ESTUDO DA CINÉTICA DA DEGRADAÇÃO TÉRMICA DE COMPÓSITOS DE NANOPARTÍCULAS NÃO-SATURADAS DE POLIÉSTER E POLIÉSTER / SILICA POR TÉCNICAS DE ANÁLISE TGA E DSC

STUDY OF THE KINETICS OF THERMAL DEGRADATION OF UNSATURATED POLYESTER AND POLYESTER/ SILICA NANOPARTICLES COMPOSITES BY TGA AND DSC ANALYSIS TECHNIQUES

دراسة حركيات التحلل الحراري للبوليستر غير المشبع و متراكبات البوليستر / جسيمات السيليكا النانوية بواسطة تقنيات تحليل TGA و DSC

FARHAN, Ahmed Jadah^{1*}

¹Department of Physics, College of Science, University of Wasit, Wasit, Iraq

* Correspondence author

e-mail: aalomairi@uowasit.edu.iq

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RESUMO

Compósitos são materiais multifásicos que possuem propriedades superiores de engenharia; a combinação de suas fases constituintes atinge essas propriedades. Os compósitos poliméricos reforçados por nanopartículas (NPCs) são novos tipos de compósitos que atraíram muita atenção recentemente e emergiram rapidamente como uma atividade de pesquisa multidisciplinar cujos resultados poderiam ampliar as aplicações dos polímeros em benefício de muitas indústrias diferentes. O objetivo da pesquisa é analisar o efeito da adição de diferentes porcentagens (10, 20 e 30%) de nanopartículas de sílica ao poliéster insaturado (UPE) e identificar a cinética de estabilidade térmica e decomposição para elas. Nesta pesquisa, os nanocompósitos foram preparados a partir de poliéster insaturado (UPE) misturado com diferentes porcentagens (10, 20 e 30%) de nanopartículas de sílica. As curvas de análise gravimétrica térmica (TGA) e calorimetria diferencial de varredura (DSC) foram obtidas a partir da degradação térmica calculada usando o Coats-Redfern. Os parâmetros cinéticos e termodinâmicos foram estudados para todas as amostras, apresentando um excelente coeficiente de correlação linear próximo à unidade usando o Minitab 16. Trabalho experimental mostrou que a degradação de compósitos obtidos a partir da análise termogravimétrica foi mais lenta que a UPE pura. A melhoria da estabilidade térmica foi atribuída ao teor de sílica. Além disso, o resultado mostrou que a decomposição sob o ambiente oxidativo para a UPE pura era muito mais rápida que o ambiente inerte.

Palavras-chave: *Decomposição térmica, Análise gravimétrica térmica, Poliéster insaturado aumentado, Nanopartículas de sílica.*

ABSTRACT

Composites are multi-phase materials that have superior engineering properties; the combination of their constituent phases achieves these properties. Nanoparticle-reinforced polymeric composites (NPCs) are new types of composites that have attracted a lot of attention recently and rapidly emerging as a multidisciplinary research activity whose results could widen the applications of polymers to the benefit of many different industries. The aim of research to analyze the effect of adding different percentages (10, 20, and 30%) of silica nanoparticles into unsaturated polyester (UPE) and identification of the thermal stability and decomposition kinetics for them. In this research, the nanocomposites were prepared from unsaturated polyester (UPE) mixed with different percentages (10, 20, and 30%) of silica nanoparticles. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves were obtained from the thermal degradation computed by using the Coats-Redfern. The kinetic and thermodynamic parameters were studied for all specimens were presented an excellent linear correlation coefficient close to unity using Minitab 16. Experimental work was showed that the degradation of composites obtained from the thermal gravimetric analysis was slower than the pure UPE. The enhancement of thermal stability was attributed to silica content. Also, the result showed that the decomposition under the oxidative environment for the pure UPE was much faster than the inert environment.

Keywords: *Thermal decomposition, Thermal gravimetric analysis, Unsaturated polyester risen, Silica nanoparticles.*

المترابكات هي مواد متعددة الأطوار لها خصائص هندسية فائقة؛ يتم تحقيق هذه الخصائص من خلال الجمع بين تلك الأطوار المكونة لها. المترابكات البوليمرية المدعمة بالجسيمات النانوية (NPCs) هي أنواع جديدة من المترابكات جذبت الكثير من الاهتمام مؤخرًا وسرعان ما ظهرت كمنشآت بحثية متعددة التخصصات يمكن أن تؤدي نتائجها إلى توسيع تطبيقات البوليمرات لصالح العديد من الصناعات المختلفة. يهدف البحث إلى تحليل تأثير إضافة نسب مختلفة (20 و 30%) من الجسيمات النانوية للسيليكا إلى البوليستر غير المشبع وتحديد الثبات الحراري وحركية التحلل لهما. في هذا البحث، تم تحضير المترابكات النانوية من البوليستر غير المشبع (UPE) الممزوج مع نسب مئوية مختلفة (10 و 20 و 30%) من جسيمات السيليكا النانوية. تم الحصول على منحنيات كل من التحليل الوزني الحراري (TGA) والمسح الحراري التفاضلي (DSC) من التحلل الحراري المحسوب باستخدام تقنية Coats-Redfern. تمت دراسة المعلمات الحركية والديناميكية الحرارية لجميع العينات وتم تمثيل معامل ارتباط خطي ممتاز قريب من الوحدة باستخدام Minitab 16. وأظهر العمل التجريبي أن تحلل المترابكات التي تم الحصول عليها من التحليل الوزني الحراري كان أبطأ من البوليستر غير المشبع النقي. يعزى تعزيز الاستقرار الحراري إلى محتوى السيليكا. أيضًا، أظهرت النتائج أن التحلل للبوليستر غير المشبع النقي تحت البيئة المؤكسدة كان أسرع بكثير منه في البيئة الخاملة.

الكلمات المفتاحية: التحلل الحراري، التحليل الوزني الحراري، راتنج البوليستر غير المشبع، جسيمات السيليكا النانوية.

1. INTRODUCTION:

Poly condensation polymers considered very practical in several usages due to their price and easily fabricated, suitable mechanical property, and higher corrosion property (Atta *et al.*, 2005). It is widely employed mainly in the area of coating, electrical application, fabrication parts of automotive, and construction fields (Selly and Mark, 1988; Kramer, 1992; Giovanilton *et al.*, 2009).

Thermal analysis is a technique used to measure a physical property of a substance and/or its reaction product as a function of temperature. Differential scanning calorimetry (DSC) is a technique used to study the thermal transition of a polymer. A sum of essential physical changes in a polymer takes place when a polymer is heated, which can be measured via DSC. These involve the glass transition temperature (Tg), melting temperature (Tm), crystallization temperature (Tc), and degradation or decomposition temperature (TD). Also, chemical changes due to polymerization and degradation reactions and other reactions affecting the specimen can be estimated (Charles and Seymour, 2008; Pearce *et al.*, 1982).

Kinetic parameter and thermodynamic prosperities and thermal stability determined by utilizing thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) which gives a very clear idea about the structure of the polymers and the behaviour of various composites under severe heat (Budrugeac *et al.*, 1996; Budrugeac, 1995).

Oxidative and thermal decomposition of polymers and composite usually occurs at higher temperature by the elimination of molecules along the polymer chain followed by random scission of the backbone chain; however, these changes produce more volatiles, gases and eventually all

the polymer convert to high molecules of polynuclear ring so-called chars (Regnier and Mortaigne, 1995; Bansal *et al.*, 1989; Gibson and Hume, 1995; Arie *et al.*, 1998). However, polyester decomposition occurs in two stages, in the first stage, the degradation of the backbone of the main chain occurs by ester change and hydrogen elimination and finally converts to volatiles, gases, and char because of its strong hydrogen bond prevent it from melting in the second stage (Mouritz and Gibson, 2007; Tagle *et al.*, 1992; Pielichowski and Hamerton, 1998).

There are numerous numbers of previous studies related to the kinetics of decomposition have been studied by many researchers, however, they concentrated on constant decomposition rate, activation energy and thermodynamic properties of different polymers and its different composite and they showed the enhancement in thermal stability of composites by using different inclusions for example:

Al-Bayaty and Farhan, (2015) studied unsaturated polyester resin (UPE) mixing with different weight percent 2, 4, and 6% of toner carbon nanopowder (TCNP) to prepare polyester composite. Non-isothermal decomposition kinetics of UPE and UPE/TCNP composites was carried out by utilizing thermogravimetric analysis (TGA). Kinetic parameters were determined for all specimens that were satisfactorily presenting good correlation with a linear correlation coefficient close to the unit using the SPSS package and were in a good agreement with published data. The experimental results show the decomposition of UPE/TCNP composites obtained from the thermal gravimetric analysis is faster comparing with those UPE specimens. This enhancement is attributed to the iron content in TCNP.

Thamer *et al.*, (2019) studied, the thermal analysis methods reported for the characterization

of epoxy/ Hexagonal Boron Nitride Nanoparticles (BNNPs) nanocomposites were conducted using Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). Non-isothermal kinetics decomposition of epoxy and epoxy/BNNPs nanocomposites were carried out by utilizing Thermogravimetric Analysis (TGA). TGA and DTG curves obtained from the decomposition were analyzed using the Coats-Redfern method. Kinetic parameters were determined for all specimens that show a good correlation with the linear correlation coefficient, where Coats and Redfern's procedure was the best to result in reasonable estimates of the kinetic parameters.

Ferreira *et al.*, (2006) Novel aluminized E-glass fiber reinforced unsaturated polyester composites, formulated initially for enhanced thermal and electrical shielding properties, were evaluated in terms of their thermal performance. The thermal degradation of these specimens was analyzed using a thermogravimetric analyzer (TGA). All samples were decomposed under dry nitrogen (N₂) at a flow rate of 40 ml/min to yield gases and solid char. Aluminized E-glass composites were compared alongside the unmetalled E-glass and unreinforced composite. The significant weight loss occurred between 200 and 400°C. The unreinforced polyester had a maximum weight loss, 1.25%/°C, happening at 360°C. For the aluminized and unmetalled E-glass composites, the maximum rate of weight loss was 0.34 and 0.55%/°C, respectively. Experimental results show the degradation of the aluminized E-glass composites obtained from TGA tests is higher compared to those of unmetalled E-glass fiber and unreinforced polyester composite. This improvement is correlated to the aluminum coating.

The aim of this current study was, therefore, to fabricate nanocomposite samples using the silica content (10, 20, 30) wt% with the unsaturated polyester resin to improve thermal stability and thermal decomposition of thermoset polyester using by Coats-Redfern method.

2. MATERIALS AND METHODS:

2.1.Composite fabrication

The materials employed to fabricate the nanocomposites are unsaturated polyester resin (UPE) as a matrix. It is a liquid with moderate viscosity, which can be cured to the solid-state by adding (Methyle EthyleKeton Peroxide, MEKP) as a hardener. At the same time, cobalt octoate acts

as a catalyst to accelerate the solidification process. The percentage of the hardener to the resin is (2%) while it is (0.5%) for the accelerator. Desirable physical properties, easily handled, quickly cured, and stable dimensions after solidification. The features of unsaturated polyester resin are given in (Table 1). Hardener: is a chemical material, which is added to thermosetting resin for the purpose of causing curing or hardening. The terms hardener and curing agent are used interchangeably. Note that these can differ from catalysts, promoters, and accelerators. Curing: To change the physical properties of the material (usually from a liquid to a solid) by chemical reaction, by the action of heat and catalysts, alone or in combination, with or without pressure. Accelerator: A chemical used to speed up a response or cure.

The term accelerator is often used interchangeably with the term promoter (Charles, 1975). Silica nanoparticles with a particle size of 100 nm were used as commercial fillers. The chemical composition of nano-silica is given in (Table 2). Atomic force microscopy (AFM) was used (CSPM scanning probe microscope) to measure the average particle size of nano-silica. The particle size distribution is shown in (Figure 1).

Samples of the polymer and nanocomposites at different Silica content (10, 20, and 30 %) are fabricated by cast molding. All content mixed thoroughly before casting, then the samples left at ambient temperature for 24 hr, and then cured, the specimens were left for 2 hr in an oven at temperature 60°C.

2.2. Kinetic theory

The Coats-Redfern method is a multi-heating rate application of the Coats-Redfern equation (Kim and Sea, 2005; Sperling, 2005) has been applied to study the kinetics of the decomposition of the polymer and its composite.

$$\ln \{[-\ln (1-\alpha)/T^2]\} = \ln(AoR/\beta Ea) \{1-(2R T / Ea)\} - (Ea/R T) \quad (\text{Eq. 1})$$

Where

α = The extent of the reaction

β = The constant heating rate

Ao = The frequency factor

R = The universal gas constant

T = The decomposition temperature

Ea = The activation energy

By plotting $\ln\{-\ln(1-\alpha)/T^2\}$ against $1/T$

for each heating, rate gives a family of straight lines of slope $-E/R$ Frequency factor directly determined from Y-axis intercept by substituting values of activation energies:

$$\text{Intercept} = \ln(AoR / \beta Ea) \{1 - (2RT / Ea)\} \quad (\text{Eq.2})$$

3. RESULTS AND DISCUSSION:

3.1. Thermogravimetric analysis

TGA and DSC is a crucial tool to study the kinetics of thermal decomposition and to describe the way were the polymer degrades and to determine the melting point and glass transition temperature and to explore the thermodynamics of thermal and to demonstrate the stability. Thermal decomposition carried out at a constant heating rate of 10 °C/min in an inert atmosphere between 35-650°C.

Figure 2 shows TGA and DSC profiles for pure polyester resin under oxidative agent; it can be seen the polymer start in losing its weight initially about 6 wt% at a temperature between 190 and 300°C then start losing significant weight 60.9 wt% between 300 and 430°C. However, this represents the first stage degradation, while the second stage starts 405°C till 462°C with a weight loss of 9.97 wt%, then the char starts to gasify. From the DSC profile observed two peaks which represent exothermic decomposition, the first small peak at 407.3°C, which represents the backbone scission followed with a prominent peak at 478.9°C, which represents the gasification of char. Figure 3 shows the profiles of pure polyester under inert conditions were initial lose weight starts 237°C till 310°C with weight lose 5.5 wt% followed by the first stage with weight lost 73.2 wt% between temperature range 310°C to 437°C and the second stage lose 18.8 wt% which ends at 641.8°C, the DSC profile also showed two peaks first at 415°C and the second one at 435°C. Table 3 shows the mass loss of polyester pure and with various weight percent of Silica content. However, there is a difference in the activation energy of oxidative and nonoxidative agents. In oxidative, the activation energy is much lower than nonoxidative, as shown in (Table 4). This is because oxygen enhances the decomposition, consequently reducing activation energies of decay.

The effect of addition Silica filler at different percentages are shown in Figure 4, (Figure 5) and (Figure 6). However, it can be seen the thermal stability increases with increasing Silica content (Figure 6) differs completely than (Figure 2) and

(Figure 3) especially at the initial stage which start 327°C with initial mass loss of composite 5.5 wt% followed with first stage decomposition which ends at 443°C with mass loss 72.5 wt%, while the stage mass loss is 12.49 wt% which is considered much lower comparing with pure polyester (Figure 3). DSC profile showed two peaks; the first appeared at 399°C, while the second at 508.2°C which is considered much higher comparing with (Figure 3), this is because of increased thermal stability.

3.2. The kinetic parameters

There are several methods to determine the kinetic parameters of the degradation process. However, the kinetic parameters were found by applying the Coats-Redfern method, as shown in Figure 7, a typical plot of $\ln(-\ln(1-\alpha)/T^2)$ against $(1/T)$ for oxidative thermal decomposition pure unsaturated polyester, for the first-order reaction. The method applied for pure unsaturated polyester, and its composites at different Silica content is shown in (Figure 8).

The thermodynamic properties were estimated by the following equations (3,4, and 5) (Straszko *et al.*, 2000; Silva *et al.*, 2004):

$$\Delta H = E - R T_{\text{peak}} \quad (\text{Eq. 3})$$

$$\Delta S = R [\ln(h Ao/kbT_{\text{peak}}) - 1] \quad (\text{Eq. 4})$$

$$\Delta G = \Delta H - T_{\text{peak}} \Delta S \quad (\text{Eq. 5})$$

Where ΔH is activation enthalpy, ΔS is activation entropy, ΔG is activation free energy of decomposition, T_{peak} is maximum peak temperature, h is Plank constant, and kb is Boltzmann constant. Table 5 shows the thermodynamics property of pure unsaturated polyester and its composites, according to the Coats-Redfern method used in determining kinetic data.

Figure 9 shows there is a linear relationship between activation energy, Ea , and Entropy, ΔS with accuracy $R^2=99.3\%$ (Turmanova *et al.*, 2008; Vlaev *et al.*, 2004). Table 5 shows that the activation energy increases with increasing entropy, and the positive values of internal energy mean the degradation process is not spontaneous (Al-Mulla, 2012).

4. CONCLUSIONS:

The thermal degradation of a silica-reinforced unsaturated polyester composite has

been successfully studied and experimentally compared to unreinforced polyester. UPE and UPE/silica were degraded in two stages, and almost 94% of the original mass was decomposed into volatiles and char. The activation energy of the nanocomposite materials was found to be higher than that of pure UPE in the oxidation environment by approximately 51.07% at 30%wt silica, and 19.12% higher than the pure UPE in the inert environment at 30%wt silica. Also, the entropy of the silica nanocomposites was higher than the pure UPE in oxidation and inert environment. DSC profiles of the silica nanocomposites showed there was a shift of decomposition peaks towards the right side because of enhancement of thermal stability for composite attributed to silica content as compared with pure UPE in oxidation and inert environment.

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Table 1. Typical properties of unsaturated polyester resin.

Property	Unsaturated Polyester (UPE)
Density (gm/cm ³)	1.05-1.4
Tensile strength (MPa)	45-103
Tensile modulus (GPa)	1.3-4.5
Cure shrinkage %	5-12
T _g (K)	340

Table 2. Chemical composition for the silica nanoparticles

material	Components %									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	Pb ₂ O ₃	Cu ₂ O
Silica	0.96	0.14	2.16	53.67	0.84	0.006	0.006	0.019	0.013	0.005

Table 3. The mass loss during decomposition for unsaturated polyester and its composite.

The samples	environment	loss first stage	loss second stage	Total mass loss
UPE pure	oxidative	430.2C°, 60.92%	642.6C°, 9.97%	70.89%
UPE pure	inert	437.2C°, 73.26%	641.8C°, 10.86%	84.12%
UPE +10% Silica	inert	438.2C°, 80.73%	643.9C°, 11.34%	92.07%
UPE +20% Silica	inert	435.9C°, 82.74%	643.7C°, 15.05%	97.79%
UPE +30% Silica	inert	443.8C°, 72.51%	643.2C°, 12.49%	85.00%

Table 4. Kinetics data of non-isothermal degradation of UPE and its composites according to Coats-Redfern method

The samples	Environment	Peak Temperature, T _p (K)	Activation Energy, E _a (kJ/mol)	Reaction rate constant, A ₀ (S ⁻¹)	R ²
UPE pure	Oxidative	652	78.0680	0.3164 x10 ⁴	99.1%
UPE pure	Inert	660	99.0030	22.260 x10 ⁴	99.7%
UPE +10% Silica	Inert	665	100.358	31.708 x10 ⁴	99.6%
UPE +20% Silica	Inert	656	111.382	308.222 x10 ⁴	98.7%
UPE +30% Silica	Inert	661	117.934	835.108 x10 ⁴	99.6%

Table 5. Thermodynamics property of UPE/Silica composites

The samples	Environment	T _{peak} ,(K)	ΔH,KJ/mol	-ΔS, J/mol	ΔG, kJ/mol
USP Pure	Oxidative	652	72.647	192.721	198.301
USP Pure	Inert	660	93.515	157.459	197.438
USP+10% Silica	Inert	665	94.829	154.758	197.743
USP+20% Silica	Inert	656	105.928	135.559	194.854
USP+30% Silica	Inert	661	112.438	127.334	113.496

Figure 1. AFM of silica nanoparticles

Figure 2. TGA and DSC curve for pure polymer under oxidative environment.

Figure 3. TGA and DSC curve for pure polymer under an inert environment

Figure 4. TGA and DSC curve for unsaturated polyester/Silica 10 wt%

Figure 5. TGA and DSC curve for unsaturated polyester/Silica 20 wt%.

Figure 6. TGA and DSC curve for unsaturated polyester/Silica 30 wt%.

Figure 7. A plot of oxidative thermal decomposition utilizing Coats-Redfern method

Figure 8. A plot of non oxidative thermal decomposition utilizing Coats-Redfern method

Figure 9. Plot of Entropy against Activation energy for thermal decomposition of UPE and its composite