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Mechanical Properties Of new Composite Unsaturated Polyesters Based on Nano Fillers for Marine application

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Abstract. Monomers of phathalic acid mono-(4-carboxy-phenyl) ester (AC1) and But-2-enedioic acid mono (2-carboxy-phenyl) ester (AC2) were synthesized from phathalic anhydride with p-hydroxy benzoic acid and maleic anhydride with salicylic acid ,respectively. The new unsaturated polyester resins were made through condensation reaction between the dicarboxylic acid and polyols in the presence of p-Toluene sulphonic acid as catalyst. In addition , solubility of prepared unsaturated polyesters was measured and the solubility of its was good in a polar protic solvents such as DMSO , CH_2Cl_2 , THF , DMF , acetone and some non-polar solvents such as Benzene and CH_3Cl , while it was a little solubility in both H_2SO_4 and HCl. The chemical structures of these monomers and new unsaturated polyesters were confirmed by FTIR , ^{1}HNMR. Thermal analysis of polyesters by thermo gravimetric analysis (TGA) reveals that these Aromatic polyesters possess thermal stability, differential scanning calorimetry (DSC). Carbon Nano and Nano TiO_2 reinforced polyester composites. The mechanical properties (tensile strength , elongation at break and hardness) were studied.

Key words: Unsaturated Polyesters, Nano Fillers, Composite, dicarboxylic cid, polyols

Introduction

Unsaturated polyesters are condensation polymers formed by the reaction of polyols and polycarboxylic acids with olefinic unsaturation being contributed by one of the reactants, usually acid. The polyols and polycarboxylic acids used are usually difunctional alcohols (glycols), and difunctional acid such as phthalic acid and maleic acid. Water is produced as by-product of the esterification reaction and is removed from the reaction mass as soon as it is formed to drive the polyesterification reaction to completion. In the last stages of the reaction, the decrease in carboxyl group concentration is slow and the increase in viscosity is fast[1,2]. These last stages are usually followed under vacuum. However, in order to avoid loss of volatile reactants an azeotropic distillation of water in the presence of added organic solvents, such as toluene or xylene may be used . The main drawbacks of this process are longer reaction time and difficulty in removing the last traces of solvent [3]. Unsaturated polyesters (UP) are the macromolecules with a polyester backbone and belong to category of the thermoset resin. These are step growth product of saturated acids (such as phthalic or isophthalic acid) and unsaturated acids (such as maleic or fumaric acid), condensed with a dihydric alcohols. The UP

resins can be easily handled in processes like hand layup, filament winding, resin transfer moulding in the liquid form. They can also be used in moulding compounds[4]. Moreover, they possess good mechanical and service properties, have excellent thermal stability and weather resistance. Hence, these resins are used in a number of application like insulation coatings, fiber reinforced plastics (FRP) products, sandwich panels, sheet moulding compounds (SMC), bulk moulding compounds(BMC), perfusion components etc.[5]. The curing of UP resin occurs as a combination of chemical kinetics and control by diffusion. The curing reaction between the styrene monomer and UP involves a free radical chain growth polymerization. During the curing process at room temperature, generally the organic peroxides (like methyl ethyl ketone peroxide(MEKP) are mostly used as catalysts (initiators) while cobalt salt is frequently used as an accelerator[6,]. The use of polymer matrix composite has found wide application in our modern day world. This is a result of the combination of properties which these materials possess. Some of the properties of polymer matrix composite include specific strength, high modulus, good fracture and fatigue properties as well as corrosion resistance[7]. One of the factors which make plastics attractive for engineering application is the possibility of property enhancement through fiber reinforced [8]. For thermoset products, the resultant resin was blended with styrene for cross-linking and small amount of peroxide as initiator. Unsaturated polyesters have been synthesized in high yield by polycondensation between dicarboxylic acid and polyols using p-toluene sulphonic acid as catalyst and xylene as solvent . Qualitative structure analysis of the polymers have been carried out by the using of FT-IR, and ^{1}HNMR spectroscopy, thermal stability were systematically investigated . Mechanical and thermal properties (TGA) and (DSC) are studied.

Experimental

Materials

   Propylene glycol, Polymethylol resin , Maleic anhydride , Phathaleic anhydride, Salicylic acid , P-Toluene sulphonic acid , Pyrogallol , Xylene , all from (MERCK) ; Tetrahydrofurane (THF) , Dimethyl sulphoxide (DMSO) , all from (MERCK) ; Methanol , Acetone , Toluene , MEKP , Hydroquinone , all form (BDH-chemicals) ; Sulfuric acid form (Sd fine-CHEM) ;Hydrochloric acid , Cobalt naphthanate , Benzene , all form (Hi-media) ; Carbon Nano , Titanium di oxide Nano , all from (NANO SHELL) ; Styrene from (KESHI) .

Instruments

     FTIR 8400S , Fourier Transform infrared spectrophotometer , SHIMADZU, Japan), (Oven ,Trivp International Crop .Italy) ,(Hot plate stir , Bibby Strlintd .UK) (Measurement of   ^{1}HNMR Spectra : recorded NMR spectra using a type of Bruker ,Ultra shield 300 Mhz, Switzerland and using (DMSO-d6) as a solvent at the university's Educational teacher-Tehran Iran) ,(Thermogravimetry analysis (TGA) were performed on a polymer laboratories co England, Model pL-TG at Iran polymer & petrochemical institute , using a heating rate of 10ºC/min in Argon atmosphere within the temperature range of (25-500ºC)(differential thermal analysis (DSC) measurement using apparatus (DSC) type (DSC 131 Evo, SETARAM) is the origin (France) in the Department of Chemistry / Faculty of Education / University of Qadisiyah). Tensile properties were measured on dumbbell-shaped sample using a tensile testing machine from (LARYEE Co)/ China. With a load cell of 20 kN and a cross-head speed of 200 mm/min and harness testing at room temperature in the Department of Chemistry / Faculty of Education / University of Qadisiyah) .

Synthesis of monomers

Synthesis of acids (phathalic acid mono-(4-carboxy-phenyl)ester (AC1)

   Fit 250-ml three necked flask with a sealed stirrer, reflux condenser and a thermometer. place (11.2 g, 0.075 mol) of phathalic anhydride acid with (25.6 g 0.185 mol) of p-hydroxy benzoic acid) in

(150 ml) of distilled water in presence of concentrated sulfuric acid with stirring and heating at a temperature between (50 - 60) °C for four hours .Then raise the beaker and put it in a cool bath ,further white precipitation of the new acid was observable. Filter off the precipitated, wash with hot and drain well water .Dried in the oven.
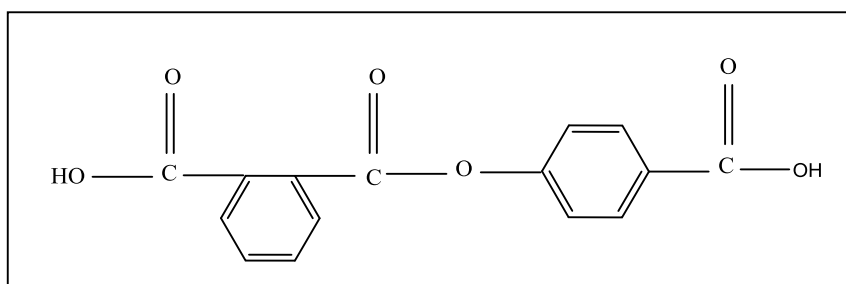
Figure (1) structure of AC1

Synthesis of But-2-enedioic acid mono (2-carboxy-phenyl) ester (AC2)

Fit 250-ml three necked flask with a sealed stirrer, reflux condenser and a thermometer. place (11.2 g, 0.114 mol) of maleic anhydride acid with (25.6 g 0.185 mol) of salicylic acid) in (150 ml) of distilled water in presense of concentrated sulfuric acid with stirring and heating at a temperature between (50 - 60) °C for four hours .Then raise the beaker and put it in a cool bath , further white precipitation of the new acid was observable. Filter off the precipitated, wash with hot and drain well water .Dried in the oven.
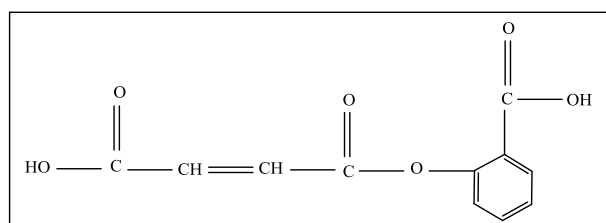
Figure (2) structure of AC2

Table (1) physical properties of monomers

| Monomers	Molecular formula	%Results	Colour	MP
AC1	$C_{15}H_{10}O_6$	75%	White	180-198 ^{o}C
AC2	$C_{11}H_8O_6$	65%	White	152-161 ^{o}C

Synthesis of unsaturated polyesters

A mixture of 1.25 mol polyols, 0.5 mol of di carboxylic acid as shown in (Table2) 0.2% p-Toluene sulfonic acid (PTSA) and Xylene as solvent was charged in a three-neck reaction kettle equipped with stirrer, thermometer, nitrogen-gas introducing tube, separator and water condenser. The mixture was mechanically stirred and heated at 120 ^{o}C under nitrogen gas stream. When reaction mass becomes clear, it was allowed to cool to 80 ^{o}C and then 0.5 mol from Maleic anhydride, (FA), AC1 or AC2 was added and continues heating at 120-220 ^{o}C until an acid number of 20 was reached. During esterification reaction, water formed as by product and was continuously removed from the reaction

mass as it inhibits the rate of reaction. The Xylene was completely distilled out and reaction product was allowed to cool. When the temperature reached to 180 $^{\circ}$C, 20 mg of hydroquinone was added as inhibitor and when resin temperature dropped below the boiling point of reactive diluent (i.e. Styrene), the polyester resin were mixed with styrene by 38 weight percent of resin [9].
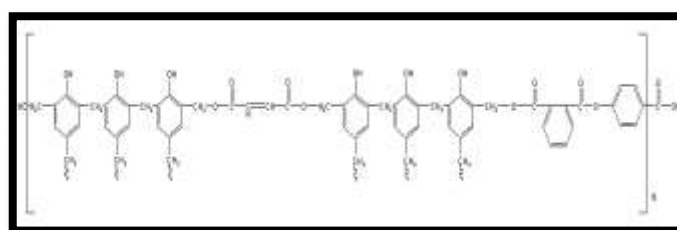
Table (2) Synthesis of UPRS

UP	Alcohols	diacids	Usaturated acid
UPRS1	Propyleneglycol	**Oxalic acid**	FA
UPRS2	Pyrogallol	AC1	AC2
UPRS3	Polymetylol resin	AC1	MA
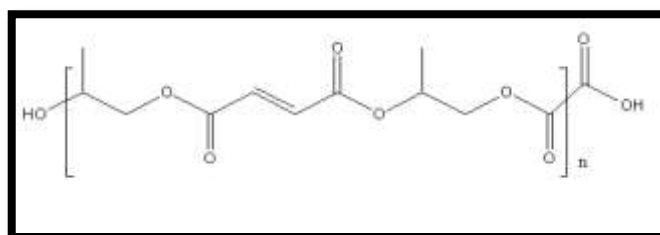
Figure (3) structure of UPRS 1
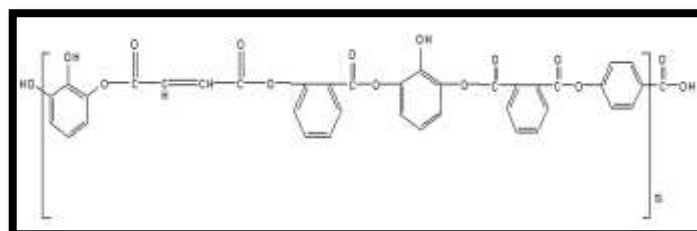
Figure (4) structure of UPRS 2

Figure (5) structure of UPRS 3

Physico – chemical Tests
Acid value Test
    Acid value of unsaturated polyester resin was determined according to the process reported by mantel eLal [10]
Tensile strength Test
    Tensile properties were tested in accordance with ASTM-D638.This test method determines the tensile properties of polymer matrix composite materials .

**Curing   of   unsaturated   polyesters   and   prepare   composites**
unsaturated polyester mixed with the monomer styrene in 38%weight of unsaturated polyester resin
ester unsaturated where styrene is working on linking polymer chains together by binding site is
saturated found in polyester unsaturated .Fillers used to modify the mechanical and thermal properties
of polyester . Carbon nanotube used to modify these polyester .where a number of models had
prepared per poly ester as additives vary ratios for each specimen. It was taking a certain weight of of
unsaturated polyesters and mixed with styrene to be supported in some fillers in a beaker then heated
at a temperature less than 120 ° C to be melted after that lifting of the heater and add filler with
stirring continous for two minutes then add 1 g of material hardener MEKP that is works on hardening
polyester [11,12].

Results and Discussion

Synthesis of monomers

Synthesis of Phathalic acid mono-(4-carboxy-phenyl) ester (AC1)

   This monomer (acid) prepared by reacting phathalic anhydride with p-hydroxy benzoic acid in
distilled water in presense H_2SO_4 as catalyst with stirring in temperature between (50-60°C) for 4
hours . After reaction compeleting , round white precipitate was formed dried and weighted .
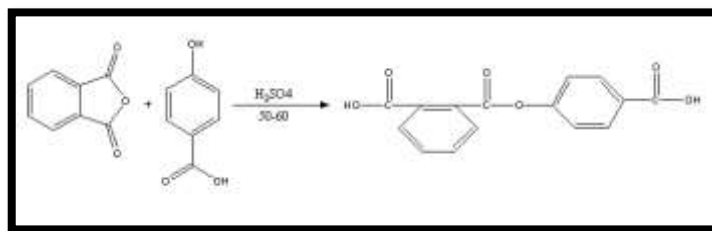
Scheme (1) synthesis of AC1

Characterization of (AC1)

FT-IR spectrum :

     The FTIR spectra of **(AC1)** as shown in (Figure 6) which indicates absorption band of (OH)
Carboxylic at (3400 cm^{-1}) ,(C-H) aromatic at (3000 cm^{-1}) , (C=O) Carboxylic acid, (C=O) in the
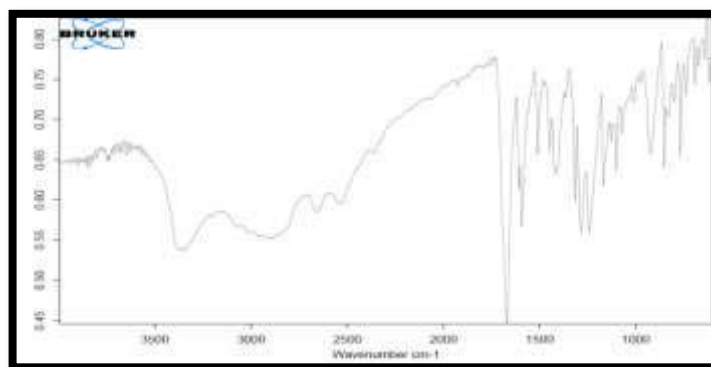ester group at (1742 cm-1) , (C=C) aromatic at (1580 cm^{-1}) , and (C-O) at (1110 cm^{-1})[13] .

Figure (6) FTIR spectra of AC1

 (**^{1}H-NMR) Spectrum of (AC1)** , is shown in Figure (7) assigns the following chemical shifts ; ($\square$ =
2.5 ppm) for (DMSO), ($\square$ = 3.34 ppm)for (H_2O), ($\square$= 6.844-7.67 ppm) for Ar-H group and($\square$= 11.5)
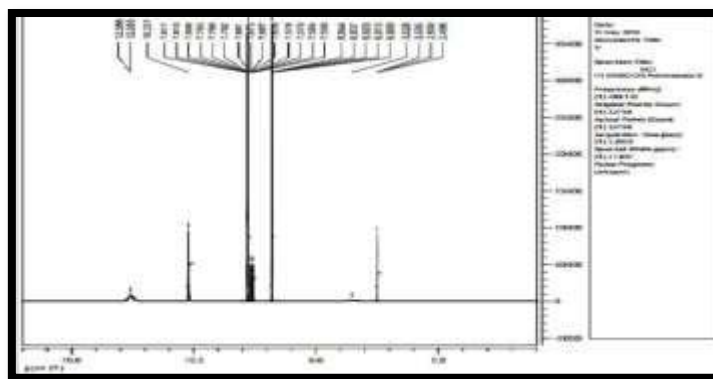for OH[13] .

Figure (7) HNMR spectra of AC1

Synthesis of But-2-enedioic acid mono (2-carboxy-phenyl) ester (AC2)

This monomer (acid) prepared by reacting maleic anhydride with salicylic acid in distilled water in presense H_2SO_4 as catalyst with stirring in temperature between (50-60°C) for 4 hours. After reaction compeleting, round white precipitate was formed dried and weighted .
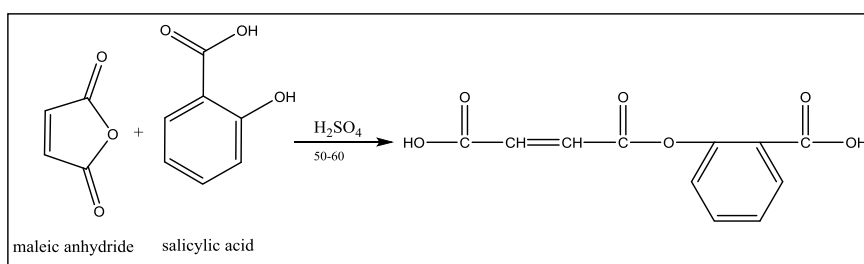
Scheme (2) synthesis of AC2

Characterization of (AC2)
FT-IR spectrum

The FTIR spectra of (AC2) as shown in (Figure 8) which indicates absorption band of (OH) Carboxylic at (3500 cm^{-1}) ,(C-H) aromatic at (3000 cm^{-1}) , (C=O) in the ester group at (1754 cm^{-1}) , (C=C) aromatic at (1525,1610cm^{-1}) , (C-O) at (1280 cm^{-1}) and (C=C) alkene at(1600cm^{-1})[13] .
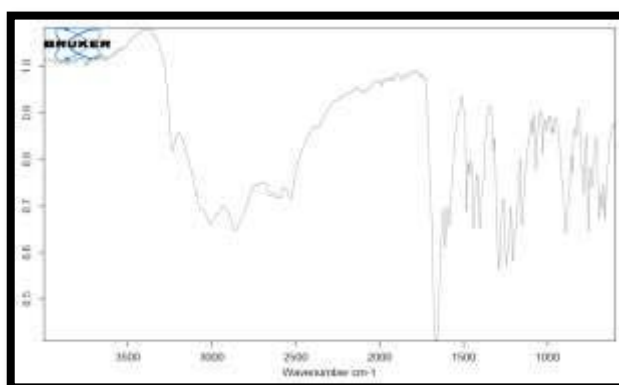

Figure (8) FTIR spectra of AC2

(**^{1}H-NMR) Spectrum of (AC2)** , is shown in Figure (10) assigns the following chemical shifts ;($\square$ = 2.4 ppm) for (DMSO),($\square$ = 3.34 ppm)for (H_2O), ($\square$= 6.844-7.804 ppm) for Ar-H group and ($\square$= 11.5) for OH[13] .
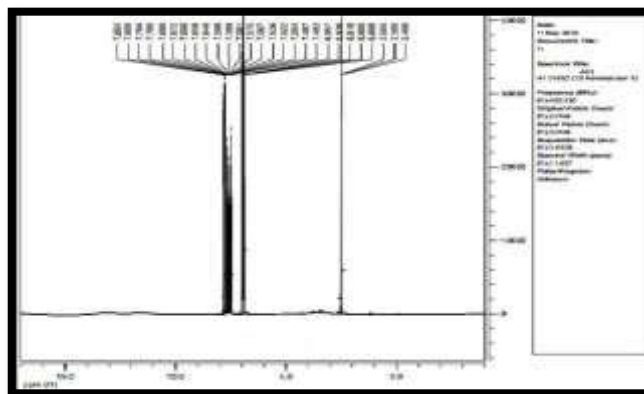

Figure (9) HNMR spectra of AC2

Synthesis of unsaturated polyesters

In this section, used polycondensation method for synthesis of a series of new unsaturated polyesters from the direct polycondensation reaction of dicarboxylic acid (oxalic acid, , AC1 and AC2) with alcohols (propylene glycol, pyrogallol, polymethylol resin) respectively , by using p-toluene sulphonic acid catalyst(0.2gm) with heating into 120°C . when the reaction become clear (fumaric acid, AC2, ,maleic anhydride) were added .These unsaturated polyesters were contain double bond in main chain for forming cross linking with styrene. These unsaturated polyesters were characterized by FT-IR and ^{1}HNMR spectra.
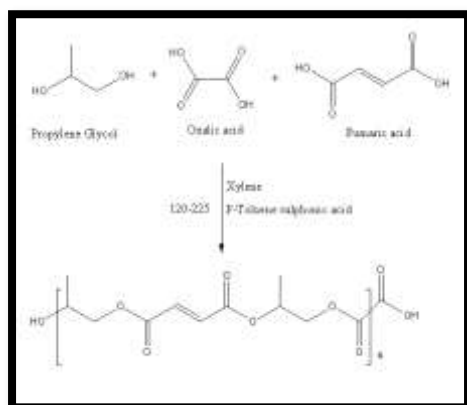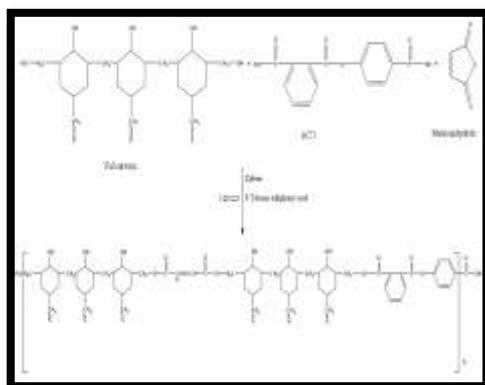

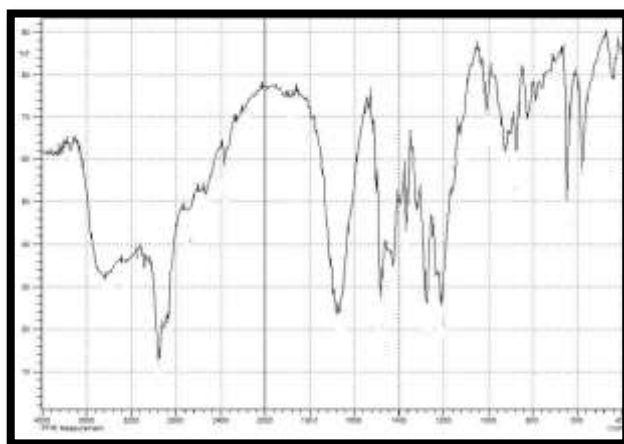**Scheme (3) synthesis of UPRS1**
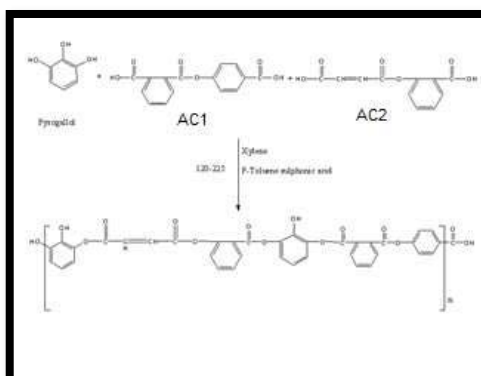
Scheme (4) Synthesis of UPRS2

Scheme (5) Synthesis of UPRS3

Characterization of (UPRS1)
FT-IR spectrum

    The FTIR spectra of **(UPRS1)** as shown in (Figure 11) which indicates absorption band of (OH) Carboxylic at (3520 cm-1), (C=O) Carboxylic acid at(1704cm-1), (C=O) in the ester group at (1735 cm-1) , and (C-O) at (1240 cm^{-1}) and (C=C) alkene at(1600cm^{-1})[13] .

Figure (10) FTIR spectra of UPRS1

Characterization of (UPRS2)

FT-IR spectrum

    The FTIR spectra of (UPRS 2) as shown in (Figure 12) which indicates absorption band of (OH) Carboxylic at (3301 cm^{-1}) ,(C-H) aromatic at (3090 cm^{-1}) , (C=O) Carboxylic acid at(1704cm^{-1}), (C=O) in the ester group at (1732 cm^{-1}) , (C=C) aromatic at (1480 cm^{-1}) , and (C-O) at (1280 cm^{-1}) , (C-H) aliphatic at (1732 cm^{-1}),(C=C) alkene at (1600cm^{-1})[13].
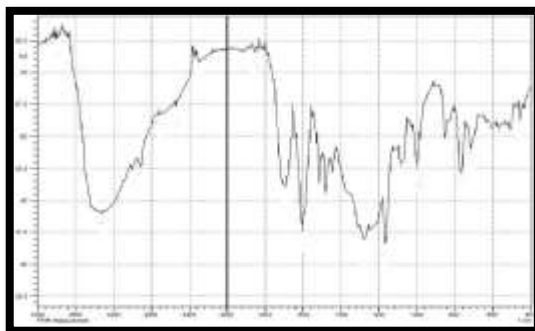
Figure (11) FTIR spectra of UPRS2

Characterization of (UPRS 3)

FT-IR spectrum

The FTIR spectra of (UPRS 3) as shown in (Figure 13) which indicates absorption band of (OH) Carboxylic at (3470 cm^{-1}) ,(C-H) aromatic at (3070 cm^{-1}) , (C-H) alkene at(3002cm^{-1}) ,(C-H) aliphatic at(2964 cm^{-1}) , (C=O) in the ester group at (1775 cm^{-1}) ,(C=C) alkene at (1600cm^{-1}) , (C=C) aromatic at (1604,1480cm^{-1}) , and (C-O) at (1203 cm^{-1})[13] .
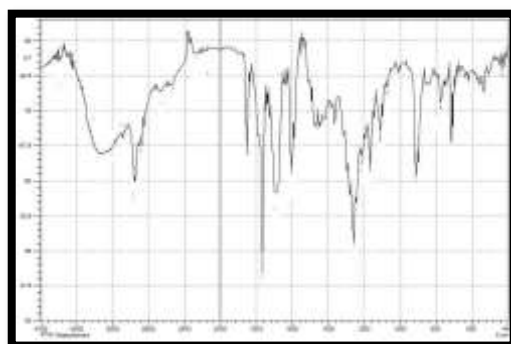
Figure (12) FTIR spectra of UPRS3

(**^{1}H-NMR) Spectrum of (UPRS 3)** , is shown in Figure (14) assigns the following chemical shifts ;($\square$ = 2.4 ppm) for (DMSO);($\square$ = 3.8 ppm) for methylene group, ($\square$= 11.5 ppm) for OH ,$\square$= 6.6-8.2 ppm) for Ar-H group and OH phenol($\square$= 5.6ppm)[13] .
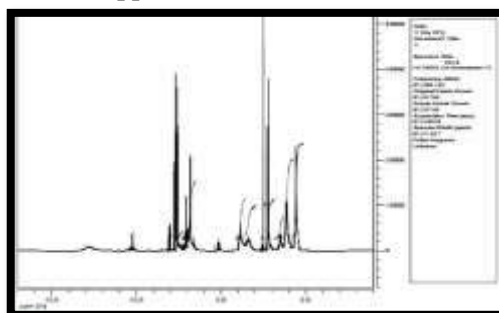
Figure (13) HNMR spectra of UPRS3

Physico – chemical tests
Acid value test

The acid value (AV) is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound, such as unsaturated polyesters (1,2 and 3). It has been observed from the results shown in the (table 3), (UPRS 3) showed an acid value higher than the (UPRS 1) and (UPRS 2) due to the length of unsaturated polyesters chain component there of these polyesters[14-15] .

Calculations:

Acid value = $\frac{v*0.1*56.1}{w}$

Where

V= Consumption of KOH solution by the blank reading (ml)

0.1 = Normality of KOH solution

W = Weight of sample (gm)

Table(3) Acid values

UPRS	Acid Value
UPRS 1	23
UPRS 2	22
UPRS 3	24

Solubility test

Unsaturated polyester showed high solubility in different type of solvents . (table4) described solubility of samples, was measured by taking the solubility (0.01 g) of the sample prepared resin and melted in (2 ml) of the solvent, The solvents used include (DMF, Acetone, Toluene, Xylene) (Polar aprotic) non-polar solvents such as (Benzene, $CHCl_3$) and other solvents such as methanol, ethanol. The solvent molecules increase with the distance between the molecular chains of the resin. The spaces between long chains with pendant side group of resin are invaded by solvent molecules as they fill the space made available by chain movements. When movements bring two chains close to proximity, short range attractive forces are therefore established resulting in restricted chain movement and thus the formation of a viscous system[16-17]. Solvent are added to deal with the problem of high viscous resin which is an obstacle in substrates wet ability .

Table (4) Solubility of UPRS

Polymer	Acetone	Benzene	$CHCl_3$	CH_2Cl_2	DMSO	DMF	THF	H_2SO_4 0.01M	Solvents HCl 0.01M
UPRS 1	++	+-	++	++	++	++	++	--	--
UPRS 2	--	--	+-	+-	++	++	--	+-	+-
UPRS 3	+-	+-	++	++	+-	++	++	++	++

(+ -) partially soluble   (++) totally soluble   (--) don't soluble

Mechanical Properties[18]
Tensile Strength

It is well known that the incorporation of Nano fillers such as carbon black Nano and TiO_2 in a polymeric matrix can markedly promote improvements in mechanical properties of Nano composite. The results shows the stepwise increasing trend of tensile strength Nano composite with increasing content of carbon Nano and Tio_2. It shows that the Nano fillers exhibit excellent tensile strength. The

tensile strength of Nano composite based on Nano fillers increased respectively. Tensile strength of UPRS composite was increased by the addition of Carbon Nano filler is higher than TiO$_2$ Nano. This can be attributed to the physical properties of this filler, where the particle size of Nano fillers is smaller with the UPRS matrix. Increasing the filler content for UPRS reduced the tensile strength of the composite , due to the poor dispersion of Nano fillers, as the partial multi-layered Nano fillers would enhance the strength little. But it can be decreased the tensile strength of the composite. .UPRS1 get mechanical properties better than UPRS 2 and the last better than UPRS3 as shown in(Table5).

Table(5) tensile streenth

FILLER	TENSILE STREGNTH		
	UPRS 1	UPRS 2	UPRS 3
C NANO	17	12	13
TIO$_2$ NANO	15	14	11

Elongation

The elongation at break obtained from the tensile tests indicates the elastic properties of the composites .Generally , high value of elongation at break is indicative of highly elastic material . The addition of Nano filler causes the matrix to lose its elastic properties and the material becomes more little . It indicates that elongation at break (%) decreases gradually with increasing filler loading. The reduction of elongation at break is due to stiffening of the polymer matrix by the filler. Further increase in filler loading causes the molecular mobility decrease due to extensive formation of physical bond between the filler particles and the polymer chain that stiffen the matrix the increase in filler loading leads the matrix progressively becoming reinforced and hence lowering elongation at break .

Table(6) Elongation at break

Fillers	Elongation at break		
	UPRS1	UPRS 2	UPRS 3
C nano	2.9	2.5	2.1
TiO$_2$nano	2.0	1.9	1.8

Modulus

Modulus of elasticity for the composites increases with the increasing Nano fillers (Carbon Nano and TiO$_2$ Nano).Because of the hardness of its composites tends to increase strongly with addition of these fillers . This belong to the small of particles size of the Nano fillers.

Table (7) Modulus

Fillers	Modulus		
	UPRS 1	UPRS 2	UPRS 3
C nano	30	37	38
TiO$_2$nano	35	39	40

Hardness

The hardness of the composites was also due to the destriction of the mobility of the UPRS matrix by the addition of the filler content .This may be attribute to increasing the surface area of the Nano fillers in contact with UPRS and decreasing the movement of polymer molecular which leade to lose of strength of material . .UPRS 3 get modulus higher than UPRS2 and the last is higher than UPRS1.

Table(8) Hardness

Fillers	Hardness		
	UPRS 1	UPRS 2	UPRS 3
C nano	30	37	38
TiO_2 nano	35	39	40

Thermal Properties
Thermo gravimetric analysis (TGA) study

Thermo gravimetric Analysis (TGA) involves determining changes in mass as   a function of temperature . It is commonly used to search degradation temperatures, absorbed content of materials, levels of inorganic and organic parts contained in a material and analysis solvent residues[19] . It employs a sensitive electronic balance from which the sample is suspended in a furnace controlled by a temperature programmer . The thermal properties of two samples of these alkyd resins were investigated by means of thermo gravimetric analysis (TGA) in Argon atmosphere at heating rate of 10 ºC/ min . The results such as T_i , T_{op} , T_f , $T_{50\%}$, % Residue at 500 ºC , and char yields at 300 ºC are summarized in (Table 9) . The temperatures of 50% weight loss of (UPRS1,UPRS2,UPRS3) as a standard indication for thermal stability of polymers were all from 300 ºC. The char yields of (UPRS 1,UPRS 2,UPRS 3) are (74 to 50 %) at 300 ºC in Argon atmosphere , which indicate they could meet temperature resistant requirements .

Table(9) TGA

UPRS	DT/$°C$				$T_{50\%}$	Residue at ^{o}C500	Char % At $300°C$
	T_i	T_{op1}	T_{op2}	T_f			
UPRS 1 C Nano	**271**	**170**	**407**	>500	>500	51%	74%
UPRS1 TiO_2 Nano	**353.4**	**290**	**409.9**	>500	>500	**72%**	70
UPRS2 C Nano	**269**	**200**	**419**	>500	>500	**75%**	50
UPRS2 TiO_2 Nano	234	214	314	>500	>500	**85%**	64
UPRS3 C Nano	**322**	**190**	**414.5**	>500	>500	**82%**	62.5
UPRS3 TiO_2 Nano	**350**	**200**	**413.9**	>500	>500	**62%**	66

DT: Decomposition temperature.
Ti: Initial decomposition temperature.
Top: Optimum decomposition temperature.
Tf: Final decomposition temperature. The final degree of dissociation temperature
T50%: Temperature of 50% weight loss, obtained from TGA .
Char% at 300 ° C: Residual weight percentage at 300 ° C in Argon by TGA
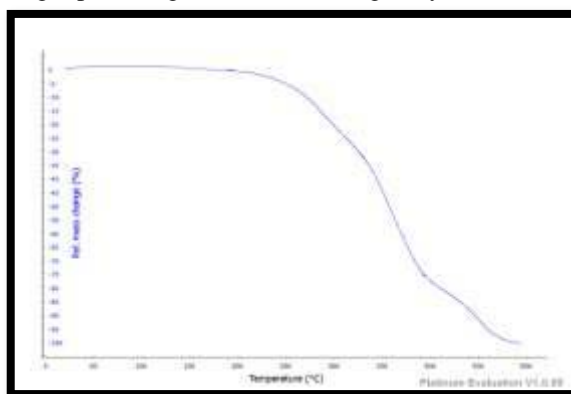

Figure (14) TGA cure of UPRS 1 supported by
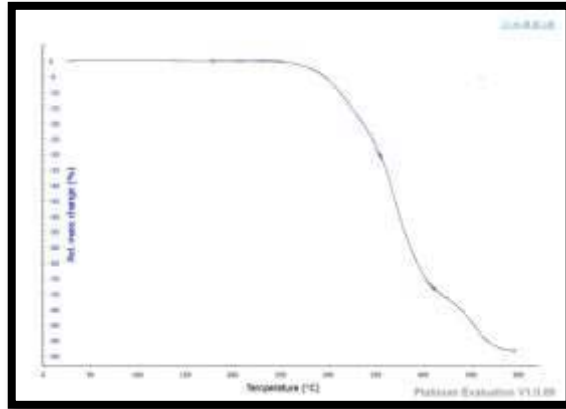TiO_2 Nano

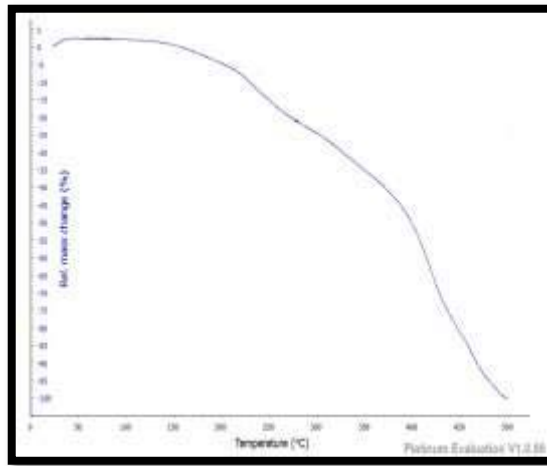Figure (15) TGA cure of UPRS 1 supported by
Carbon Nano

Figure (16) TGA cure of UPRS 2 supported by Carbon Nano
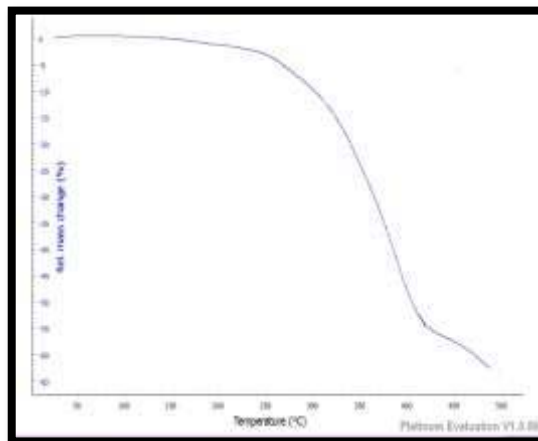

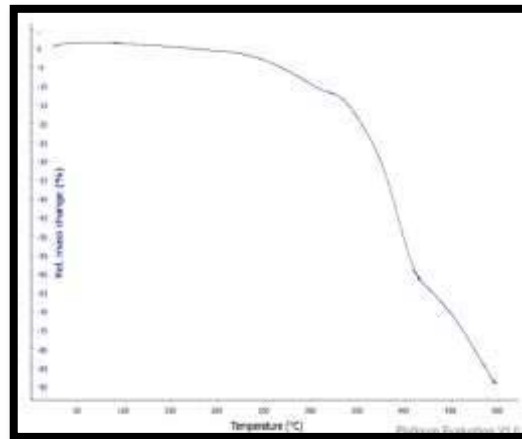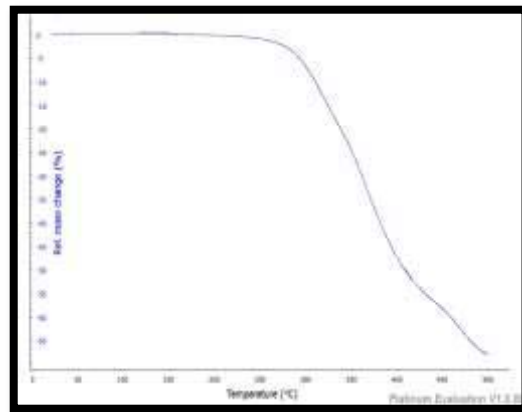Figure (17) TGA cure of UPRS 2 supported by TiO$_2$ Nano

Figure (18) TGA cure of UPRS 3 supported by Carbon Nano

Figure (19) TGA cure of UPRS 3 supported by TiO$_2$ Nano

Differential Scanning calorimeter analysis (DSC) study

Differential Scanning Calorimetry,is a technique of thermal analysis that investigates how material's heat capacity (Cp) is transformed by temperature. A known mass sample is heated or cooled and the variations in its heat capacity are observed as alterations in the heat flow. This allows to reveal transitions such as melts[20] glass transitions (Tg), and the melting point (Tm) the degree of crystallization (Tc) This test was applied to the prepared samples , Shows the (Figure 22) for the sample of (UPRS 1 C Nano), the results showed the value of the glass transition (Tg) of the mixture (68°C), referring to obtain the flow temperature and then increases endothermic the sample to reach the melting point (Tm) at (469°C) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (360°C) . It also shows a (figure 22) for the sample of (UPRS 1 TiO$_2$ Nano) and the results showed the value of the glass transition (Tg) of the combination (49°C) referring to an increase in the flow temperature and then increase endothermic the sample to reach the melting point (Tm) at (452°C) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (361.3°C). It also shows a (figure 23) for the sample of (UPRS 2 C nano) and the results showed the value of the glass transition (Tg) of the combination (85°C) referring to an increase in the flow temperature and then increase endothermic the sample to reach the melting point (Tm) at (467°C) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (310 °C). It also shows a (figure 24) for the sample of

(UPRS2 TiO2 Nano) and the results showed the value of the glass transition (Tg) of the combination (50ºC) referring to an increase in the flow temperature and then increase endothermic the sample to reach the melting point (Tm) at (478 ºC) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (390 ºC). It also shows a (figure 25) for the sample of (UPRS3 C Nano) and the results showed the value of the glass transition (Tg) of the combination (41.8ºC) referring to an increase in the flow temperature and then increase endothermic the sample to reach the melting point (Tm) at (464 c º) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (335 ºC). It also shows a (figure 26) for the sample of (UPRS 3 TiO$_2$ Nano) and the results showed the value of the glass transition (Tg) of the combination (49ºC) referring to an increase in the flow temperature and then increase endothermic the sample to reach the melting point (Tm) at (471.8 c º) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (335 ºC).

Table (10) shows the degree of glass transition, melting point and the degree
of crystallization in the differential thermal analysis of UPRS

	Samples	Tg (ºC)	Tm (ºC)	Tc (ºC)
UPRS 1	**10 % C Nano**	**68**	**469**	**360**
	10% TiO$_2$ Nano	**49**	**452.4**	**361.3**
UPRS 2	**10 % C Nano**	**85**	**467**	**310**
	10% Tio$_2$ Nano	**50**	**478**	**390**
UPRS 3	**10 % C Nano**	**41.8**	**464**	**335**
	10% TiO$_2$ Nano	**49**	**471.8**	**335**

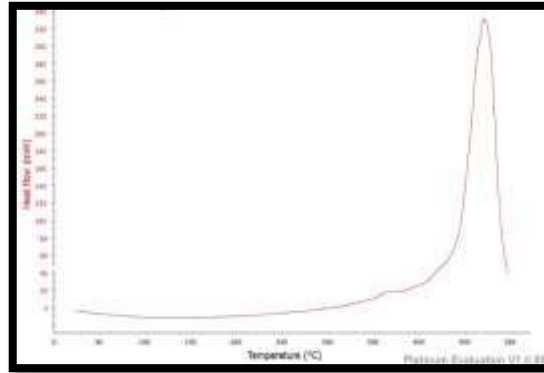Tg : Degree glass transition

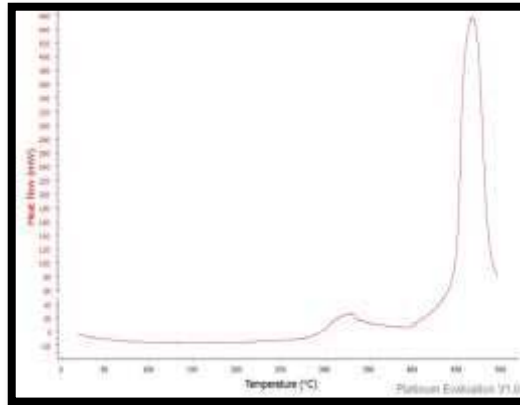Tm : Melting Ponit

Tc : Degree of crystallization
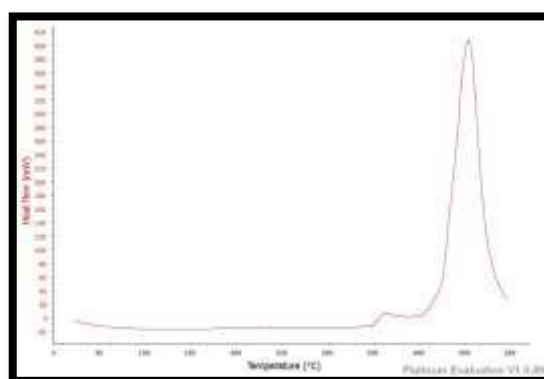
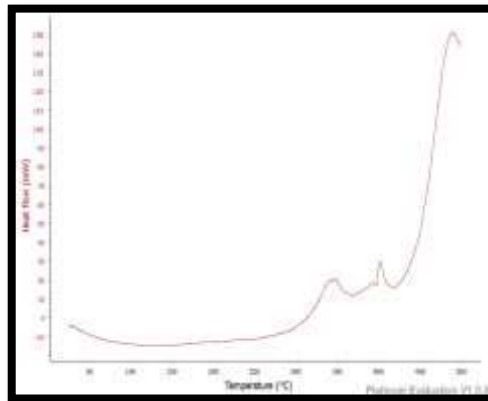**Figure (20)** DSC cure of UPRS 1 supported by TiO$_2$ Nano
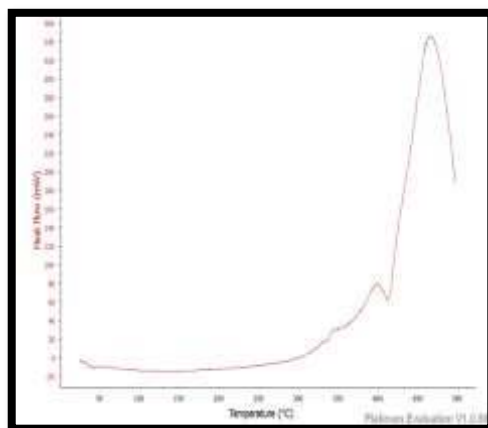
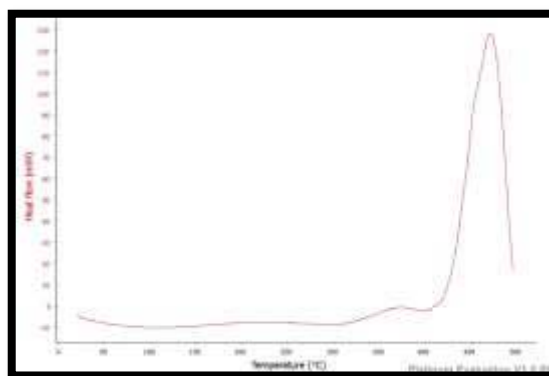**Figure (21)** DSC cure of UPRS 1 supported by Carbon Nano

Figure (22) DSC cure of UPRS 2 supported by Carbon Nano

Figure (23) DSC cure of UPRS 2 supported by TiO$_2$ Nano

Figure (24) DSC cure of UPRS 3 supported by Carbon Nano

Figure (25) DSC cure of UPRS 3 supported by TiO$_2$ nano

Conclusions

In this study , new unsaturated polyesters were prepared from reacting diols with dicarboxylic acids and unsaturated carboxylic acid in the presence of p-Toluene sulphonic acid as catalyst and xylene as solvent .It show physiochemical properties such as solubility, acid value .Unsaturated polyesters show good solubility in solubility in various solvents . It shows cross linking with styrene . It show good mechanical and thermal properties when it supported by some fillers such as carbon Nano and TiO$_2$ Nano. In general mechanical and thermal properties of UPRS1 is better than UPRS3 and the last is better than UPRS2 .

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