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Study The Thermal Properties And Effect Of Acidic Solutions To Unsaturated Polyester Composite With Iron Filings

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ABSTRACT

Polymeric composites of liquid polyester as a base material were prepared and studied with iron filings powder as a support material, in a ratio of (1:1), using the (TGA) and (IGA) techniques to study their thermal properties.
The (TGA) values correspond to the weight ratio values at 330 °C (Wt%) and there is no agreement between the IGA values and the weight ratio values at 330 °C. There was a compatibility for the TGA values with the weight ratio values at 330 °C (Wt%) and there was no agreement between the IGA values with the weight ratio values at 330 °C, i.e. the isothermal gravimetric analysis (IGA) could not be considered a good measure of thermal stability.
The values of the weight ratio at 330 °C (330 Wt%), the (TGA) values and the isothermal gravimetric analysis (IGA) values were found to be close to all networks treated at temperatures (23,53,83,123,153). The reason for this is that the unsaturated polyester contains iron filings powder, so it is not effect with heated. It was found that the neutral medium had more influence on the weight ratio values at 330 °C (Wt%). The Fuoss equation was used to calculate the energy of activation for all studied polymeric networks.

Keywords: Thermal gravimetric Analysis, Unsaturated polyesters, iron filings, polymeric compounds , activation energy, thermally stable Polymers, isothermal gravimetric Analysis

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INTRODUCTION

The idea of the current research started from the increasing importance of composite materials in our daily life because they carry distinctive properties that qualify them to be a basic material in many modern industries and that technological development depends on progress in this field and as a result of this development there is a need to replace the traditional materials used such as metals in industry into materials An alternative that has good engineering and thermal properties for use in various applications. Hence the idea of improving mechanical properties (shock resistance, stiffness, elastic modulus, compressive strength) and the ability to work at high temperatures. Therefore, it was necessary to work on producing materials that contain more than one support material that improves the properties of the final product, The composite material is composed of the base material (unsaturated polyester) with the support material which is (tungsten carbide) with different weight ratios (0, 0.75, 1.5, 2.25, 3%) respectively, we found that the hardness value increased with increasing the weight fraction to obtain its higher value. By 3% (Esraa et al., 2019, Yolanda Bautista et al., 2018),
Unsaturated polyester (UP) composed of maleic anhydride, phthalic anhydride and 1,2-propylene glycol has been prepared as an adhesive base component. Fillers are widely used in order to reduce cost and to control shrinkage in adhesive formulations, Four types of fillers of the same particle size (50 mesh) and different chemical properties, silica, alumina, talc, and kaolin were used. Best results as an adhesion strength were obtained with the kaolin filler(Adil K. Hussien et al., 2018), Two groups of Nano composites were prepared by Hand Lay-up method. The first group consists from (UP) reinforced by hybrid nanoparticles consisting of a mixture of zirconium oxide and yttrium oxide (30 mol%Y2O3- ZrO2) with particles size (83.98nm). The second group consists of (UP) reinforced by zirconia nanoparticles (ZrO2) with particle size (47.23nm). This reinforce a good compatibility between unsaturated polyester resins and reinforcement nanoparticles, which enhancement the mechanical properties(Sihama et al., 2018), Novel aluminised E-glass fibre reinforced unsaturated polyester composites, originally formulated for enhanced thermal and electrical shielding properties were evaluated in terms of their thermal performance. The thermal degradation of these specimens was analysed using a thermogravimetric analyser (TGA). The samples were heated from ambient temperature to 500 °C at a heating rate of 20 °C/min. All specimens were decomposed under dry nitrogen (N2) at a flow rate of 40 ml/min to yield gases and solid char. Aluminised E-glass composites were compared alongside the unmetallised E-glass and unreinforced composite. The major weight loss occurred between 200 and 400 °C. The unreinforced polyester had a maximum weight loss1.25%/°C, occurring at 360 °C. For the aluminised and unmetallised E-glass composites, the maximum rate of weight loss was 0.34 and 0.55%/ °C, respectively. Experimental results show the degradation of the aluminised E-glass composites obtained from TGA tests is higher compared to those of unmetallised E-glass fibre and unreinforced polyester composite. This improvement is correlated to the aluminium coating (Ferreira, J.M. et al.2006)
datepalm fibers and rice husks waste particleboards a sin solation boards were manufactured. The boardswere fabricated from unsaturated polyester resin as a matrix reinforced by rice husk and date palm fibers prepared The results showed that thermal and acoustic in solation properties increase with increased the volume fraction of

date palm fiberand rice husks in hybrid composite, where as decrease with increased fiber length, more over the thermal insulator of the polyester composite reinforced with rice husk gave a better thermal insulator whereas polyester composite reinforced by date palm fibers gave the best acoustic insulation (Ammar et al., 2016).

Experimental

Models of polymeric complexes

After carrying out some a number of practical experiments, they were suitable for numbers in laboratory conditions, percentage (2:1, solid: unsaturated polyesters). Polymeric compounds were prepared from unsaturated polyester and iron filings powder in a ratio of 1:1, and this ratio was increased all studied (McCaffery E. L.,1970). Where the unsaturated polyester liquid is mixed with iron filings powder for 30 minutes until the homogeneity between the iron scrap powder is complete and then the substance is added The mixture is hardened and mixed well and then poured into molds to obtain chips (1 ± 0.1 mm). They are separated from the molds by sharp pieces into small pieces suitable for the required study (Ebtehag Z. Sulyman et al.,2019).

Heat treatment of models

Samples groups were thermally treated for 10 hours at 5 the following temperatures: 23, 53, 83,123 and 153°C. After the end of the specified period, the samples were removed from the oven and kept in a dry place.

Acid treatment of models

Different groups of samples were treated in three acid media with three different acidity (pH: 5, 7, 9) and after the expiration of the specified time (48 hours) the samples were removed from the solutions, washed with water and dried in air only at laboratory temperature and then kept in a dry place

Thermal stability of polymeric compounds

The thermal stability (resistivity) of polymeric compounds was studied using TGA Thermo gravimetric analysis and IGA Isothermal Gravimetric Analysis. The thermal stability of the various models was measured by comparing the temperature at the beginning and the end of the decomposition and the weight ratio of the polymer remaining in the middle of the beginning and the end, and the following definitions were given:

Initial Decomposition Temperature – (IDT)

Complete Decomposition Temperature – (CDT)

The weight ratio is at 330°C -(Wt%)$_{330}$

The CDT and IDT values were measured from the intersection of the TGA tangents at the change points with the straight part of the curve at the beginning and end of the decomposition. The value of (Wt%)$_{330}$ was determined from the intersection of the column falling on the curve at a degree of 330°C (Tager, A.,1978).

The thermo gravimetric analysis curves were obtained through a laboratory-implemented device depending on the source (Perrin D. D. et al.,1980). Also, a thermo gravimetric constant temperature analysis (IGA) device was used, and before entering the model for measurement, the temperature was fixed at 330°C, and then entered into the model after that and the weight change curves were recorded with time at this temperature. And the implemented device was used to measure (TGA) .

The (CDT) and (IDT) values were measured from the intersection of the TGA tangents at the change points with the straight part of the curve at the beginning and end of the decomposition. The value of (Wt%)$_{330}$ was determined from the intersection of the column falling on the curve at a degree of 330°C .

Figure (1) indicates the thermo gravimetric analysis curves of the treated (hardened) polymeric composites at five different temperatures. It indicates the composition of the unsaturated polyester compound with iron filings powder. The reference values (CDT, IDT% Wt) extracted from the aforementioned figures were included in Tables (1), For the sake of comparison, we reviewed the results of the gravimetric analysis of the ester models (alone) and treated at temperatures ranging between 23 - 153°C and pH values ranging Between (5-9), where it was found that the (IDT) values were less than 153°C in all these treatments, while the (CDT) values ranged between 338 -480°C and did not reach 500°C. The average values of (Wt%)$_{330}$ did not exceed 30% (**Citation** Al-Lami HS, et al.2006), Where it was found that the (IDT) values are less than 153 °C in all these treatments, while the (CDT) values ranged between 338-480 °C and did not reach 550°C except in rare cases. The average values of (Wt%)$_{330}$ did not exceed 65% (Ebtehag Z .Sulyman,2011).

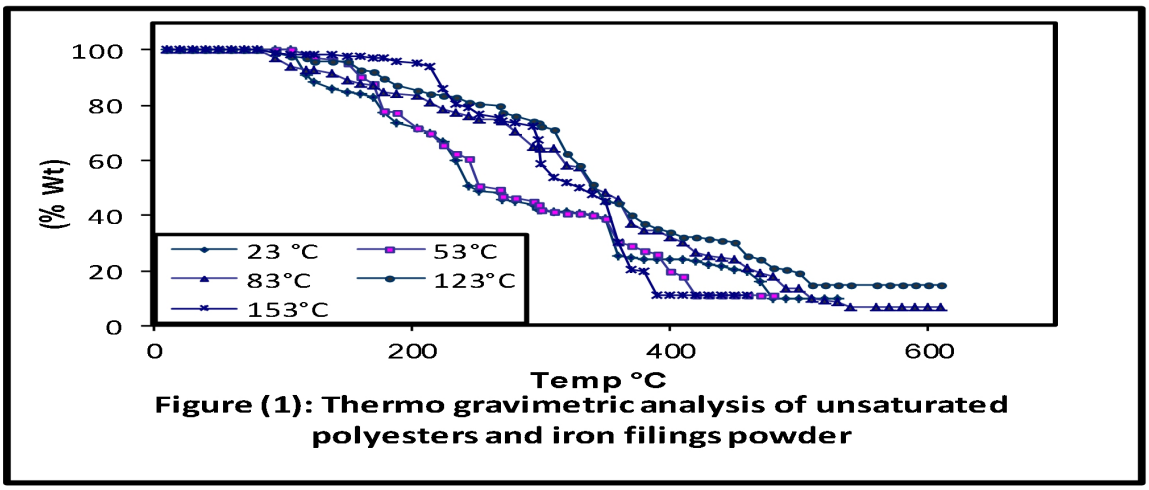

Figure (1): Thermo gravimetric analysis of unsaturated polyesters and iron filings powder

Table (1): Some values of the thermal stability of polymers taken from the thermo gravimetric analysis curves

Composite	Process	Temperature at	Weight ratio

	temperature (°C)	Initial Decomposition Temperature **IDT**	Complete Decomposition Temperature **CDT**	(Wt%) at 330°C
UPE-IFP	23	137	480	55
	53	137	458	46
	83	138	447	34
	123	124	338	32
	153	124	367	31

From a note in Table (1) and by comparing the values of (IDT, CDT, Wt%) for all polymeric compositions with polyester alone, a remarkable increase in these values is observed due to the presence of iron filings powder with polyester and by extrapolating in Table (1) for the values of (IDT) and for all the polymeric compounds, the following is observed:

1. The (IDT) values of the iron filings containing polymeric compounds were high
2. A significant effect of increased curing temperature on the (IDT) values is observed, as the higher the curing degree, the lower its value .

A significant effect of increased curing temperature on the (IDT) values is observed, as the higher the curing degree, the lower its value.

3. The (CDT) values for polymeric compounds with iron filings powder are relatively high in all polymeric compounds.
4. A significant effect of increased curing temperature on (CDT) values is observed, as the higher the degree of curing, the lower its value .
5. By comparing the mean values of $(Wt\%)_{330}$ with the average values of each of the (IDT) and (CDT), it is noted that they are more consistent (relatively) with the values of (CDT), which indicates that the values of (IDT) are not necessarily a good measure of thermo polymeric compounds .

Thermal stability of compounds treated at different pH

Figure (2) indicates the thermo gravimetric analysis curves of the polymeric compounds treated at three different pH degrees. The reference values for the beginning and end of the decomposition and the residual weight at 330°C were extracted and listed in Table(2)

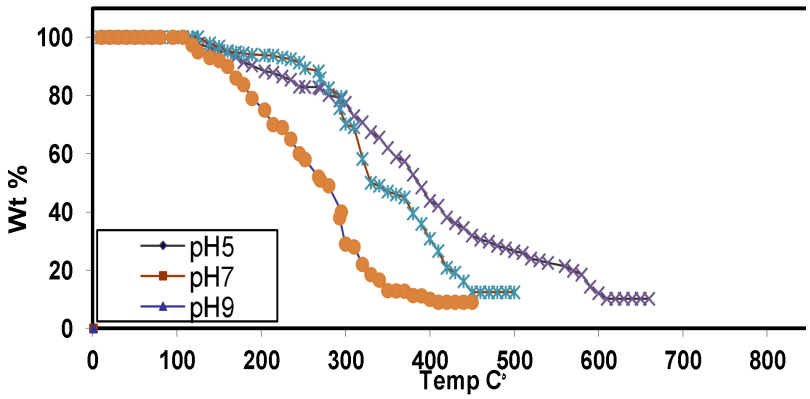

Figure 2: Thermo gravimetric analysis of polymeric compos unsaturated polyesters with iron filings powder UPE-IFI treatment at different pH

Table (2): Some values of thermal stability of UPE-IFP polymeric compounds for treatment at different pH

Composite	Acid state pH	Temperature at		Weight ratio (Wt%) at 330°C
		Initial Decomposition Temperature **IDT**	Complete Decomposition Temperature **CDT**	
UPE-IFP	pH_5	117	421	31

	pH_7	**138**	**451**	**46**
	pH_9	**117**	**412**	**12**

By extrapolating the (IDT) values in Table (2) for all compounds, it was found that these values are relatively higher in the neutral environment than in the acidic and basic surroundings. This can be attributed to the influence of the bonds due to acid or base decomposition(Sabar, D. A, et al., 2018),values of $(Wt\%)_{330}$ are in agreement with the values of the iron filings powder It was high By extrapolating the CDT values of the polymeric compounds (Table 2), it is noted that they gave the highest values in the neutral medium compared to the basic and acidic medium

Reviewing the residual weight values of $(Wt\%)_{330}$, it is noted that the highest values were in the neutral medium R. compared to the basic and acidic medium(Mohammed, By comparing these values with the).K. , et al., 2018 values of CDT, IDT, it is observed that the values of $(Wt\%)_{330}$ correspond to the values of IDT and CDT in the neutral medium.

Isothermo gravimetric Analysis (IGA)

All measurements were made at a degree of 330°C. Rapid weight loss is observed in all the graphs in the first minutes of the measurement and after a period of time to semi-constant weights, as the graphs take a more straight form. This behavior is explained on the basis that all polymers begin a rapid loss of some small molecules (such as, H_2O, H_2 , O_2 ... etc.) at the beginning of heating (Ebtehag Z .Sulyman,2005), and at the same time the incomplete polymeric structures integrate or the free radicals used (as a result of the disintegration of some bonds) with each other forming New covalent bonds increase the stability of the compound, thus preventing This prevents the separation of other particles, and thus the loss decreases and the weight ratio reaches a semi-stable state. From figures (3 and 4), two important values were extracted, firstly the time taken to reach a constant weight and secondly, the remaining weight ratio after an hour of heating (Yang, Li, Z,2015) , and these values are listed in Table (3).

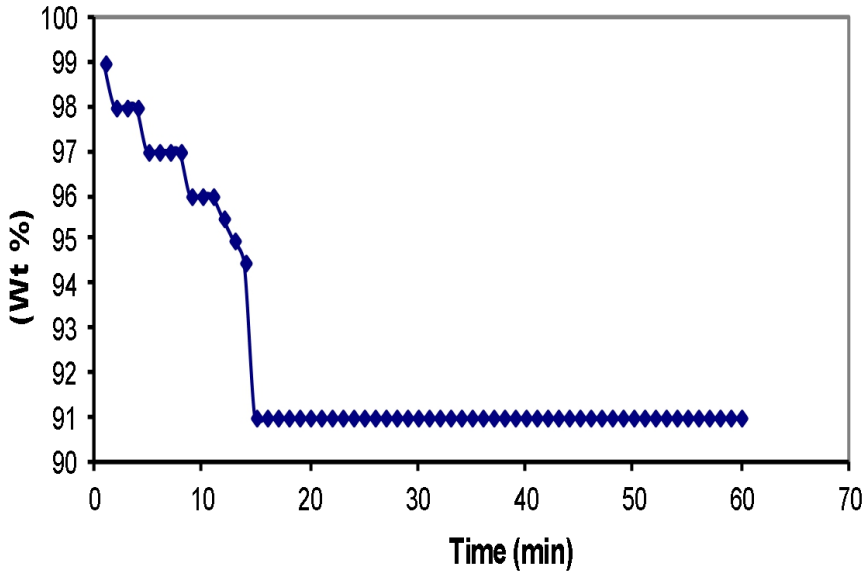

Figure 3: Thermogravimetric decomposition (IGA) For unsaturated polyester UPE at 330°C

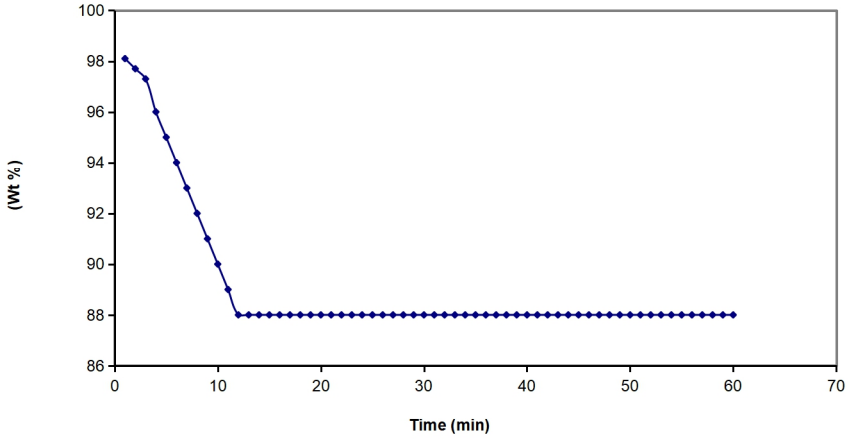

Figure 4: Thermo gravimetric decomposition (IGA) For polymeric compositions with iron fillings powder(UPE-IFP) at 330°C

Table (3): The constant weight ratio and the time taken to reach these ratios adapted from IGA measurements at 330°C

Composite	W %	Time (mint)
UPE	92	17
UPE-IFP	58	26

1- The time taken to reach a constant weight was 26 minutes compared to 17 minutes for unsaturated polyesters alone. This behavior can be explained by the presence of iron filings powder within the polymeric complexes, which delays the formation of the final composition due to interstitial interactions of the iron filings powder with the unsaturated polyesters in the composites.

2- The value of the residual weight in the polymeric compound was lower than it is in the unsaturated polyesters alone. The reason may be attributed to the fact that the presence of the polymer alone helps it to form more dense and compact mesh structures than it is in the case of the compound with the powder, which gives it greater relative thermal resistance

Energy of activation

The energy of activation for the dissociation process at its inception and for all studied polymeric composites was calculated using the Fuoss equation and according to the following equation Yang,(Fuoss,I.,1964)

$E = RT_i^2 / W_i (dw_i / dT_i)$

Where: E = dissociation activation energy, Ti = dissociation initiation temperature, Wi = weight ratio at Ti, R = gas constant, dwi / dTi = slope of the tangent at the dissociation point.

1- The values of the primary dissociation activation energy shown in Tables (4,5) have been included and if we take into consideration that increasing the activation energy can be considered as a measure of the stability of the polymer then the following can be observed:

2- This energy of composites treated at low temperatures is higher than that treated at higher temperatures (Table 4).

3- It was found that this energy of the treated compounds in the neutral environment is relatively higher than in the acidic and basic surroundings (Table 5).

4- These results are broadly identical to the results obtained when studying the stability of polymeric networks in constant and variable temperature, by a percentage of up to 70% Almost taking into account that all the measurements were made manually and with the help of laboratory-manufactured thermal devices and in conditions that are often far from idealism, and despite our use of this method to find the activation energy, we have many reservations about its use because the Foss equation is based on specific values The starting temperature of Ti dissociation and the slope of the tangent at the dissociation point (dwi / dTi) and assuming that the weight ratio of the polymer (%Wt) remains constant before the dissociation (the curve runs in a straight line) until it reaches the dissociation point Ti, after which the curve is gradually taken down and then the value of Ti is measured at the point of dissociation. The intersection of both lines and in fact the equation is used in the ideal case because most (TGA) curves do not initially run straight (parallel to the base).In 90% of cases, the weight loss is not uniform most of the time. Therefore, the difference in the determination of the Ti values as well as the tangent gradient values of Ti leads to large

differences in the measured activation energy values depending on these two value.

Table (4):The values of activation energies for dissociation of treated polymeric compounds in degrees Various thermals (kJ/ mol)

Polymeric compounds	Curing temperatures (°C)	Activation energies kJ/ mol
UPE-IFP	25	20.5
	50	17.4
	80	15.9
	120	10.3
	150	6.1

Table (5): The values of activation energies for the dissociation of the treated networks in degrees Different acidity (kJ / mol)

Polymeric compounds	PH degrees	Activation energies (kJ/ mol)
UPE-IFP	PH_5	16.3
	PH_7	38.0
	PH_9	12.3

CONCLUSIONS

1. The (IDT) values of polymeric composites containing UPE-IFP were high, a remarkable effect of increased curing temperature on the IDT values is observed
2. The (CDT) values of polymeric composites UPE-IFP are relatively high.
3. It is noted that there is a significant effect of increased curing temperature on the (CDT) values of the UPE-IFP polymeric composites.
4. No significant effect of increased treatment temperature was observed on (CDT) values, as they fluctuated more and less for others in a way that did not lead to a general conclusion.
5. By comparing the average values of $(Wt)_{330}$ with the average values of each of the (IDT), (CDT) notes that they are more consistent (relatively) with the values of (CDT), which indicates that the IDT values are not necessarily a good measure of thermal stability.
6. The values of (IDT) for all polymeric complexes in acidic media were found that these values in neutral medium are relatively higher than in acidic and basic media.
7. Also, the CDT values in the neutral medium are relatively higher than in acidic and basic media.
8. It is noted that the weight values of $(Wt\%)_{330}$ are the highest in the neutral medium compared to the acidic and basic medium.
9. By comparing the values of (CDT) and IDT, it was found that the values of $(Wt\%)_{330}$ correspond to the values of (CDT) in the neutral environment indicating that the values of (IDT) do not determine the dissociation of the polymer.
10. The time taken to reach a constant weight of unsaturated polyesters with UPE-IFP iron filings was 26 minutes compared to 17 minutes for unsaturated polyesters alone, meaning that the weight values $(Wt\%)_{330}$ of UPE-IFP were lower than those of unsaturated polyesters.
11. Activation energy can be considered as a measure of polymer stability. It was found that the activation energy of UPE-IFP compound polymers trea
12. ted at lower temperatures is higher than that of high temperature treatment.
13. It was found that the activation energy of the treated UPE-IFP complex in neutral medium is relatively higher than in the acidic and basic media.

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