

SYNTHESIS, CHARACTERIZATION, AND PROPERTIES OF NEW UNSATURATED POLYESTERS RESINS REINFORCED WITH SOME FILLERS (CARBON NANO, NANO TiO₂, TiO₂ AND ZnO) FOR COMPOSITE APPLICATION

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ABSTRACT

The unsaturated polyester resin considered at the present time a significant matrix resin for thermosetting polymer compound. The Major objective of this study was to synthesize and characterize new unsaturated polyester resins for composite applications. Four types of new monomer polyester resins were synthesized, including: phthalic acid mono-(4-carboxy-phenyl) ester (AC1), but-2-enedioic acid mono-2-carboxy-phenyl) ester (AC2), phthalic acid mono-(2-carboxy-phenyl) ester (AC3) and but-2-enedioic acid mono (2-carboxy-phenyl) ester (AC4). These monomers were synthesized from salicylic acid and phthalic anhydride, phthalic anhydride and p-hydroxybenzoic acid, maleic anhydride and p-hydroxy benzoic acid in the presence H₂SO₄ as catalyst. The chemical structures were confirmed by FTIR and ¹HNMR spectroscopy. New unsaturated polyesters were synthesized by the condensation reaction between (ethandiol, triethanol amine and ethylene glycol) and acids (phthalic acid mono-(4-carboxy-phenyl) ester (AC1), phthalic anhydride, phthalic acid mono-(2-carboxy-phenyl) ester)(AC1) with (maleic anhydride and but-2-enedioic acid mono (2-carboxy-phenyl) ester) in presence p-toluene sulphonic acid as catalyst. All of these unsaturated polyesters show good solubility in common organic solvents, such as (DMSO, CH₂Cl₂, THF, DMF, acetone and some non-polar solvents as Benzene and CH₃Cl. Thermal analysis of polyesters by thermo gravimetric analysis (TGA) reveals that these Aromatic polyesters possess thermal stability, differential scanning calorimetry (DSC) were also studied. Unsaturated polyesters supported with some Nano fillers such as carbon Nano, TiO₂ Nano and TiO₂ and Zinc oxide for composite applications. The results showed that the new unsaturated polyesters reinforced fillers (Carbon Nano, Nano TiO₂, TiO₂ and ZnO) composites exhibit high mechanical properties at 20% wt. of loading filler.

KEYWORDS: Unsaturated Polyester Resin, Composite, Nano Fillers, Mechanical Properties

INTRODUCTION

Unsaturated polyester resins are frequently cast-off as matrices for fiber-reinforced composites. Commercial organizations are generally provided as fairly low molecular mass, unsaturated linear polyesters, melted in a polymerizable monomer, like styrene, giving cross linking components by responding to the unsaturated resin in an essential addition reaction. Hence, condensing agents, low profile additives, inert and reinforcing fillers are to be put in the compost for the sake of changing the presentation of the creation. As a final point, initiators, inhibitors, and extra additives are to be put to regulate the reaction kinetics. To gain this is through two step practice; firstly unsaturated as well as saturated acids or anhydrides are responded to diols in a polycondensation reaction, then the second step is the resulting linear polyester prepolymer is liquefied in styrene to be resin just like syrup [1].

Then the resin is, at the end, handled in a rigid thermo set in an open radical copolymerization between styrene and the double bonds in the polyester chain.

The practice of treatment of thermo sets contains two major steps: first, the time of heating the liquid resin (whichever pure or in the formula of compounds together with fillers) and second the treatment response in the mould. A composite material has been defined as: a substance consisting of two or more materials, insoluble in one another, which are combined to form a use full engineering material possessing certain properties not possessed by the constituents[2,3]. Such materials offer advantages over conventional isotropic structural materials such as steel, aluminum, and other types of metal. These advantages include high strength, low weight, good fatigue strength and corrosion resistance. In addition, by changing the arrangement of the fibers, the properties of the material can be tailored to meet the requirements of specific design [4]. The scheme of a structural component that is used in compound encompasses material as well as structural scheme. Dissimilar to convene, the characteristics of the compound material might be schemed concurrently with the organizational features. Compound aspects (e.g., rigidity, thermal enlargement, etc.) are endlessly diverged over a broad variety of standards, below the regulation of the schemer [5]. Many works have been devoted to use of particulate fillers in composite in the recent past. For carbon Nano, TiO₂Nano, TiO₂ and ZnO are the most commonly particles used to reinforce polymers. In general, particles enhanced the stiffness of the composite to a limited extent [6]. Particle fillers are extensively manipulated to develop the characteristics of matrix materials. The effect of putting unsaturated polyester considered as a matrix material with the alumina regarded as a filler of particle size (30µm) having diverse weight division a number of its perfunctory and thermal aspects are considered due to the arranged samples. Consequently the outcome of stretchy strength and rigidity assessments displayed an upsurge with the upsurge of weight division being non- linear connection [7, 8]. sFor thermo set 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 with oils using p-toluene sulphonic acid as catalyst and xylene as solvent. Qualitative structure analysis of the polymers has been carried out by the using of FT-IR, and ¹HNMR spectroscopy, thermal stability was systematically investigated. Mechanical and thermal properties (TGA) and (DSC) are studied.

The aim of this work is to:-

- Prepare and testing samples of particular composite, which consists of unsaturated polyester resin matrix, with Carbon Nano, Nano TiO₂, TiO₂ and ZnO.
- Evaluation of mechanical properties of the composites.

EXPERIMENTAL PART

Materials

Ethanediol, Maleic anhydride, Phathaleic anhydride, P- Toluene sulphonic acid, Pentaerythritol, Xylene, all from (MERCK); Triethanol amine, Propylene glycol, Ethanol, all from (Scharlab S.L); 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 naphtha ate, Benzene, all form (Hi-media); Carbon Nano, Titanium di oxide Nano, all from (NANO SHELL); Zinc Oxide, Titanium di oxide, all from (ENGLAND CHEMICAL COMPANY); Styrene from (KESHI).

Instruments

FTIR 8400S, Fourier Transform infrared spectrophotometer, SHIMADZU, Japan), (Oven, Trivp International Crop. Italy),(Hot plate stir, BibbyStrlindt.UK) (Measurement of 1 HNMR Spectra : recorded NMR spectra using a type of Bruker, Ultra shield 300 Mhz, Switzerl 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 10°C/min in Argon atmosphere within the temperature range of 25-500°C)(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 strength instrumental, Hardness instrumental.

Synthesis of Monomers

Phthalic 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 phthalic anhydride acid with (25.6 g 0.1 mol) of p-hydroxy benzoic acid) in (150 ml)) of distilled water in the 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.

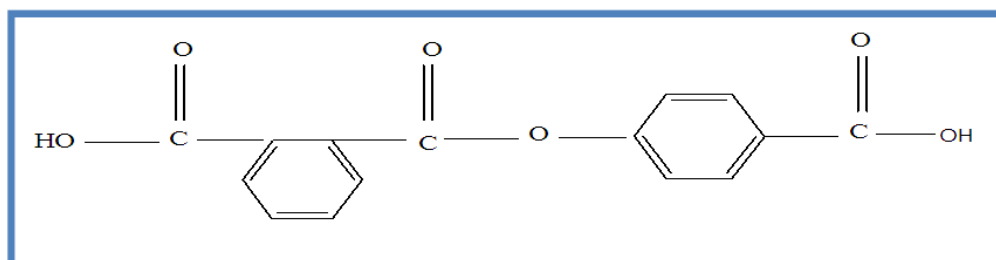


Figure 1: Structure of AC1

But-2-Enedioic Acid Mono-2-Carboxy-Phenyl) Esterac2

Fit 250-ml three necked flask with a sealed stirrer, reflux condenser and a thermometer. Place (11.2 g0.075 mol) of phthalic anhydride acid with (25.6 g 0.1 mol) of maleic acid) in (150 ml)) of distilled water in the 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.

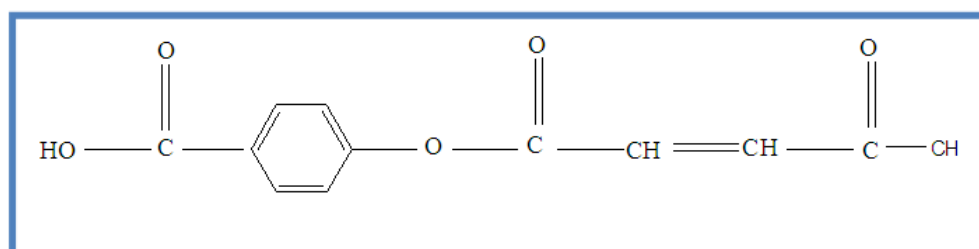


Figure 2: Structure of AC2

Phthalic Acid Mono-(2-Carboxy-Phenyl) Ester AC3

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 0.1 mol) of p-hydroxy benzoic acid) in (150 ml)) of distilled water in the 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.

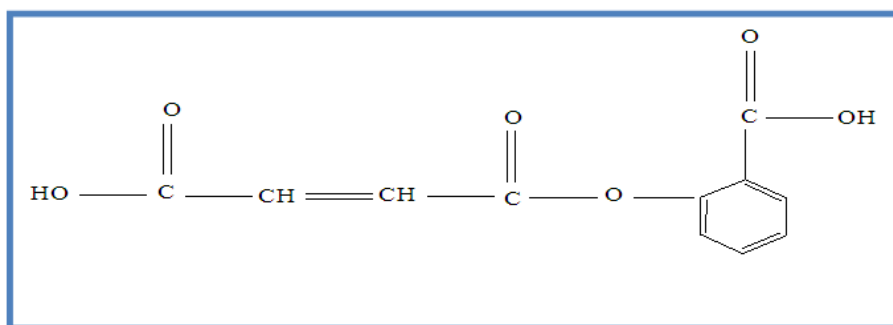


Figure 3: Structure of AC3

But-2-enedioic Acid Mono (2-Carboxy-Phenyl) Ester AC4

Fit 250-ml three necked flask with a sealed stirrer, reflux condenser and a thermometer. Place (11.2 g, 0.067mol) of phthalic acid with (25.6 g 0.1 mol) of p-hydroxy benzoic acid) in (150 ml)) of distilled water in the presence of concentrated sulfuric acid with stirring and heating at a temperature between (50 and 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.

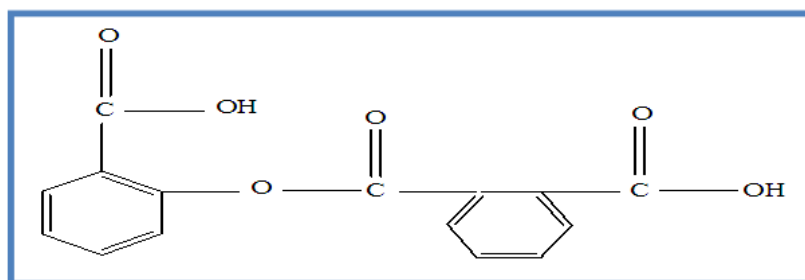


Figure 4: Structure of AC4

Table 1: Physical Properties

Monomer	الصيغة الجزيئية	%Results	Colour	MP
AC1	C ₁₅ H ₁₀ O ₆	75%	White	198-180°C
AC2	C ₁₁ H ₈ O ₆	55%	White	196-187°C
AC3	C ₁₁ H ₈ O ₈	65%	White	161-152°C
AC4	C ₁₅ H ₁₀ O ₆	55%	White	162-154°C

Synthesis of Unsaturated Polyesters (UPRS1, UPRS2, UPRS3)

As given in(Table1), a combination of (1.25 mol) polyols, 0.5 mol of dicarboxylic acid 0.2% p- Toluene sulfonic acid (PTSA) and Xylene being a solvent has been indicted in a Kettle of the three necks used for response and is fortified with stirrer, thermometer, nitrogen-gas presenting tube, isolator as well as water condenser. Then combination,

automatically, moved and heated at 120°C underneath the nitrogen gas stream. Once reacted mass turn out to be pure, then it is exposed to cool to 80 °C and after that to (0.5 mol) Maleic anhydride(MA)or AC3 or AC4is to be put and endures heating at120-220 °C up until an acid of number 20 is grasped. Throughout esterification response water is fashioned being an occasional outcome and was unceasingly detached from the response mass as it hinders the degree of response. Thus the Xylene was totally purified out and response outcome was permissible to cool. After the temperature touches 180 °C, 20 mg of hydroquinone was put considered inhibitor. Then, once the resin temperature released under the boiling degree of responsive diluent (i.e. Styrene), we mix the polyester resin with styrene by 38% weight percent of resin [9].s

Table 2: Synthesis of UPRS

Up	Alcohols	Diacids	Unsaturated Acid
UPRS1	Ethandiol	AC1	MA
UPRS2	Triethanolamine	Phathalic anhydride	AC4
UPRS3	Ethylene glycol	AC3	AC2

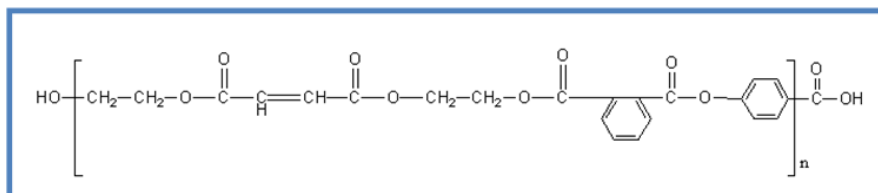


Figure 5: Structure of UPRS 1

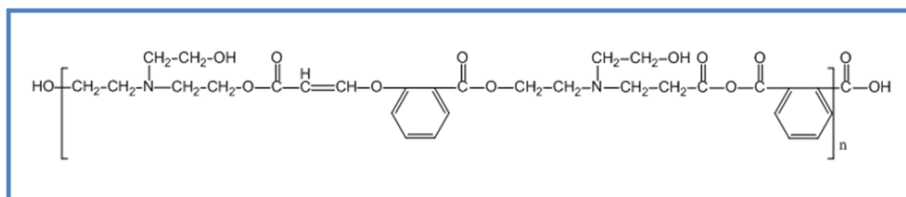


Figure 6: Structure of UPRS 2

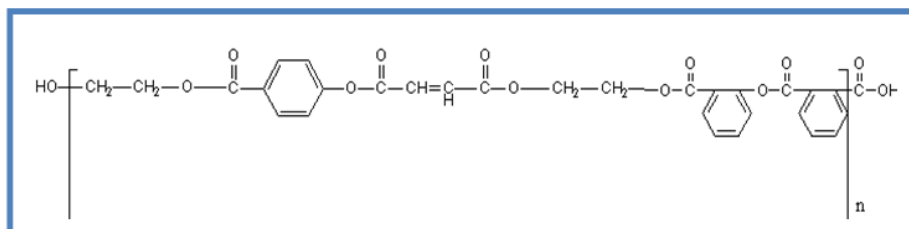


Figure 7: Structure of UPRS 3

Physico – Chemical Tests

Acid Value Test

Acid rate of unsaturated polyester resin is to be decided conferring to the course stated by mantel eLal.12.

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

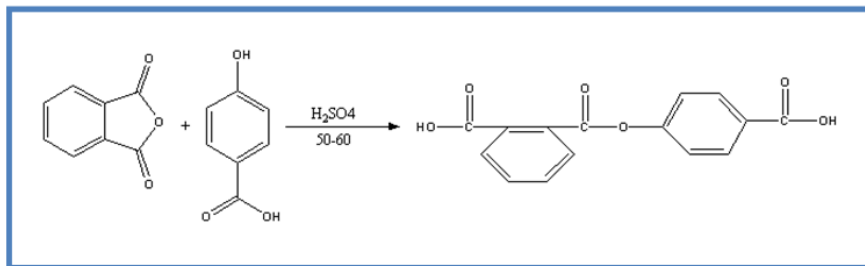
Unsaturated polyester mixed with the monomer styrene in 38% weight present of unsaturated polyester resin ester unsaturated where styrene is working on linking polymer chains together by binding site is saturated found in polyester unsaturated. Fillers used to modify the mechanical and thermal properties of polyester. Carbon nanotube used to modify these polyester. Where a number of models had prepared per polyester as additives vary ratios for each specimen. It was taking a certain weight 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 heat and add filler with stirring continuously for two minutes then add 1 g of material hardener MEKP that is works on hardening polyester [10].

RESULTS AND DISCUSSION

Synthesis of Monomers

Phthalic Acid Mono-(4-Carboxy-Phenyl) Ester AC1

This monomer (acid) prepared by reacting phthalic anhydride with p-hydroxy benzoic acid in distilled water in the presence H_2SO_4 as a catalyst with stirring in temperature between (50-60°C) for 4 hours. After the reaction completing, round white precipitate was formed, dried and weighted [11].



Scheme 1: Synthesis of AC1

Characterization of (AC1)

FT-IR Spectrum

The FTIR spectra of (AC1) as shown in (Figure 8) 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})

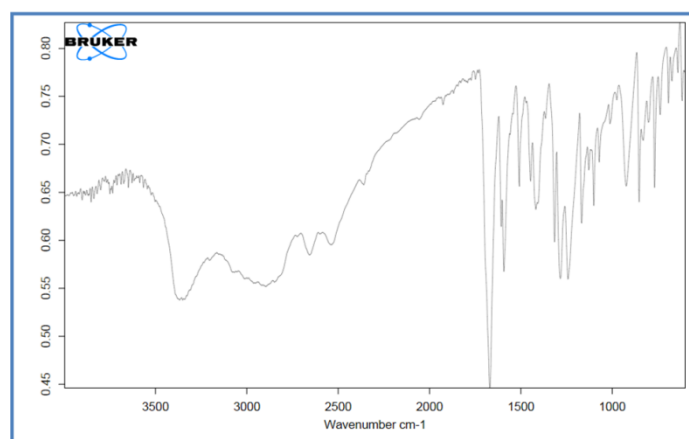


Figure 8: FTIR Spectra of AC1

(¹H-NMR) Spectrum of (AC1), is shown in Figure (9) assigns the following chemical shifts ; (□ = 2.5 ppm) for (DMSO), (□ = 3.34 ppm) for (H₂O), (□ = 6.844-7.67 ppm) for Ar-H group.

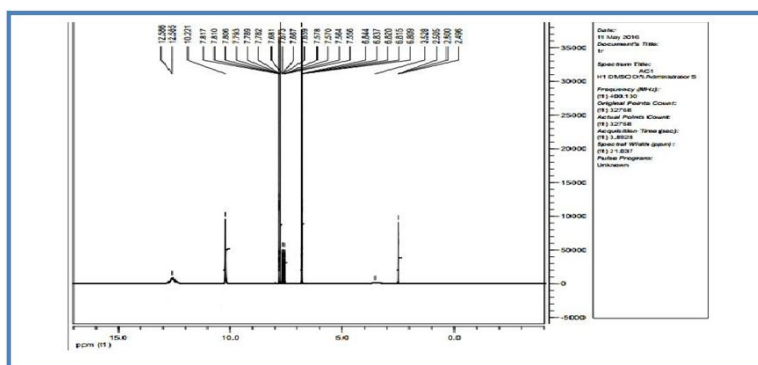
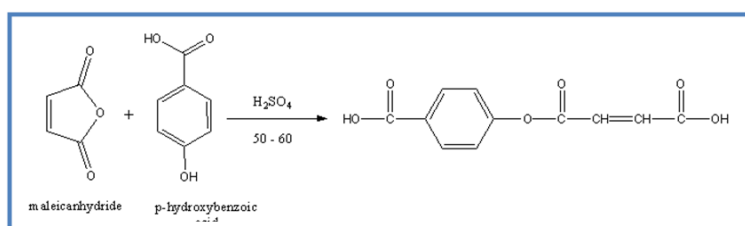


Figure 9: HNMR Spectra of AC1

But-2-enedioic Acid Mono-2-Carboxy-Phenyl) Esterac2

This monomer (acid) prepared by reacting phthalic anhydride with p-hydroxy benzoic acid in distilled water in the presence H₂SO₄ as a catalyst with stirring in temperature between (50-60°C) for 4 hours. After the reaction completing, the 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 show in (Figure 12) which indicates absorption band of (OH) Carboxylic at (3552 cm⁻¹), (C-H) aromatic at (3000 cm⁻¹), (C-H) aliphatic at (3050cm⁻¹), (C=O) in the ester group at (1754 cm⁻¹), (C=C) aromatic at (1520,1640 cm⁻¹), and (C-O) at (1280 cm⁻¹).

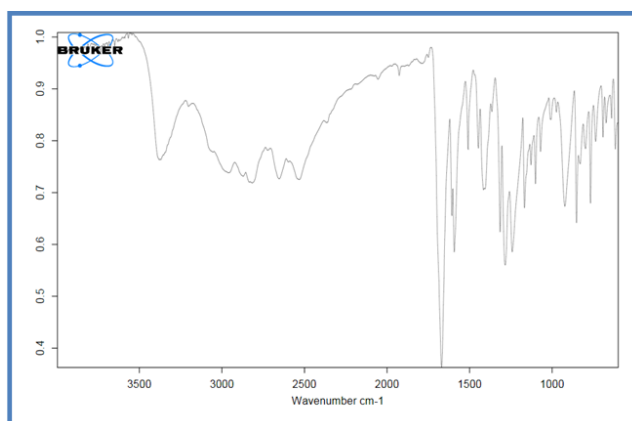
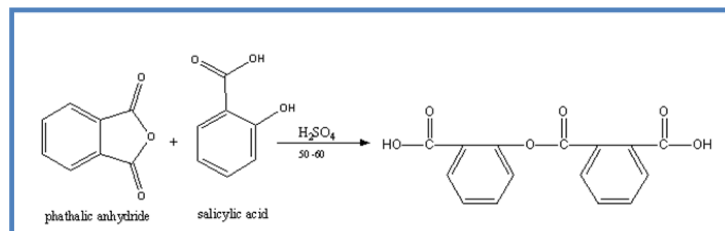


Figure 10: FTIR Spectra of AC2

Phthalic Acid Mono-(2-Carboxy-Phenyl) Ester AC3

This monomer (acid) prepared by reacting phthalic anhydride with p-hydroxy benzoic acid in distilled water in the presence H_2SO_4 as a catalyst with stirring in temperature between (50-60°C) for 4 hours. After reaction completing, the round white precipitate was formed, dried and weighted.



Scheme 3: Synthesis of AC3

Characterization of (AC3)

FT-IR Spectrum

The FTIR spectra of (AC3) as shown in (Figure 13) 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 ($1525, 1610\text{ cm}^{-1}$), and (C-O) at (1280 cm^{-1}).

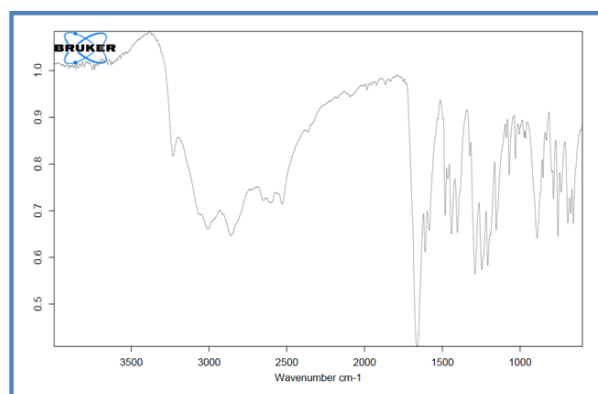


Figure 11: FTIR Spectra of AC3

(**1H -NMR**) Spectrum of (AC3), is shown in Figure (14) assigns the following chemical shifts ; ($\delta = 2.4\text{ ppm}$) for (DMSO), ($\delta = 3.34\text{ ppm}$) for (H_2O), ($\delta = 6.844\text{--}7.804\text{ ppm}$) for Ar-H group.

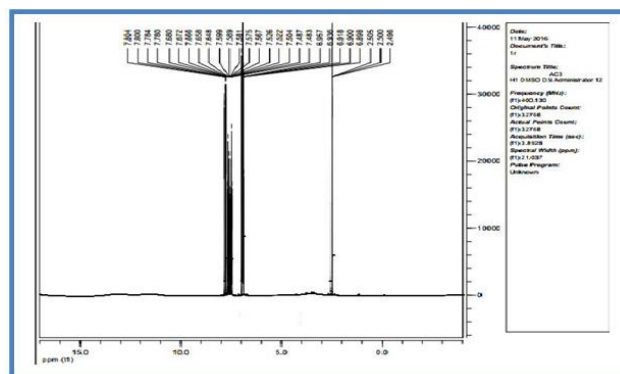
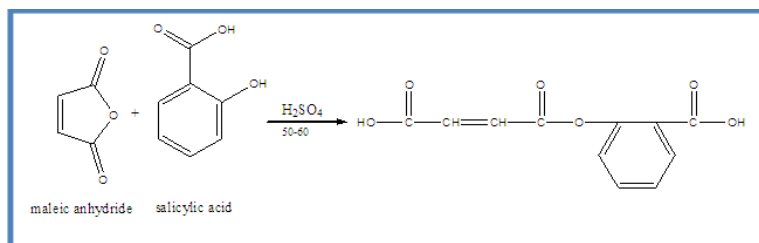


Figure 12: 1H -NMR Spectra of AC3

But-2-enedioic Acid Mono (2-Carboxy-Phenyl) Ester AC4

This monomer (acid) prepared by reacting phthalic anhydride with p-hydroxy benzoic acid in distilled water in the presence H₂SO₄ as a catalyst with stirring in temperature between (50-60°C) for 4 hours. After the reaction completing, the round white precipitate was formed, dried and weighted.



Scheme (4): Preparation of AC4

Characterization of (AC4)

FT-IR Spectrum

The FTIR spectra of (AC1) as shown in (Figure 15) which indicates absorption band of (OH) Carboxylic at (3517 cm⁻¹), (C-H) aromatic at (3000 cm⁻¹), (C=O) Carboxylic acid at (1700 cm⁻¹), (C=O) in the ester group at (1754 cm⁻¹), (C=C) aromatic at (1522, 1612 cm⁻¹), and (C-O) at (1240 cm⁻¹).

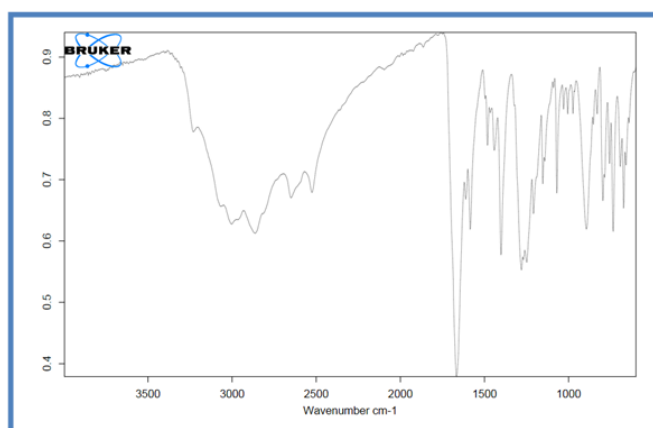
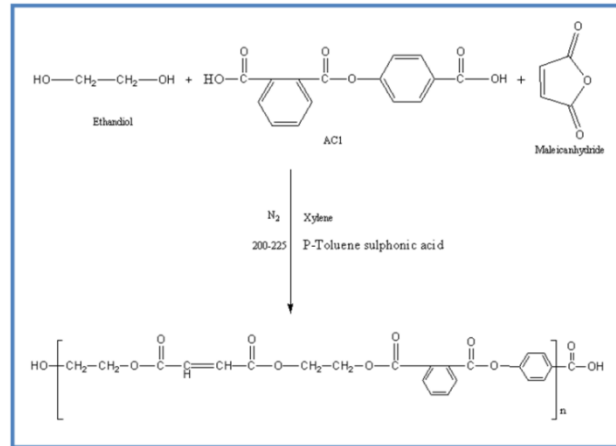


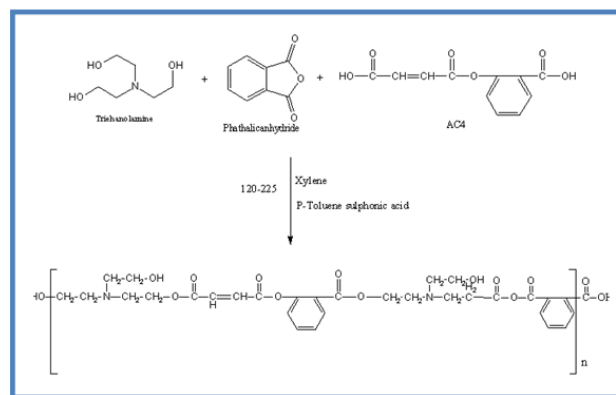
Figure 13: FTIR Spectra of AC4

Synthesis of Unsaturated Polyesters

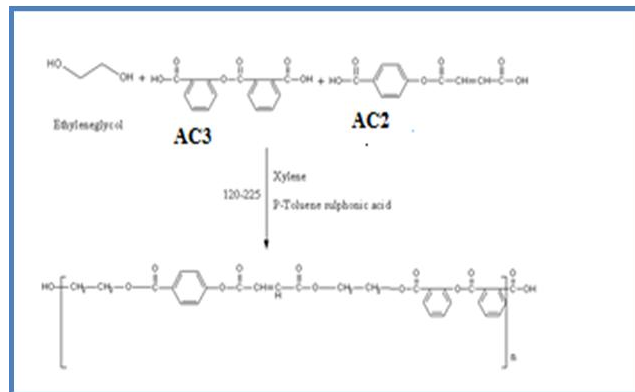
In this section, used polycondensation method for synthesis of a series of new unsaturated polyesters from the direct polycondensation reaction of dicarboxylic acid (AC1, phthalic anhydride, AC4) with alcohols (ethandiol, triethanolamine, ethleneglycol) respectively, by using p-toluene sulphonic acid catalyst (0.2gm) with heating into 120°C. When the reaction becomes clear (Maleic anhydride, AC4, AC2) was added. These UPRS were contained double bond in the main chain for forming cross linking with styrene. These UPRS were characterized by FT-IR and ¹HNMR spectra.



Scheme (5) Synthesis of UPRS 1



Scheme (8) Synthesis of UPRS 2



Scheme 7: Synthesis of UPRS 3

Characterization of (UPRS1)

FT-IR Spectrum

The FTIR spectra of (UPRS1) as shown in (Figure15) which indicates absorption band of (OH) Carboxylic at (3400 cm⁻¹), (C-H) aromatic at (3100 cm⁻¹), (C=O) Carboxylic acid at (1704 cm⁻¹), (C=O) in the ester group at (1754 cm⁻¹), (C=C) aromatic at (1522, 1612 cm⁻¹), and (C-O) at (1240 cm⁻¹).

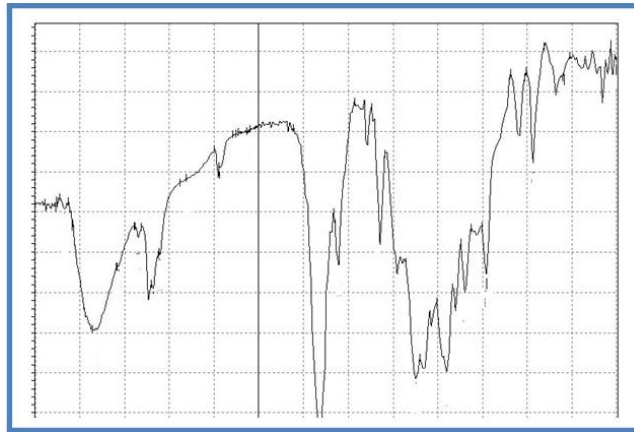


Figure (14): FTIR Spectra of UPRS 1

(¹H-NMR) Spectrum of (UPRS 1), is shown in Figure (8) assigns the following chemical shifts; ($\delta = 2.5$ ppm) for (DMSO), ($\delta = 3.34$ ppm) for (H₂O), ($\delta = 4.3$ ppm) for methylene group, ($\delta = 6.8-7.9$ ppm) for Ar-H group.

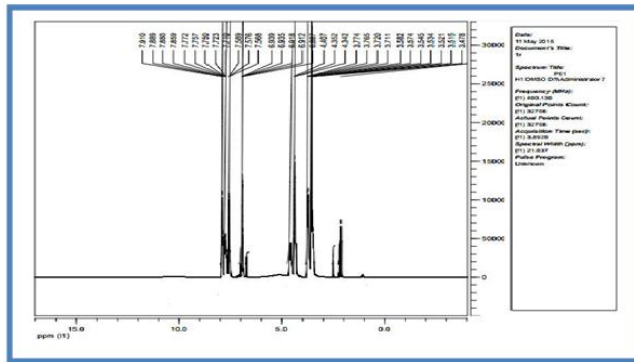


Figure 15: HNMR Spectra of UPRS1

Characterization of (UPRS2)

FT-IR Spectrum

The FTIR spectra of (UPRS 2) as shown in (Figure16) which indicates absorption band of (OH) Carboxylic at (3450 cm⁻¹), (C-H) aromatic at (3100 cm⁻¹), (C=O)Carboxylic acid at(1704cm⁻¹), (C=O) in the ester group at (1740 cm⁻¹), (C=C) aromatic at (1468cm⁻¹), and (C-O) at (1288 cm⁻¹), (C-N) at (1072cm⁻¹)

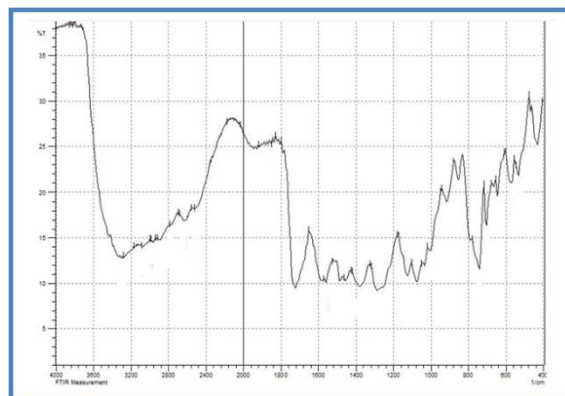


Figure 16: FTIR Spectra of UPRS 2

(¹H-NMR) Spectrum of (UPRS 2), is shown in Figure (10) assigns the following chemical shifts ; (δ = 2.4 ppm) for (DMSO), (δ = 3.34 ppm)for (H₂O),;(δ = 3.9 ppm) for methylene group, (δ= 6.7-8.2 ppm) for Ar-H group.

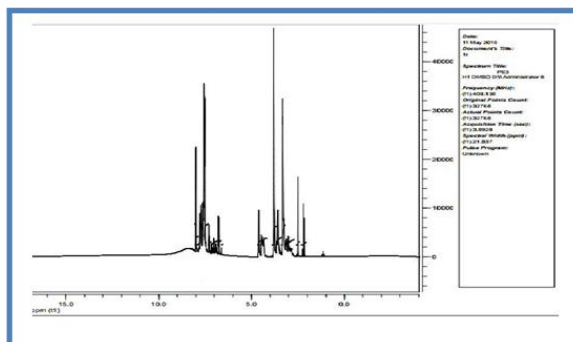


Figure 17: HNMR Spectra of UPRS 2

Characterization of (UPRS 3)

FT-IR Spectrum

The FTIR spectra of (UPRS 2) as shown in (Figure17) which indicates absorption band of (OH) Carboxylic at (3470 cm⁻¹), (C-H) aromatic at (3102 cm⁻¹), (C-H) alkene at (3032cm⁻¹), (C-H) aliphatic at (2860cm⁻¹), (C=O) in the ester group at (1733 cm⁻¹), (C=C) alkene at (1600cm⁻¹), (C=C) aromatic at (1480cm⁻¹), and (C-O) at (1203 cm⁻¹).

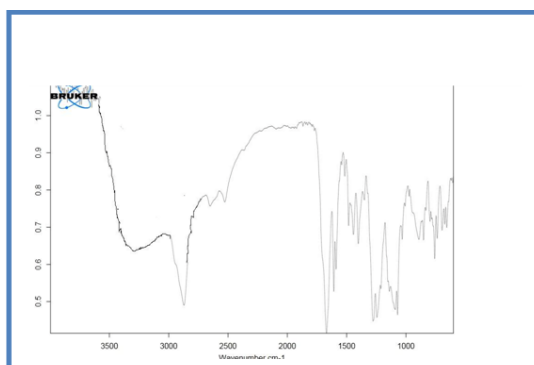


Figure 18: FTIR Spectra of UPRS3

(¹H-NMR) Spectrum of (UPRS 3), is shown in Figure (10) assigns the following chemical shifts ; (δ = 2.4 ppm) for (DMSO), (δ = 3.34 ppm)for (H₂O),;(δ = 3.9 ppm) for methylene group, (δ= 6.7-8.2 ppm) for Ar-H group.

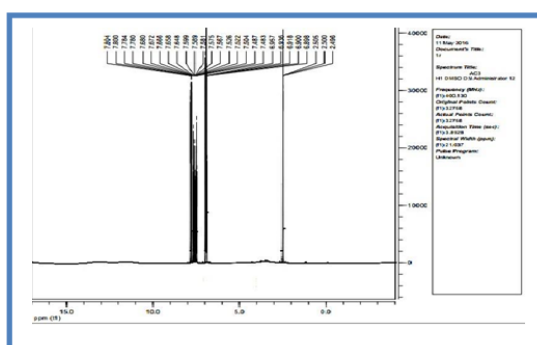


Figure 19: HNMR Spectra of UPRS3

Physico – Chemical Tests

Acid Value Test

Acid rate of unsaturated polyester resin is to be decided conferring to the course stated by mantel eLal.12 Almost one gram (precisely assessed) of the tester was melted in 50ml of acetone in 250ml narrowed bottle. Then waiting for few minutes, the solution was titrated with 0.1 N alcoholic potassium hydroxide solution, through the use of phenolphthalein being an indicator. Complete decision was done at the alike time deprived of a tester. The rate of the acid is stated as the no. of milligrams of potassium hydroxide demanded to counterbalance one gram of resin tester.

Calculation

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

Where

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

0.1 = Normality of KOH solution

W = Weight of sample (gm)

The acid value of unsaturated polyester resins is reported in table (2).(UPRS 2) showed an acid value higher than the (UPRS 1) and (UPRS3) due to the length of unsaturated polyesters chain component there of these polyesters[12,13].

Table 3: Acid Value

UPRS	Acid Value
UPRS 1	24
UPRS 2	28
UPRS 2	22

Solubility Test

Unsaturated polyester showed high solubility in different type of solvents. (Table10) 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, CHCl₃) and other solvents such as methanol, ethanol. There is an increase in the solvent molecules with the detachment between the molecular chains of the resin. There is also an invasion to the spaces between elongated chains together with suspended side group of resin through solvent molecules as they fill the space was accessible by chain actions. When actions bring two chains near to nearness, short range striking services are therefore recognized bringing about in limited chain action and consequently leading to the foundation of a viscous scheme [14, 15]. Then they add solvents, so that they can deal with the issue of great viscous resin which is a difficulty in substrates wet aptitude.

Table 4: Solubility Test

Polymer	Solvents								
	Acetone	Benzene	CHCl ₃	CH ₂ Cl ₂	DMSO	DMF	THF	H ₂ SO ₄ 0.01M	HCl 0.01M
UPR _S 1	++	+-	++	++	++	++	++	--	--
UPR _S 2	--	--	+-	+-	++	++	--	+-	+-
UPRS 2	+-	+-	++	++	+-	++	++	++	++

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

Mechanical Properties

Tensile Strength

The amount of the power demanded to wrench something such as rope, wire, or a structural beam in relation to the top where it destroys is called tensile strength. So the tensile power of a material is the all-out amount of tensile pressure that it can measure earlier to failure. Tensile strength of UPRS 1 composite was increased by the addition of Carbon Nano filler is higher can be attributed to the physical properties of this filler, where the particle size of Nano fillers is small and the particle size of non-Nano fillers is larger, with the UPRS matrix. Increasing the filler content for UPR1 reduced the tensile strength of the composite. But it can be decreased the tensile strength of the composite. But it can be decreased when the filler is not Nano such as TiO_2 and ZnO . UPRS1 get mechanical properties better than UPRS2 and the last better than UPRS3.

Table 5: Tensile Strength

FILLER	TENSILE STRENGTH		
	UPRS1	UPRS2	UPRS 3
C NANO	17	14	13
TiO_2 NANO	15	12	11
TiO_2	12	10	9
ZNO	10	9	8

Elongation

Elongation at disruption, likewise named as fracture strain, which is the ratio between altered length and original length afterward breaking of the test sample. It shows the ability of a material to repel fluctuations of shape deprived of crack construction. The elongation at break is decided by stretchy testing in agreement with EN ISO 527. The elongation at break obtained from the tensile tests indicates the elastic properties of the composites. Generally, a high value of elongation at break is indicative of highly elastic material. The addition of filler causes the matrix to lose its elastic properties and the material becomes more brittle. The fillers increased the value of the elongation at break. Where the Nano fillers (carbon Nano and Nano TiO_2) gained the UPRS high elongation because the diffusion of its in easily between the chains of UPRS that is belong to small particle size of its. Where carbon Nano mixes with UPRS in a good manner better than TiO_2 Nano.

Table 6: Elongation at Break %

Fillers	Elongation at break		
	UPRS1	UPRS2	UPRS 3
C Nano	2.9	2.5	2.1
TiO_2 nano	2.0	1.9	1.8
TiO_2	2.0	1.9	1.7
ZnO	1.9	1.8	1.5

Modulus

Modulus of elasticity is the diminutive from the Latin word modus meaning measure or manner. For the composites increases with the increasing filler (ZnO and TiO_2). Because of this the hardness of its composites tends to strongly increase with the addition of these fillers. This belongs to the large particle size of the fillers, but it doesn't effect when the fillers are Nano (Carbon Nano and Nano TiO_2) because the particle size of these fillers is smaller and the surface area is larger than not Nano fillers.

Table 7: Modulus

Fillers	Modulus		
	UPRS 1	UPRS 2	UPRS 3
C Nano	30	37	38
TiO ₂ nano	35	39	40
TiO ₂	37	39	42
ZnO	33	35	40

Hardness

Hardness is the measurement of how the solid matter resists and is to different types of enduring shape alter when a compressive power is used. Certain resources (e.g. metals) are harder than others (e.g. plastics). Macroscopic hardness is generally categorized by solid intermolecular bonds, yet the performance of hard resources underneath power is difficult; consequently, there are diverse amounts of hardness: scratch hardness, indentation hardness, as well as rebound hardness. Hardness is thus reliant on ductility, elastic stiffness, plasticity, strain, strength, toughness, viscoelasticity, and viscosity. The familiar samples of solid substance are ceramics, concrete, certain metals, as well as super hard materials that can be compared with lenient substance.

The hardness of the composites was also due to the destruction of the mobility of the UPRS matrix by the addition of the filler content. This may be attributed to the increased surface area of the Nano fillers in contact with UPRS and decreasing the movement of polymer molecular which lead to rose of strength of material. Where the surface area of Nano fillers is larger than non-Nano fillers. UPRS3 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	39	37	38
TiO ₂ nano	35	33	40
TiO ₂	37	30	31
ZnO	33	35	33

Thermal Properties

Thermo gravimetric analysis (TGA) study

Thermo gravimetric Analysis (TGA) involves determining changes in mass as a function of temperature. It is quite normal to quest squalor heats, engrossed component of substances, stages of inorganic and organic fragments embodied in a substantial and examination solvent remains. 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 an Argon atmosphere at a heating rate of 10 °C/ min. The results such as T_i, T_{op}, T_f, T_{50%}, % Residue at 500 °C, and char yields at 300 °C 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 °C. The char yields of (UPRS1, UPRS2, UPRS3) are (53%, 70%, 80%) at 300 °C in Argon atmosphere, which indicate they could meet temperature resistant requirements. Weight residue of UPRS at 500 °C.

Table 9: TGA

Alkyd Resin	DT/°C				T _{50%}	Residue at °C300	Char % At 200°C
	T _i	T _{op1}	T _{op2}	T _f			
UPRS1 CNano	271	170	407	>500	>500	51%	74%
UPRS1 ZnO	298	210	405	>500	>500	52%	81%
UPRS1 TiO ₂	329	233	398	>500	>500	70%	75
UPRS1 TiO ₂ Nano	353.4	290	409.9	>500	>500	72%	70
UPRS2 CNano	269	200	419	>500	>500	75%	50
UPRS2 ZnO	339.5	201	445	>500	>500	72%	76
UPRS2 TiO ₂	334	244	428	>500	>500	80%	56
UPRS2 TiO ₂ Nano	234	214	314	>500	>500	85%	64
UPRS3 CNano	322	190	414.5	>500	>500	82%	62.5
UPRS3 ZnO	328	145	411	>500	>500	60%	66
UPRS3 TiO ₂	330	180	417	>500	>500	65%	64
UPRS3 TiO ₂ Nano	350	200	413.9	>500	>500	62%	66

DT: Decomposition temperature.

T_i: Initial decomposition temperature.

T_{op}: Optimum decomposition temperature.

T_f: Final decomposition temperature. The final degree of dissociation temperature

T_{50%}: Temperature of 50% weight loss, obtained from TGA.

Char% at 500 ° C: Residual weight percentage at 300 ° C in Argon by TGA

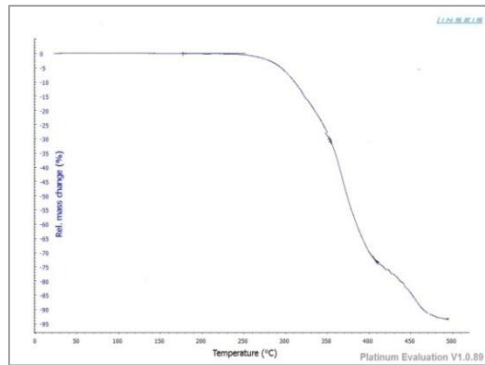


Figure (20) TGA Curve of UPRS1 Supported by Carbon Nano

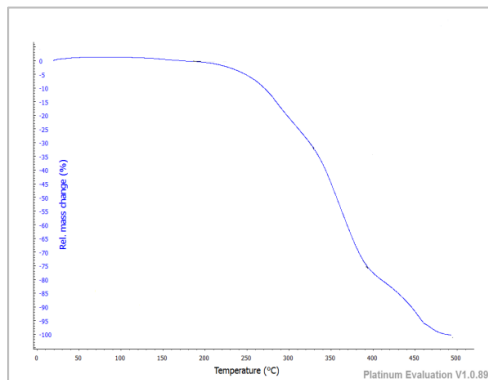


Figure 21: TGA Curve of UPRS1 Supported by TiO₂Nano

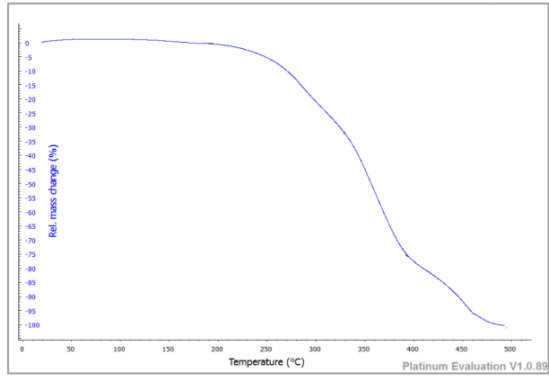


Figure 22: TGA Curve of UPRS 1 Supported by ZnO

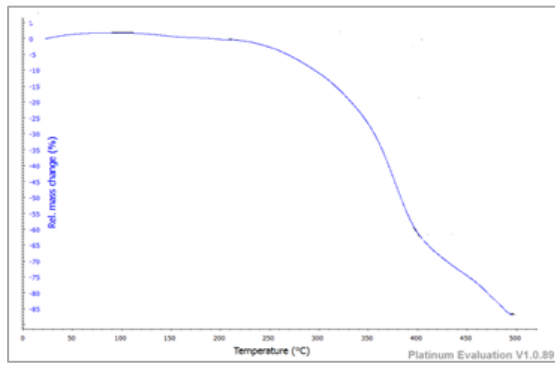


Figure 23: TGA Curve of UPRS1 Supported by TiO₂

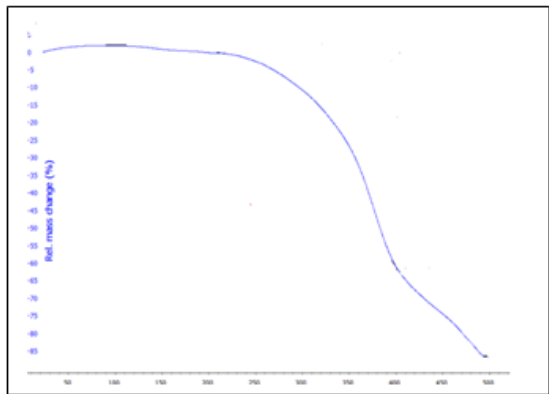


Figure 24: TGA Curve of UPRS2 Supported by ZnO

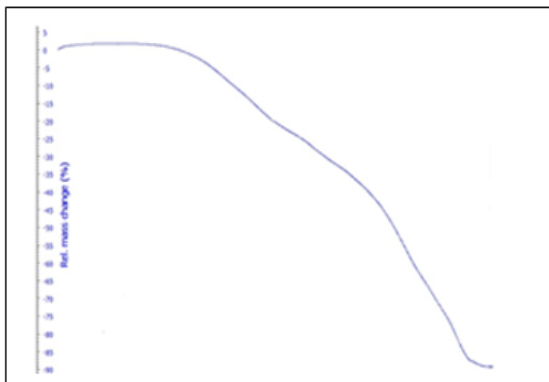


Figure 25: TGA Curve of UPRS 2 Supported by TiO₂

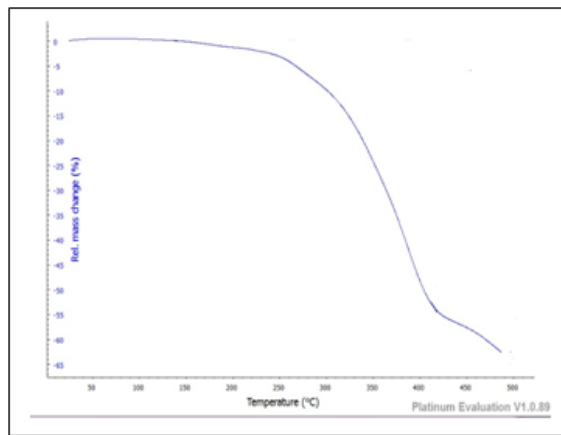


Figure 26: TGA Curve of UPRS2 Supported by ZnO

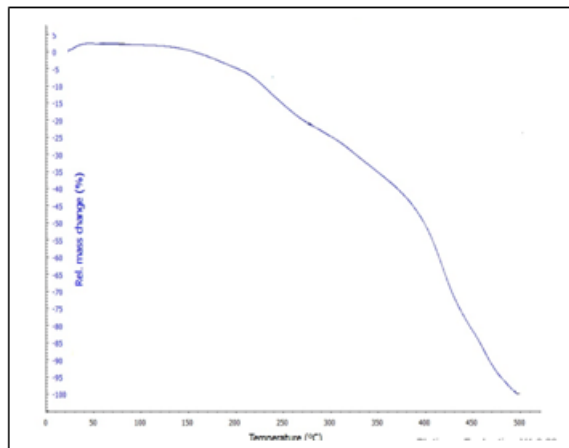


Figure 27: TGA Curve of UPRS2 Supported by TiO₂

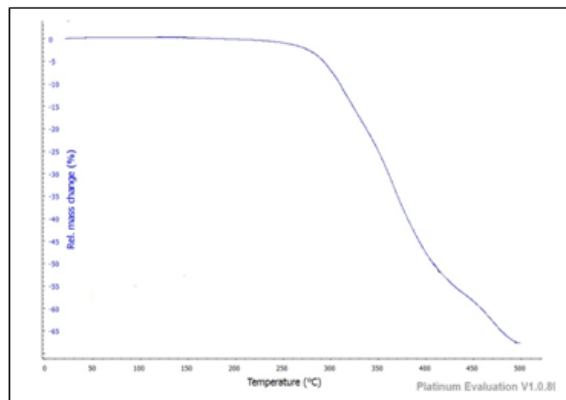


Figure 28: TGA Curve of UPRS3 Supported by TiO₂Nano

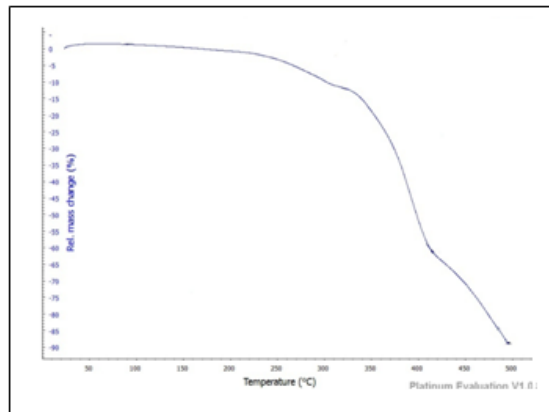


Figure 29: TGA Curve of UPRS3 Supported by Carbon Nano

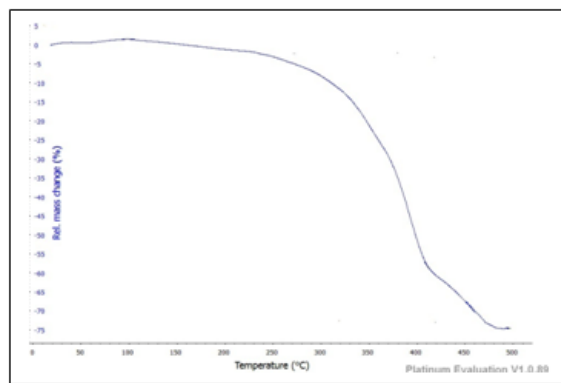


Figure 30: TGA Curve of UPRS2 Supported by ZnO

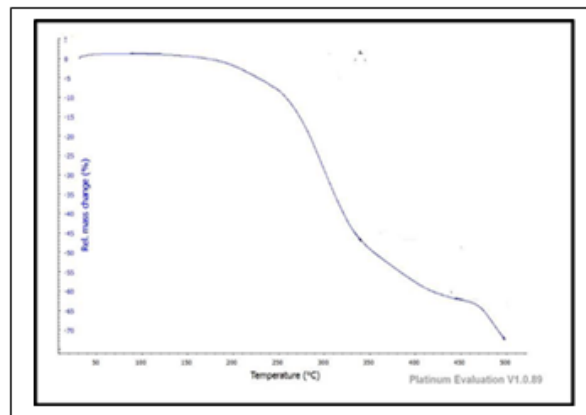


Figure 31: TGA Curve of UPRS3 Supported by TiO₂

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 glass transitions (T_g), and the melting point (T_m) the degree of crystallization (T_c)⁽¹⁴⁾. this test was applied to the prepared samples, Shows the (curve 24) for the sample of (UPRS 1 C Nano) The results showed the value of the glass transition (T_g) of the mixture (68c °), referring to obtain the flow temperature and then increases endothermic the sample to reach the melting point (T_m)

at (469c °) 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 (curve 25) for the sample of (UPRS 1 TiO₂) and the results showed the value of the glass transition (Tg) of the combination (43c°) referring to an increase in the flow temperature and then increase endothermic the sample to reach the melting point (Tm) at (446.7 c °) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (340 c°).It also shows a (curve 26) for the sample of (UPRS 1 TiO₂ Nano) and the results showed the value of the glass transition (Tg) of the combination (49c°) 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 (curve 27) for the sample of (UPRS 1 ZnO) and the results showed the value of the glass transition (Tg) of the combination (90c°) referring to an increase in the flow temperature and then increase endothermic the sample to reach the melting point (Tm) at (481 c °) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (395 c°).It also shows a (curve 28) for the sample of (UPRS 2 C Nano) and the results showed the value of the glass transition (Tg) of the combination (85c°) 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 (curve 29) for the sample of (UPRS 2TiO₂) and the results showed the value of the glass transition (Tg) of the combination (48c°) referring to an increase in the flow temperature and then increase endothermic the sample to reach the melting point (Tm) at (430 c °) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (320 c°).It also shows a (curve 30) for the sample of (UPRS 2ZnO) and the results showed the value of the glass transition (Tg) of the combination (35c°) referring to an increase in the flow temperature and then increase endothermic the sample to reach the melting point (Tm) at (448.7 c °) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (320 c°).It also shows a (curve 31) for the sample of (UPRS 2 C Nano) and the results showed the value of the glass transition (Tg) of the combination (41.8c°) referring to an increase in the flow temperature and then increase endothermic the sample to reach the melting point (Tm) at (464 c °) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (335 c°).

It also shows a (curve 32) for the sample of (UPRS 2 TiO₂) and the results showed the value of the glass transition (Tg) of the combination (54c°) referring to an increase in the flow temperature and then increase endothermic the sample to reach the melting point (Tm) at (487.3 c °) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (400.7 c°).It also shows a (curve 33) for the sample of (UPRS 2 TiO₂ Nano) and the results showed the value of the glass transition (Tg) of the combination (49c°) referring to an increase in the flow temperature and then increase endothermic the sample to reach the melting point (Tm) at (471.8 c °) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (335 c°).It also shows a (curve 34) for the sample of (UPRS 2ZnO) and the results showed the value of the glass transition (Tg) of the combination (40c°) referring to an increase in the flow temperature and then increase endothermic the sample to reach the melting point (Tm) at (450 c°) completely dissolve and then less the sample heat absorption rate and by a curved appointed degree of crystallization (Tc) of the mixture was (394 c°).

Table 10: Shows the Degree of Glass Transition, Melting Point and the Degree of Crystallization in the Differential Thermal Analysis

Samples		Tg (c°)	Tm (c°)	Tc (c°)
UPRS 1	10 % C Nano	68	469	360
	10 % TiO ₂	43	446.7	340
	10% TiO ₂ nano	49	452.4	361.3
	10% ZnO	90	481	395
UPRS 2	10 % C Nano	85	467	310
	10 % TiO ₂	48	84	320
	10% ZnO	35	448.7	320
UPRS 3	10 % C Nano	41.8	464	335
	10 % TiO ₂	54	487.3	400.7
	10% TiO ₂ nano	49	471.8	335
	10% ZnO	40.6	450	394

Tg: Degree glass transition

Tm: Melting Point

Tc: Degree of crystallization

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 insolubility in various solvents. It shows cross linking with styrene. It shows good mechanical and thermal properties when it's supported by some fillers such as carbon Nano, TiO₂Nano, TiO₂ and ZnO. In general, mechanical and thermal properties of UPRS1 better than UPRS 2 and the last is better than UPRS 2.

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