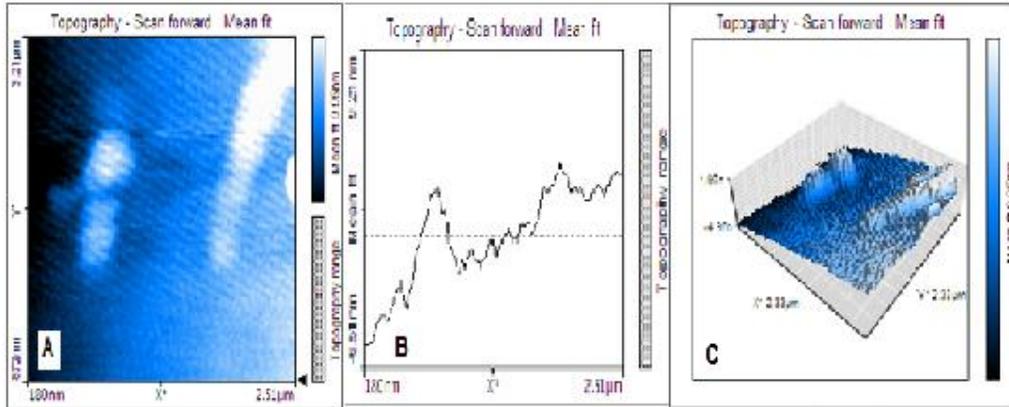


FIGURE 9: (A) AFM 2D image graphene oxide functionalized with polyaniline
 (B) AFM Topography- scan image of graphene oxide functionalized with polyaniline
 (C) AFM 3D image graphene oxide functionalized with polyaniline

These results are supported with SEM images figures (10A) and (10B). The images were show the accumulation of the sheets and look like a bulky shape.

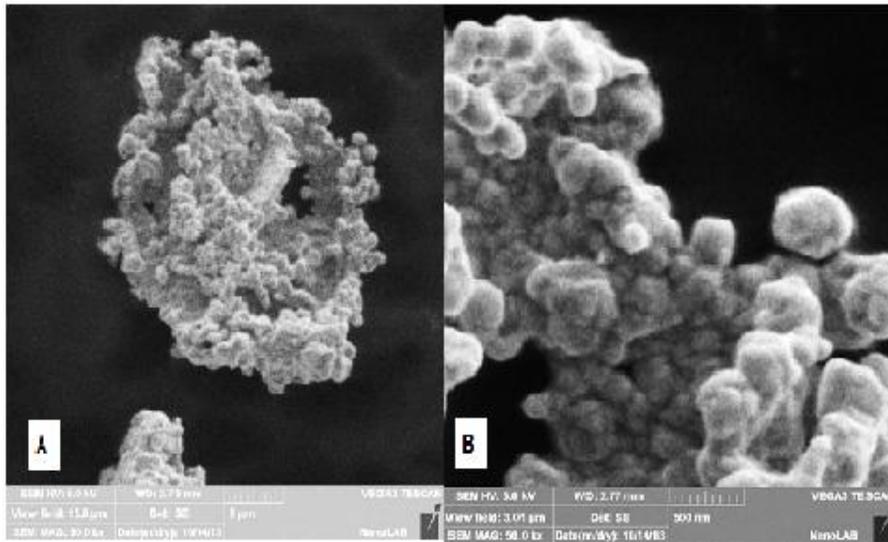


FIGURE 10: (A) SAM 2D image graphene oxide functionalized with Polyaniline
 (B) SAM 2D image graphene oxide functionalized with polyaniline

Study the effect of the nanosheets on the liquid crystalline phases

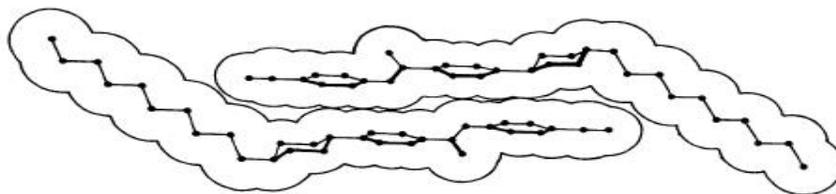


Figure 11:

Nanosheets on the liquid crystalline phases

To study the effect of the nanosheets on the liquid crystalline phases, prepared graphene oxide and graphene oxide functionalized with polyaniline were added as described in section Figure (11), The addition was at the lower eutectic points of the binary (60% A) systems. It is worth noting, that in the two mixtures were appeared a new enantiotropic smectic phase. The figures (12-1) to (12-2) were show the smectic (S_x) phase at different temperature. The appearance of the smectic phase may

illustrate with reorientation of the liquid crystal molecules. These almost may align parallel to the nanoparticle and functionalized nanoparticles. This particular alignment has two effects: first on is the surface energy and on the interaction between the nanosheets and the liquid crystalline molecules, the latter is smaller than the surface energy. The liquid crystal molecules tend to splay rather than bend around the particle, which decreases the energy since splay is allowed for smectic liquid crystals D^[15-18].

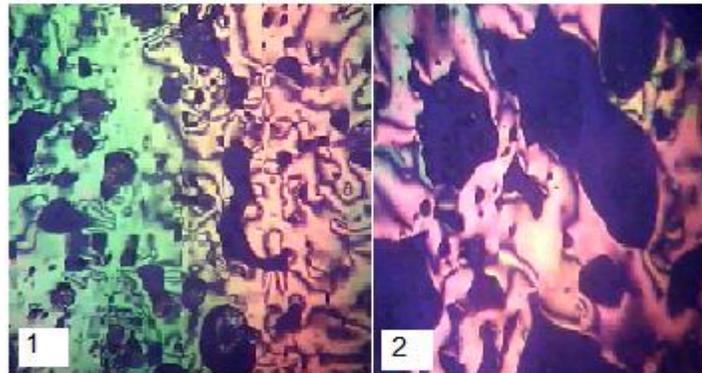


FIGURE 12:1. Transition smactic at smactic (S_x) texture of mix D with graphene oxide functionalized at (220) °C (60X). **2.** Transition smactic at smactic (S_x) texture of mix D with garphene oxide at(217) °C (60X)

Electrical Properties of liquid crystals binary systems

Dielectric permittivity

In this work were divided the data and the figures, each group were show the results of binary pure system measured in 400 and 4000Hz. The figures were depicted

the real, imaginary-permittivity and the Ac conductivity of the measurements, these measurements were performed of binary (60%) pure system measured at the eutectic point concentration with the transition temperatures of Cr-N (146), N-I (268°C).

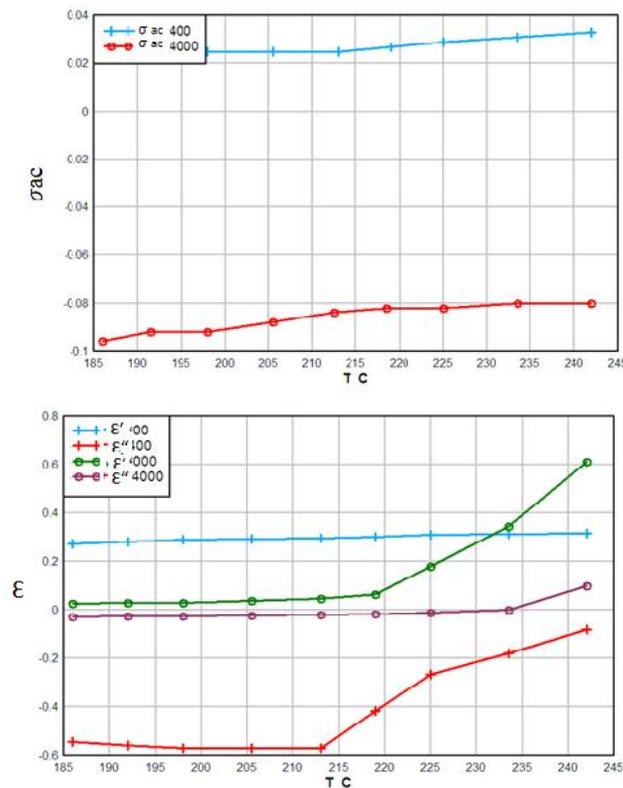


FIGURE 13: Mixture D pure conductivity 400&4000 Hz **Figure (14):** Mixtures D pure permittivity 400 4000 Hz

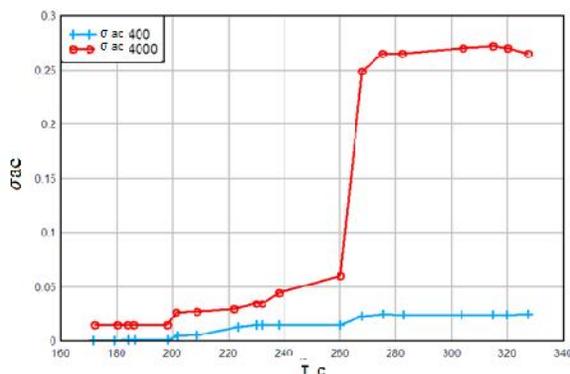


FIGURE 15: Mixture D with graphene oxide functionalized with Polyaniline conductivity 400&4000 Hz

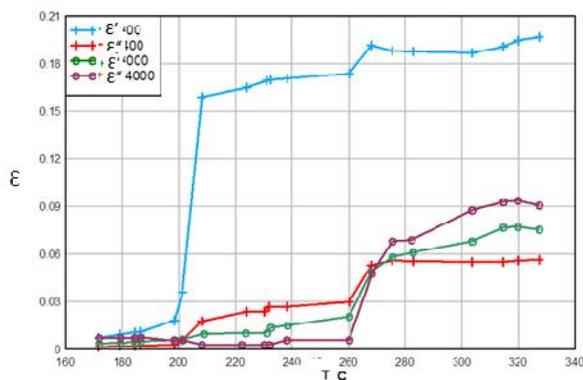


FIGURE 16: Mixture D with graphene oxide functionalized with Polyaniline permittivity 400&4000 Hz

The figures of (14) and (16) illustrated the behavior of ϵ' and ϵ'' of binary liquid crystalline mixture systems with graphene oxide functionalized with polyaniline nanosheets respectively at the eutectic point concentration (60 %) the measurements were performed in smectic, nematic and isotropic phase. All values of ϵ' and ϵ'' were at 400Hz higher than at 4000Hz and increased with increasing of the temperatures except ϵ'' at 4000Hz decreased with the temperatures increasing. The above figures shows changes (jumps) in the components of the permittivity at isotropic / nematic and Nematic /smectic phase transitions. These changes reflect the molecular reorganization that takes place at transitions between different liquid crystal phases. The interpretation of the dielectric properties can be carried out through the differences in orientational order in the phases; this will affect the internal field factors and short range dipole - dipole interactions. Polar mesogens dipole - dipole association is an important contributor to the physical properties of liquid crystal phases, and this is particularly important in smectic and nematic phases, where translational order can affect the dipole- dipole correlation factors^[19-21]. An interesting feature were appeared in the studied concentrations of the eutectic temperature of the mixture in binary, tertiary-system a smectic X phase, this phase was builds its existence after the addition of nanosheets. In order to study the dynamic behavior of this phase were performed by dielectric permittivity at 400 and 4000 Hz with different nanosheets. The figures (14) to (16) shows the limits of dielectric permittivity as a function of temperature in the isotropic, nematic and smectic phases calculated from the experimental data according to Eq. xx. A considerable drop in the permittivity was observed at the isotrope – nematic and nematic- smectic phase transitions. The permittivity was considerably in the isotropic phase for the mixtures higher than the permittivity observed in the mixture containing nematic and smectic phases. This may lead to the conclusion that the dipole moments exhibit parallel correlations with electric field direction in the isotropic phase of the mixtures. Within the smectic and nematic phases the permittivity was practically approximately with little differences or constant. These values were in agreement with the values reported for the pure nematogens as well as in binary mixtures^[22,23].

Conductivity of samples

The binary pure systems figure (13), were doped with graphene oxide functionalized with polyaniline show figure (15), at frequency 4000Hz higher σ_{AC} than in 400 Hz and show a jumps at the transition temperatures, the conductivity were in $Sx < N < I$ phase. This can be described by the hopping of charge transfer, and can be attributed to electronic charge transfer through graphene oxide functionalized with polyaniline. This assumes that the distance of hopping is a minimal distance between then eighboring nanosheets. Similar behavior of σ_{AC} curves for other liquid crystalline – Carbone nanotube system was described^[24].

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