Preparation of unsaturated polyester/nano ceramic composite and study electric, thermal and mechanical properties

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Abstract

The composites were manufactured and study the effect of addition of filler (nanoparticles SiO_2 treated with silane) at different weight ratios (1, 2, 3, 4 and 5) %, on electrical, mechanical and thermal properties. Materials were mixed with each other using an ultrasound, and then pour the mixture into the molds to suit all measurements. The electrical characteristics were studied within a range of frequencies (50-1M) Hz at room temperature, where the best results were shown at the fill ratio (1%), and thermal properties at (X=3 %), the mechanical properties at the filler ratio (2%).

تصنيع متراكبات بولي استر الغير المشبع /نانو سيراميك ودراسة الخواص الكهربائية و الحرارية و الميكانيكة

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الخلاصة

تم تصنيع المركبات ودراسة تأثير إضافة الحشو (الجسيمات النانوية SiO_2 المعالجة سطحيا) بنسب وزنية مختلفة (5 و 4 (1, 2, 3,)%، على الخصائص الكهربائية والميكانيكية والحرارية. خلطت المواد مع بعضها البعض باستخدام جهاز الموجات فوق الصوتية، ثم صب الخليط في قوالب لتتناسب جميع القياسات. درست الخصائص الكهربائية ضمن مجموعة من الترددات (50-1M) Hz في درجة حرارة الغرفة، حيث أظهرت أفضل النتائج عند نسبة التعبئة (1%) والحرارية عند (X=3%)، الخواص الميكانيكية عند نسبة حشو (2%).

Introduction

Recently, nano-technology and scientific interest has created a remarkable result of a new future for the using nanomaterial at (10^{-9} meters). Nano particles could be leading to enhance features radically from traditional materials grain size for similar chemical composition. Nano-particles were using to design new products that work on the unique levels [1-5]. Unsaturated polyester has a molecular weight of low and contains bond carbon double, which is used to be the Overlap links to create additional polymers. This can illustrate overlap process and double in unsaturated polyester. Effective sites in polyester are bond carbon double (Carbon-Carbon) and this bond is called unsaturated, so the polyesters is thermosetting containing these bonds

are called unsaturated polyesters. Unsaturated polyesters possess distinctive qualities of the work of which easily mold release and lamination. Of the most important applications is the ground tiles industry: paint, coating is used in underwater pipelines, aircraft and automotive and marine coatings. Electrical are materials, used in electrical wires and cables and insulators insulating high voltages. Transmission optical line, enter in the sunglasses industry and in the microscope [6-8]. The unsaturated polyester resin that using and chemical composition shown in Fig.1 [9].
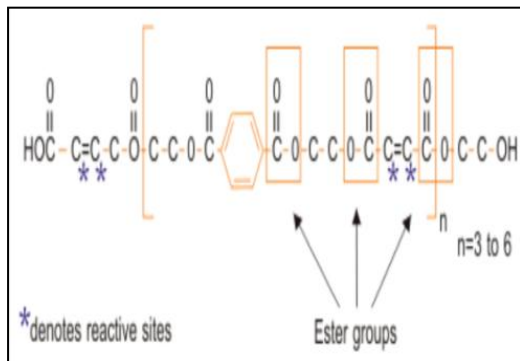

Fig.1: Unsaturated polyester [9].

The composite is classified as microscopic crusting, when it's complete delaminated sheet filler in primary size of the nanometer scale, where arise spaces between of the platelets causes loss patrol the arrangement for platelets completely. This happens when the electrostatic forces of interaction between the plates has been completely overcome by the polymer chains in the composite material as shown in Fig. 2 [5]. This research aims to study the properties of unsaturated polyester resin, reinforced surface treatment silica nanoparticles for use in industrial fields.
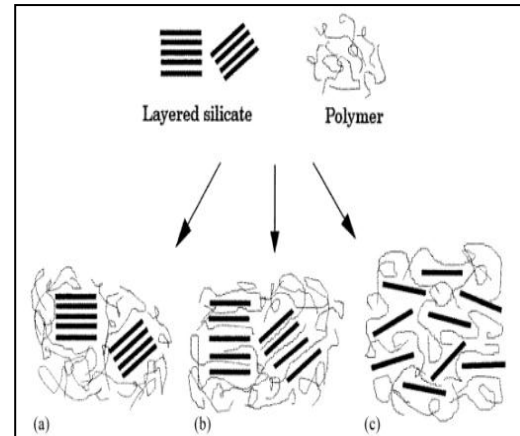

Fig.2: Schematic representation of the different types of composite materials generated on the basis of the interactions of the silicate layers with polymer matrices. (a) the separation of the small boat stage, (b) nanocomposite intercalated and (c) nanocomposite crusting [5].

A number of ceramics, polymers, such as isolators and / or capacitors are used; because they have a high degree of stability in its dimensions and distinctive mechanical properties. Characteristic applications comprise in power lines and electrical insulation, the rules of the switch, and light vessels. Since some the polymers have greater dipole moments, so, its own a dielectric constant (K) less than ceramic. The values (K=2 and 5) for polymers, commonly used these materials to insulate wires and generators, in addition to that, it used in some of the capacitors [10-12].

Materials and characterizations
Materials

Unsaturated polyester was used in this research as matrix matreial, where physical state (Liquid), density (1-1.3) g/cm^3 and color (yellow). The resin from company (Saudi Industrial Resins Limited).

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Use silicon oxide nanoparticles (SiO₂) as filler. Particle size (10-30 nm), purity (99%), treated with silane coupling.

Preparation of samples

Pure UP prepared with hardener material using a methyl ethyl ketone peroxide (MEKP) addition ratio is (0.5 gm), to (100 gm) of UP resin. It has been used an auxiliary material for solidification process (cobalt Actoate), at addition ratio (0.02 gm) to (100 gm) of resin [13].

UP/nanocomposite samples were prepared by weight Nano SiO₂ in different percentage (1, 2, 3, 4 and 5) wt% mixed with Up by ultrasonic instrument for 3 minutes and keep for 24 hours to hardening, thereafter samples were placed in an oven electric at 70 °C to complete the hardening process. Table 1 shows the weight ratios (%) of silicon oxide nanoparticles (SiO₂) additives for unsaturated polyester resin.

Table 1: Weight ratios of unsaturated polyester resin, silicon oxide nanoparticles (SiO₂, Catalyst % and Hardener %.

UP % (Unsaturated polyester resin)	Nano(SiO₂)% filler	Catalyst %	Hardener %
97.96	1	0.04	1
96.96	2	0.04	1
95.96	3	0.04	1
94.96	4	0.04	1
93.96	5	0.04	1

Tests

1-Electrical properties

The test includes the dielectric constant, loss tangent ($\tan\delta$) and the imaginary dielectric constant at voltage 10 mV, ranging from (50 Hz-1 MHz), using LCR meter model (RS-232,Taiwan, LCR-8000G, Drive Signal Level AC(20 Hz-5MHz) (0.01V~2Vrms), as shown in Fig.3. The dielectric constant, loss tangent ($\tan\delta$) and the imaginary dielectric constant were calculated by using the equations as following [13]

$$K = \frac{dC}{A\varepsilon_o} \qquad (1)$$

where
K: Dielectric constant, d: thickness of samples, C: the capacitance

$$\tan\delta = \frac{k'}{K} \Rightarrow k' = \tan\delta * K \qquad (2)$$

k': Imaginary dielectric constant, where the $\tan\delta$ values are taken from the LCR meter instrument.

Fig.3: LCR meter.

2- Mechanical properties.

The stress-strain properties by using tensile instrument, as in Fig.4 according to ASTEM (D882). Modulus of elasticity, tensile strength, percent

elongation at break and percent elongation yield were tested by this instrument and the initial gauge length speed were fixed at 0.001mm/min. Young modulus calculated by eq.

Young modulus= stress/ stress   (3)

Fig.4: Tensile instrument.

Impact strength testing was carried out by impact device, on non-notch samples, Impact strength was obtained from the following relation

Impact Strength= Fracture energy (KJ) / Area (m^2)   (4)

Hardness

The shore hardness (D) instrument was using to measure the resistance of the material plastic deformation at the surface areas of which when a vertical force pressed on the sample surface using indenter tool under a stationary load, a large of plastic distortion occurs. Readings appear on the screen of the device indicate the value of the hardness under examination and taken three readings for a more accurate result. Fig.5 refers to hardness shore D.

Fig.5: Hardness shore D.

3- Thermal properties

C-Therm TCi^{TM} Thermal Conductivity Analyzer technique was used in this study to measure the thermal conductivity of the samples. This technique is based on the method of transient plane source method. Non-invasive nature of C-Therm sensors allow for testing materials of any size in the site or in the lab without destroying the sample. Moreover, the test can be done in seconds with a consistent and accurate result. Fig.6 shows an image C-Therm TCi^{TM} Thermal Conductivity Analyzer device (SETARAM Instrumentation).

Fig.6: C-Therm TCi^{TM} thermal conductivity analyzer device.

Differential Scanning Calorimeter DSC

The device of the type (DSC-60/Shimadzu) was used that gives a comprehensive survey of the temperature of the specimen and includes the glass transition of amorphous polymers which is characterized by the gradual change of thermal capacity with the change of temperature that depends on the heating rate.

Rustle & discussions
1- Electrical properties

Fig.7 shows dielectric constant values (K) with applied frequencies (50- 1M) Hz in (R.T). The figures show correspond in dielectric constant value for all ratios(X=1, 2, 3 and 4) %

respectively. The dielectric constant values at F≈ $(1 – 4)*10^5$ Hz have a little change at high frequencies, this because the dipoles at little frequencies respond to the vicissitudes in electric field. At high frequencies only electronic polarization is remains dominant. The (K) increases for unsaturated polyester resin which contains fillers (surface treatment silica nanoparticles) increases, this called interfacial polarization. In general, Fig.8 shows that, the (K) at 50Hz, decreases with increases of the amount percent of fillers(surface treatment silica nanoparticles) in samples, However, this behavior changes at 1MHz becomes random with increasing ratios of added fillers, leads to change the space charge polarization and consequently decreases the dielectric constant values, but at comparing the dielectric constant values with the standard values at frequency (1MHz) of the polymer(unsaturated polyester resin), we find at all ratios of added fillers the dielectric constant values are greater than standard values at 50Hz.

Table 2 shows the dielectric constant values with the standard at 50 and 1 MHz. Samples manufactured (composite) are generally higher (dielectric constant values) compared to polymeric materials. In essence they contain ions and polar groups that contribute to the higher (K) of their own. Air has of (K=1.02) which fills the spaces and this value is fixed in isolators at low and high electrical frequencies [10]. A low (K) is required mainly as insulators named inert electrical materials. Ranging applications in isolated conductors carrying the signal from each other, and the rapid spread of the signal, an insulator interfaces to reduce time (T_{RC}) factor and power dissipation in high -rate. They are in need of very dense multilayer IC's, where the coupling between very close to the metal lines need to repression to prevent deterioration in the performance of the device. This role involves electronic packaging; they separate interlayers and provide isolated paths to connect electronic devices in IC's [10].
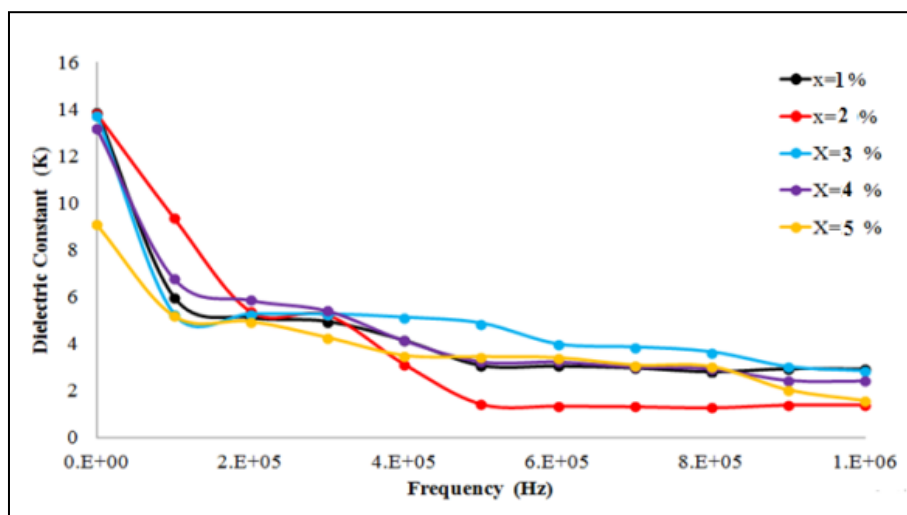

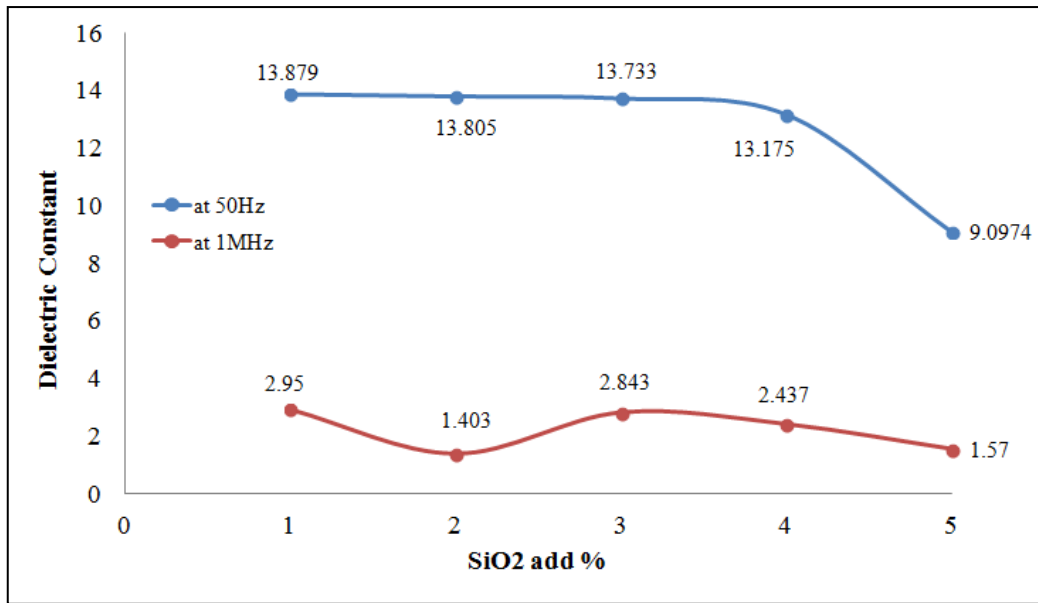**Fig.7: The (K) values with frequencies for composites (unsaturated polyester resin with filler.**

Fig.8: Dielectric constant (K) for UP/ nano SiO₂ composite (unsaturated polyester resin with filler) at 50Hz and 1MHz.

The (K`) is plotted with frequencies (50-1 M) Hz in Fig.9. In general, Increases of (f $>10^4$) Hz lead to the decreases of the Imaginary Dielectric Constant (K`), due to an increase in energy loss and this occurs due to the rotation of polar groups.

Fig.9 refers to absorption energy maxima at f= $4x10^5$Hz, this exhibits high values of (K`) at this frequency depending on Eq. (tanδ=K`/K), this zone corresponds as a rule to the area of noticeable relaxation losses. Also note that all of Fig. 10.
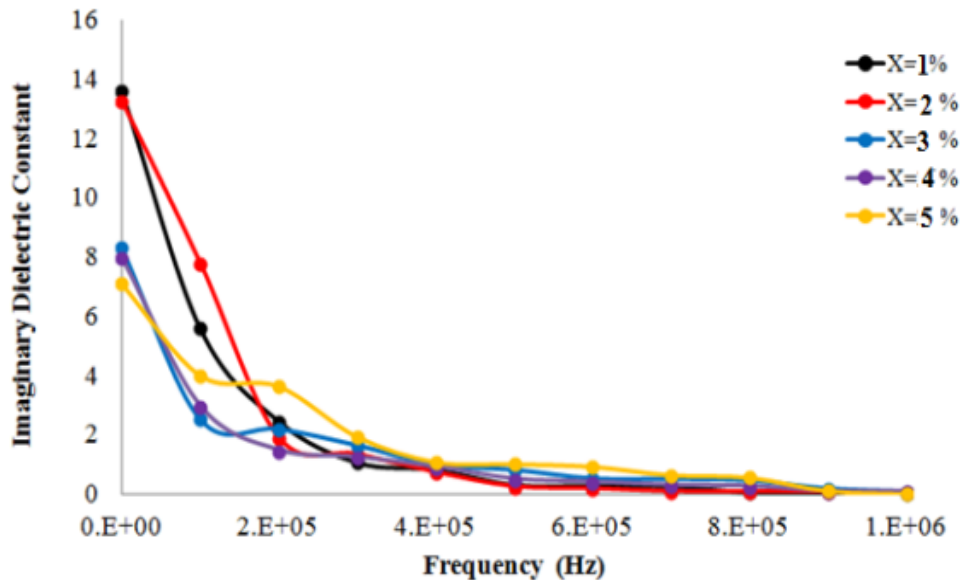
Fig.9: The (K`) values for UP/nano SiO₂ composite (unsaturated polyester resin with filler).
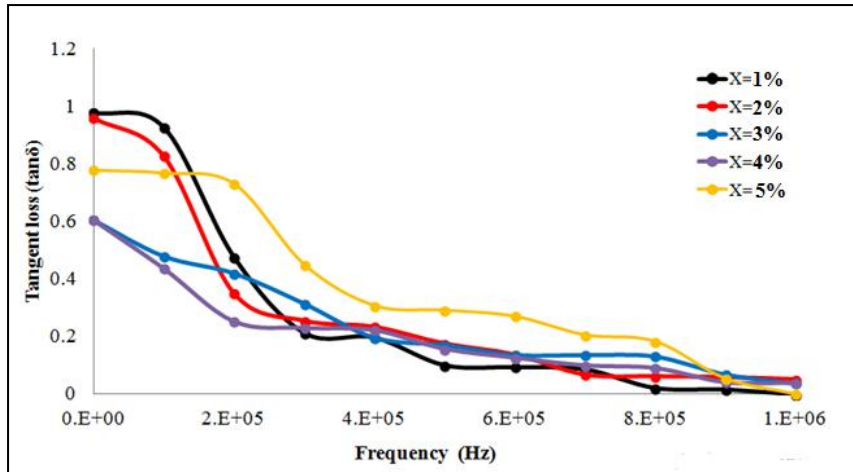
Fig.10: Tanδ for composites (unsaturated polyester resin with filler.

Table 2: Dielectric constant and tanδ values at 50 and 1MHz.

X(%) nano SiO_2	0 [14]	1		2	3	4	5
Dielectric constant at 50Hz	10.7	13.879		13.805	13.733	13.175	9.0974
Dielectric constant at 1MHz	-	2.95		1.403	2.843	2.437	1.57
tanδ	0.0125	0.0002		0.0522	0.0373	0.0399	0.0004

2- **Mechanical properties.**

Fig.11 shows the curves of (stress-strain) of UP appear that less elastic modulus because the resin from of brittle materials in terms of resistance to tensile, while at add nano SiO_2 at X= (1, 2, 3, 4 and 5%) lead to improve or increasing elastic modulus as shown in Fig.12 Due to the effect of the spacing between the particles and case agglomeration Additive material, which causes an increase in the rate of free path and that appear in Table 3.
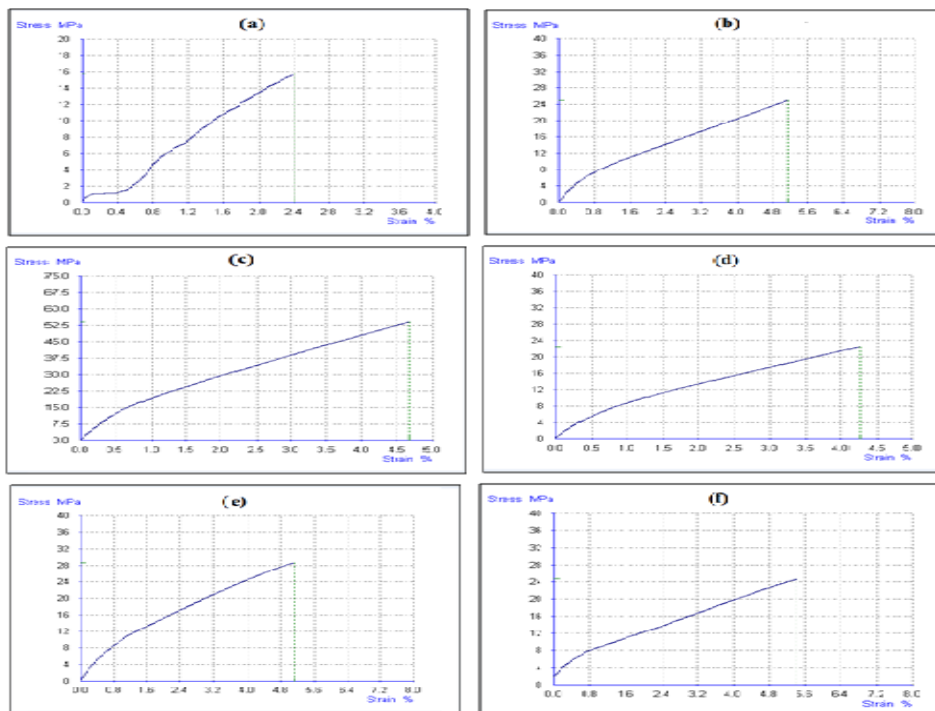

Fig.11: (a, b, c, d, e and f) (stress-strain) curves for pure UP and UP/ nano SiO_2 composite at X= (0, 1, 2, 3, 4 and 5%).
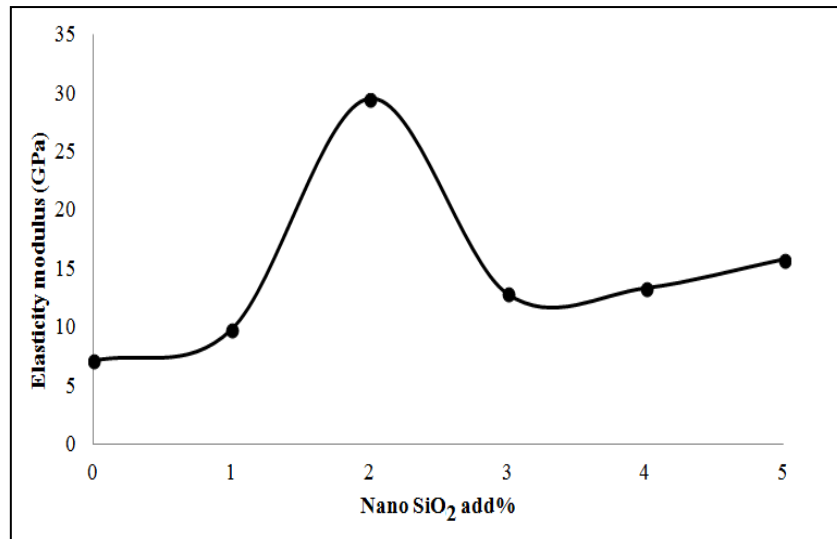
Fig.12: Elasticity modulus with filler for all samples.

Yield strength was estimation from Fig.13 for specimens, where Yield= (Yield load/original area). Yield was a measuring of the strength that the material can withstand before suffering macroscopic plastic deformation. For most materials, for example, minerals, taken as a Point on the stress-strain curve of the line when it becomes non-linear (elastic limit).However, the plastic is taken as the height of the stress-strain curve. The yield strength is a key feature when designing parts. Often added fillers because it increases the yield strength of the polymer, and this effect called reinforcement if the modulus is also improving. The explanation for strengthening lies in the fact that the addition of filler really changed the polymer phase. It has been shown that the polymers react with the surface of the filler, interphase and the formation of polymer adsorbed [13].

Note that the yield strength increases with fillers compared with the value of the yield strength of the polyester without adding. There are several factors that determine the level of reinforcement achieved by adding filler included, the volume fraction of the filler and added that the surface area of the filler, the shape of the particles, and the level of adhesion between polymer and the filler as well as the nature of the interphase between the two phases and the thickness. This should be the improvement is due to the large area of the filler such as the properties of the filler. Large surface increases polymer adhesion filler and thus improves the yield strength [10].

Table 4 Elasticity modulus (GPa), Tensile (MPa), Max Force (N), Elongation% and for composites (unsaturated polyester resin with filler (silica nanoparticles)).
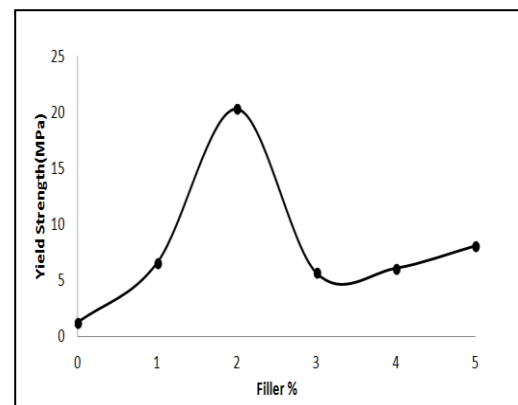

Fig.13: Yield strength with filler for samples.

Plotted the fracture energy and impact strength with ratios additive in Figs.14 and 15. Fig.14 show that the fracture energy (KJ) is higher in UP/ nano SiO_2 composite for (X=2% silica nanoparticles) than fracture energy

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unsaturated poly ester (x=0). When strengthening the polymeric material in Nano particles, the surface fracture energy of these polymers will increase, as these particulate fillers will work to hinder the growth of micro-cracks where the increase of toughness is by fillings ability on the impediment the fracture and turn it causing increased surface area of the fracture, when adding nanosilica particles at X= 2%, become obstruction process the

fracture less, due to decreases in the inter distance and therefore nanoparticles working on the distribution of stress to give more space. Either impact strength values at the rest of the ratios may explain the material matrix is not sufficient to bind silica nanoparticles and distributed homogeneously within the polymer composite at these concentrations leading to weakness in the polymer composite structure in general.
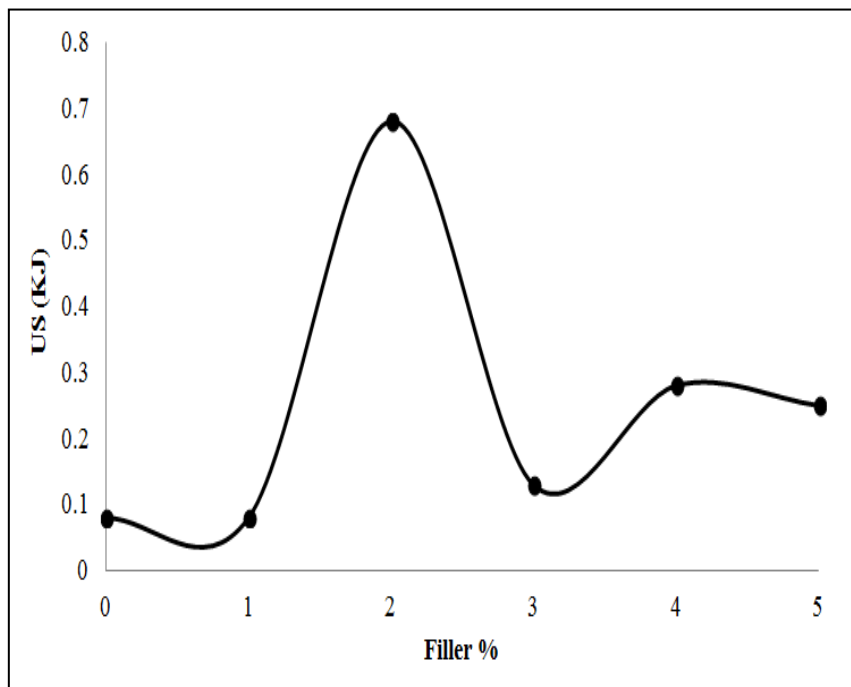
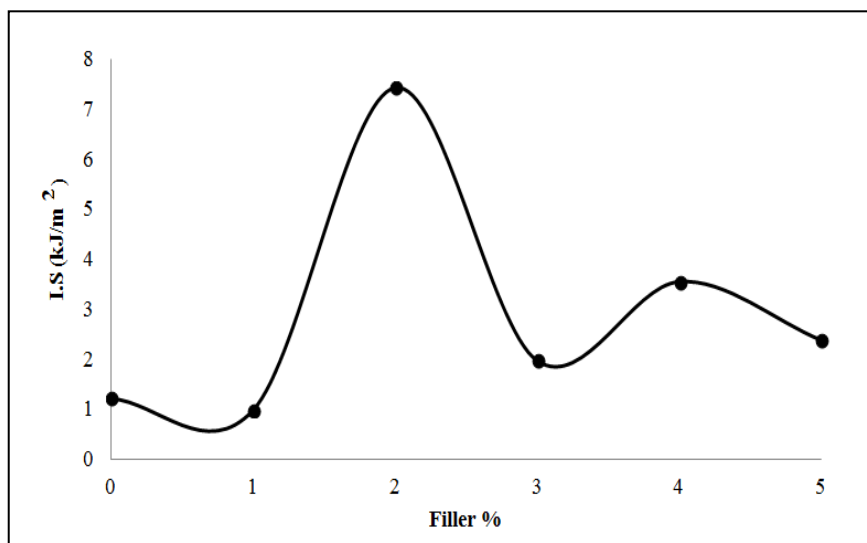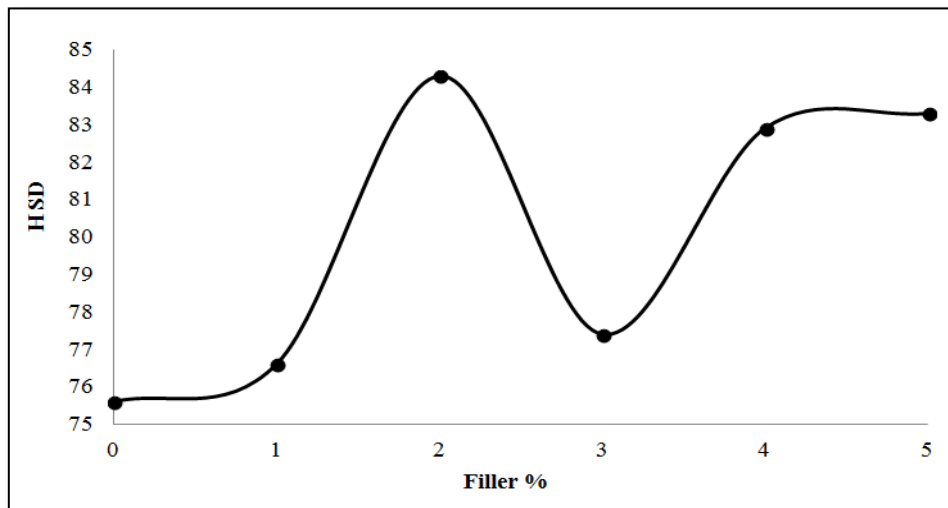*Fig.14: Fracture energy (KJ) with filler for all samples.*

Fig.15: Impact strength with filler for all samples.

Table 3: Elasticity modulus (GPa), Tensile (MPa), Max Force (N), Elongation% and for composites (unsaturated polyester resin with filler (silica nanoparticles)).

X(%) nano SiO$_2$	Elasticity modulus (GPa)	Ultimate Tensile Strength (MPa)	Max Force(N)	Elongation at max (%)
0(pure)	7.1429	15.76	1301	2.4
1	9.795	25.06	2103	5.16
2	29.474	54.1	2000	4.680
3	22.70	12.857	1686	4.260
4	28.77	13.333	1898	5.12
5	24.68	15.789	2295	5.40

Composites possessed hardness value higher than the value of the unsaturated polyester with increased the ratios added as shown in Fig.16

due to the silica Nano particles itself has high strength and hardness, which led to increased hardness composites.

Fig.16: Hardness shore D with filler for all samples.

Table 4: Fracture energy (KJ), Impact strength (KJ/m^2) and Hardness shore D for composites (unsaturated polyester resin with filler (silica nanoparticles)).

X (%) nano SiO$_2$	Fracture Energy (KJ)	I.S (KJ/m^2)	HSD
0	0.08	1.205	75.6
1	0.08	0.97	76.6
2	0.68	7.42	84.3
3	0.13	1.96	77.4
4	0.28	3.54	82.9
5	0.25	2.4	83

3- Thermal properties

Fig.17 Illustrates the behavior the thermal insulation of the composites at increasing the ratio of Nano silica addition. There is an increase and

decrease in the thermal conductivity value with the increasing of Nano silica addition, the highest value of thermal conductivity (k=0.88W/m.k) at X= 2%, the lowest value

(k= 0.33 W/m.k) at X= 3%, is due to thermal energy transmission (Phonons), where Nano silica has taken sites between the polymer molecules become part of structure which made thermal energy transport (Phonon) at 10% higher than at the rest of ratios, especially at x=3% because the problem of agglomeration between the polymeric chains this agglomeration leads to reduce transmission all phonon, thermal conductivity became less. From same Fig.17 shows the results of the thermal diffusivity for the samples of

composites (unsaturated polyester resin with filler (silica nanoparticles) adding). It can be noticed from the figure for the samples that the value of the thermal diffusivity increased and decreased with the increasing of filler. Figs.18-22 show the DSC parameter such as Tg and Cp of UP/ nano SiO_2 composite, note from the curves how to change temperature glass transition for UP/nano SiO_2 composites. Table 5 Thermal properties for composites (unsaturated polyester resin with filler (silica nanoparticles) adding).
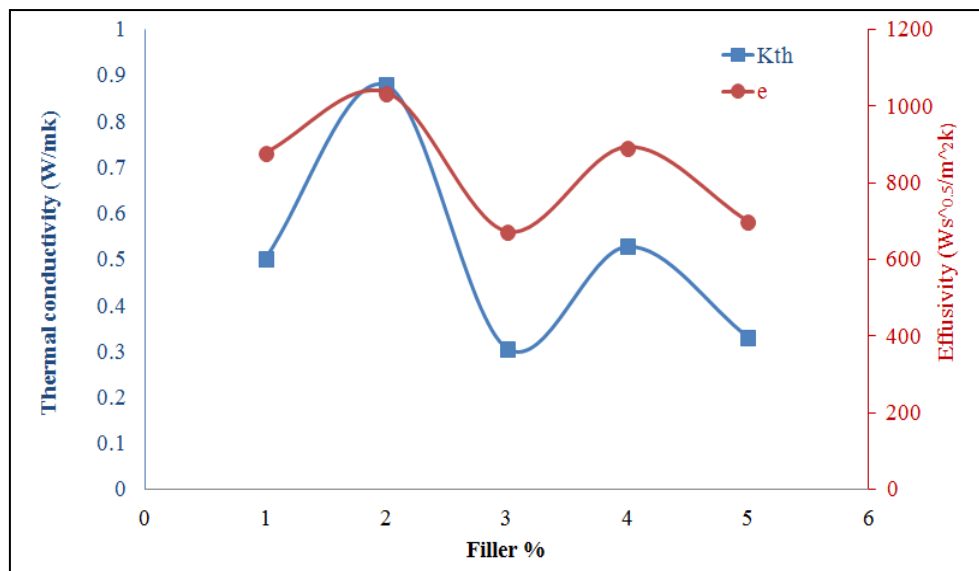

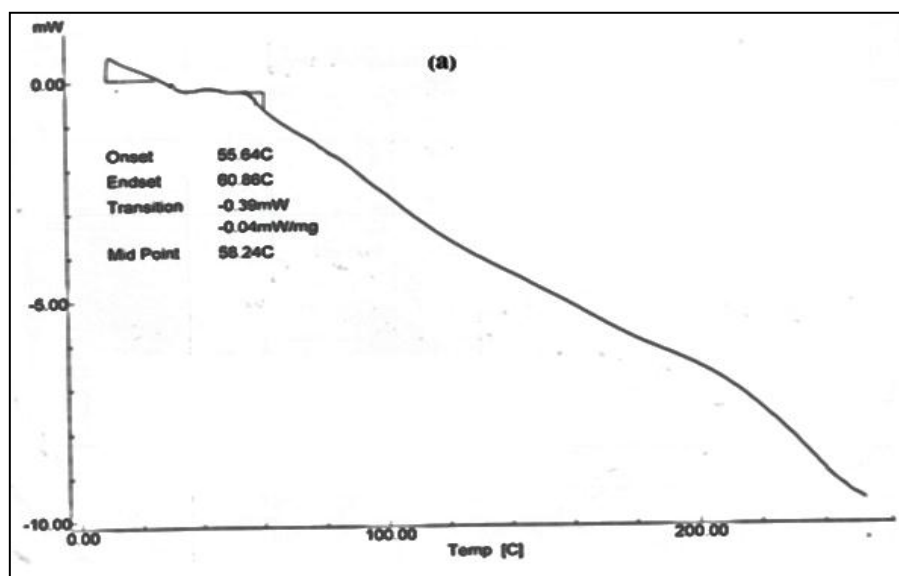*Fig.17: Thermal conductivity for UP/ nano SiO₂ composite with ratios of added fillers.*

Fig.18: (Temperature glass transition) curves for UP/ nano SiO₂ composite at X= (1%).
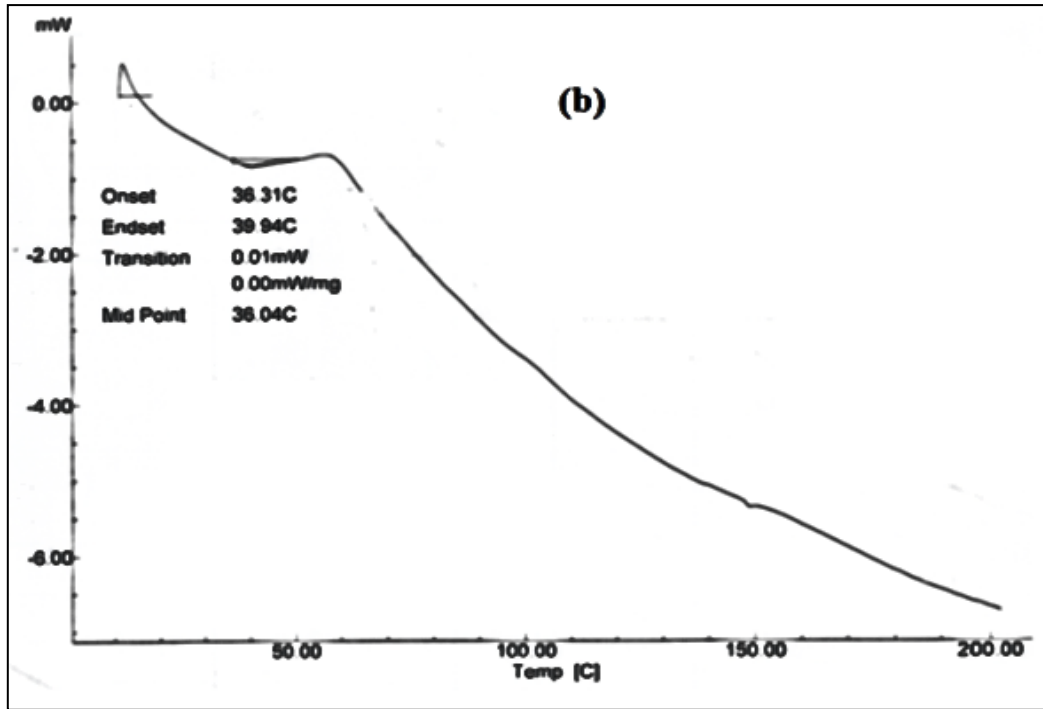
Fig.19: (Temperature glass transition) curves for composites (unsaturated polyester resin with filler (2%).
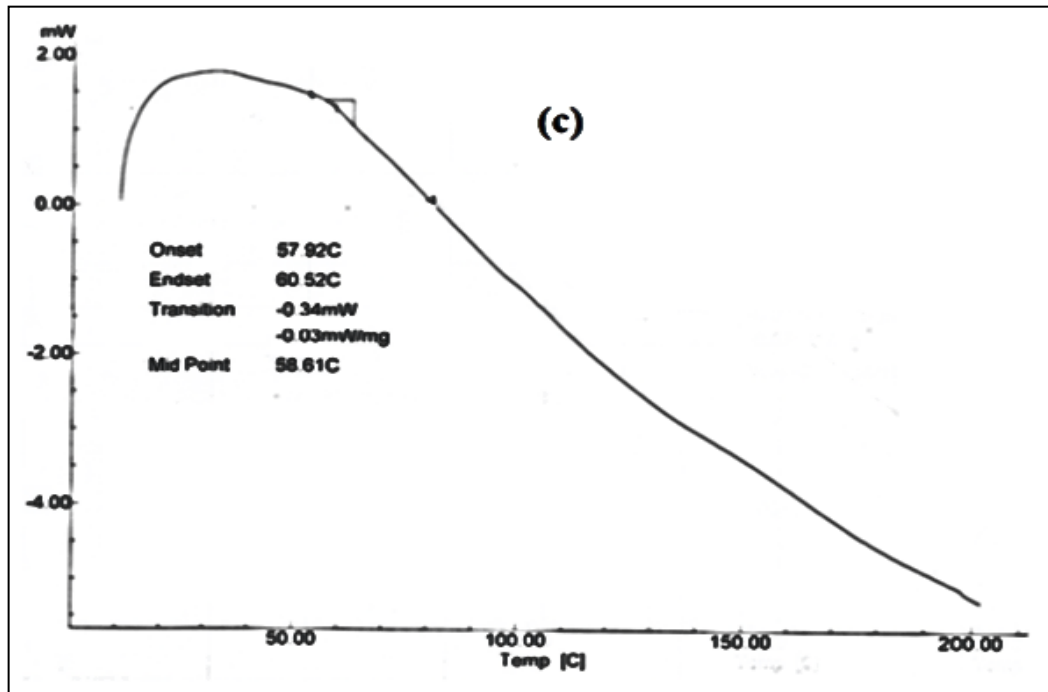

Fig.20: (Temperature glass transition) curves for UP/ nano SiO₂ composite at X= (3%).
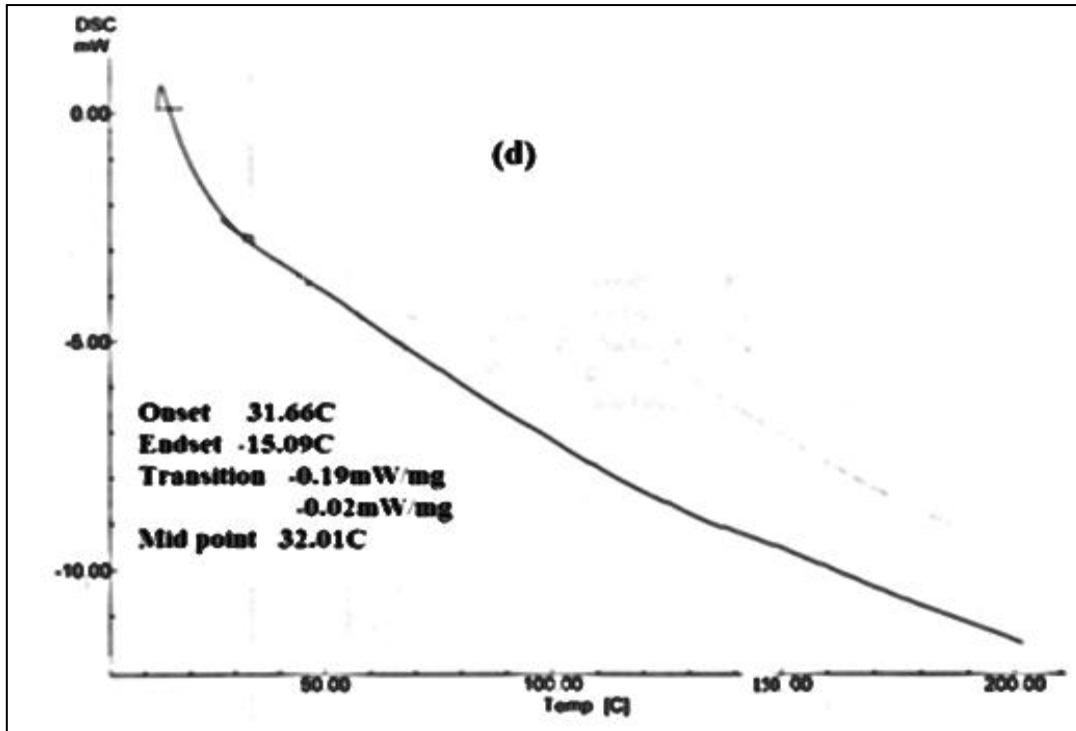
Fig.21: (Temperature glass transition) curves for UP/ nano SiO₂ composite at X= (4%).
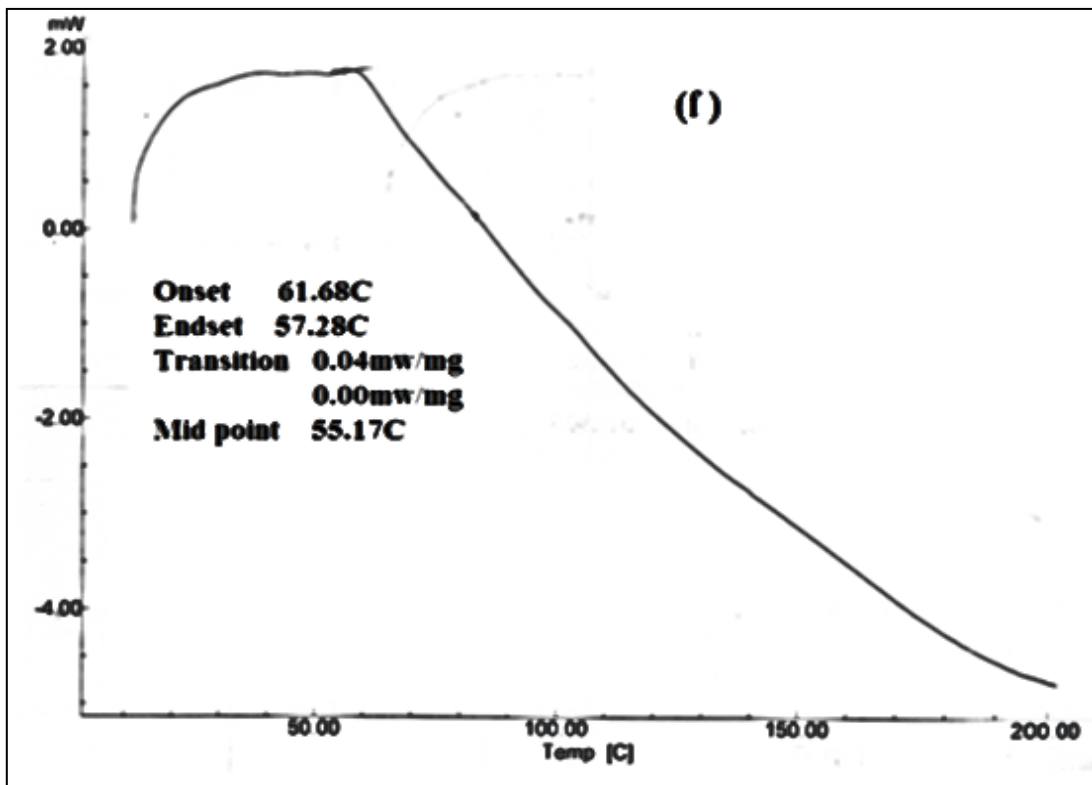

Fig.22: (Temperature glass transition) curves for UP/ nano SiO₂ composite at X= (5%).

Table 5: Thermal properties (K_{th}(W/m.K), E(W/$S^{0.5}m^2$K), Cp(J/Kg.K , Tg) for UP/ nano SiO$_2$ composite at X= (1, 2, 3, 4 and 5%).

X(%) nano SiO$_2$	K_{th}(W/m.K)	E(W/$S^{0.5}m^2$K)	Cp(J/Kg.K)	Tg
1	0.502167	878.416	11.45617	58.24
2	0.88	1035.314	9.094941	36.04
3	0.307	674.4	12.96087	58.61
4	0.52833	894.0167	13.07278	55.17
5	0.330833	700.25	12.56662	32.61

Discussions

1- The electrical properties of UP/nano silica composite samples were evaluated. The investigation revealed that the composite samples exhibited better dielectric constant and dissipation factor when compared to the neat resin, as especially when x= 1%, because tanδ=0.0002 at 50Hz.

2- Improve the mechanical properties of the values of the unsaturated polyester resin aft Improve the mechanical properties of the values of the unsaturated polyester resin after strengthen it silica as especially when x= 2%,where can used it in the made the packaging materials heavy duty.

3- The best thermal conductivity and Tg values for UP/ nano SiO$_2$ composite samples at X= (3%), because of high thermal insulation where the thermal conductivity is equal 0.307 to the addition Tg=58.61 to give it a high thermal stability.

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