Avrupa Bilim ve Teknoloji Dergisi
Sayı 15, S. 460-465, Mart 2019
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Araştırma Makalesi

www.ejosat.com ISSN:2148-2683

European Journal of Science and Technology
No 15, pp. 460-465, March 2019
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Research Article

Kinetics of Fluorescein Sodium Salt /Polystyrene (FFS/PS) Composites by TG Technique

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(First received 1 February 2019 and in final form 18 March 2019)

(**DOI:** 10.31590/ejosat.521174)

REFERENCE: Dere, A. (2019). Kinetics Of Fluorescein Sodium Salt /Polystyrene (Ffs/Ps) Composites By TG Technique. *European Journal of Science and Technology*, (15), 460-465.

Abstract

The fluorescein sodium salt (FSS) /polystyrene (PS) composites were prepared by powder metallurgy method (PM). The thermal behavior of the composites was characterized by thermogravimetric analysis (TG) technique. It is observed that the composites decompose in two steps. The kinetic parameters (activation energy, frequency factor) and thermodynamic parameters (enthalpy $\Delta H\#$ change, entropy change $\Delta S\#$ and Gibbs free energy change $\Delta G\#$) were calculated from the TG curves. Eight $g(\alpha)$ functions for decomposition mechanism (DM) were used to evaluate the kinetic parameters and analysis of experimental results suggests that in the first decomposition step, the actual DM is D3 type which is the three-dimensional diffusion mechanism for the first decomposition step of the composites. But, in the second decomposition step, it was observed that the decomposition mechanism is from one-dimensional diffusion (D1) to the random nucleation mechanism (F1).

Keywords: Composite, Kinetic-Thermodynamic Parameters, Thermal Analysis.

TG Tekniği ile Floresin Sodyum Tuzu / Polistiren (FFS / PS) Kompozitlerinin Kinetiği

Öz

Floresin sodyum tuzu (FSS) / polistiren (PS) kompozitleri toz metalurjisi metodu (PM) ile hazırlandı. Kompozitlerin termal davranışı, termogravimetrik analiz (TG) tekniği ile karakterize edildi. Kompozitlerin iki adımda bozunduğu gözlendi. Kinetik parametreler (aktivasyon enerjisi, frekans faktörü) ve termodinamik parametreler (entalpi $\Delta H\#$ değişimi, entropi değişimi $\Delta S\#$ ve Gibbs serbest enerji değişimi $\Delta G\#$) TG eğrilerinden hesaplandı. Bozunma mekanizması (DM) için sekiz $g(\alpha)$ fonksiyon kinetik parametreleri değerlendirmek için kullanıldı ve deneysel sonuçların analizi, birinci bozunma adımında, gerçek DM'nin kompozitlerin birinci bozunma adımı için üç boyutlu difüzyon mekanizması olan D3 tipi olduğunu göstermiştir. Fakat, ikinci bozunma aşamasında, bozunma mekanizmasının bir boyutlu difüzyondan (D1), rastgele çekirdeklenme mekanizmasına (F1) olduğu gözlendi.

Anahtar Kelimeler: Kompozit, Kinetik-Termodinamik parametreler, Termal Analiz.

1. Introduction

The thermal analysis techniques such as differential scanning calorimetry (DSC) and thermogravimetry analysis (TG) methods have been widely used to determine thermal behavior of the solid materials [1-6]. In general these methods are used to constantly measure the changes occurring in the physical properties of a material. Differential thermal analysis (DTA) and differential scanning calorimetry

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(DSC) are of particular importance. Both procedures permit the amount of heat to be determined that are taken up from or emitted to the surroundings per unit time during isothermal procedures or during heating and cooling. In this manner heat capacities, melt enthalpies, transition temperatures, heat capacity etc, can be measured and from this information further indications regarding phase transitions, crystallization processes etc. can be derived.

Thermogravimetry is a process in which a substance is decomposed in the presence of heat, which causes bonds the molecules to be broken. The TG technique has been widely used to determine non-isothermal decomposition kinetics because of simplicity and the information afforded by a simple thermogram.

The thermal behavior of the composites plays an important role in determining the transport mechanism, thermal stability and practical applications. The thermodynamic parameters are very important for the studying of heat transport phenomena mechanism in various solid state compounds such as composites.

This study is mainly aimed to determine kinetic and thermodynamic parameters and possible decomposition mechanism in these materials.

2. Material and Method

2.1. Composites fabrication and thermal analysis measurements

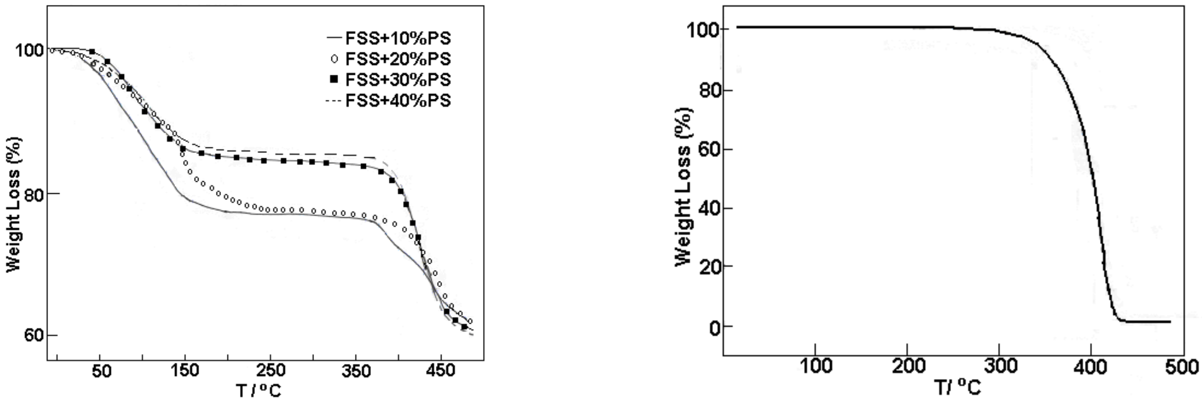
The fluorescein sodium salt (FSS) and polystyrene (PS) were purchased from the Sigma–Aldirch. Polystyrene of varying compositions (10-40%wt.) is mixed at room temperature until the PS powder surrounded the FSS particles. Four mixtures were prepared at different compositions as FSS+10%PS, FSS+20%PS, FSS+30%PS, and FSS+40%PS by powder metallurgy technique. Each mixture was cold compacted in a floating die using hydraulic press at compaction pressure of 50 MPa. The compacts were in shape of pellets of 10 mm diameter. The compacts were sintered in a furnace at 140 ºC in nitrogen atmosphere.

TG analyzer of the composites was carried out using a TG-50 Schimadzu thermogravimetric instrument. The composites (about 10 mg) were heated to 500 ºC with a heating rate of 20 ºC/min under nitrogen atmosphere using an aluminum crucible.

3. Results and Discussion

The TG curves of the composites indicate that the composites decompose in two steps in the investigated temperature range (Fig. 1a). The decomposition of FSS+10%PS composite starts at 307 K and this step continues up to 433 K, when a rest appears in the curve and in this step the fluorescein sodium salt (FSS) decomposes. The next decomposition step starts at 633 K and continues up to 773 K corresponding to decomposition of the PS when compared TG curve of polystyrene. Beyond 773 K there is no weight loss. Similarly, the other composites decompose two steps. The decomposition temperatures ranges for each step are given in Table 1.

The onset decomposition temperature of the second step increases when the PS content in the FSS was increased, the decomposition starts at higher temperatures and the composites exhibited higher transition glass temperature. Thus, in the second step, the onset decomposition temperature increases due to the interfacial interaction between FSS and PS when compared to PS (see Fig. 1b)



(a) (b)

Fig. 1 a) The TG curves of the composites b) The TG curve of PS

Table 1. The kinetic and thermodynamic parameters for the composites (TG)

Composite	*Dec. Range(°C)*	*$\Delta H^{\#}$(kJ/mol)*	*$\Delta S^{\#}$ (J/mol.K)*	*$\Delta G^{\#}$ (kJ/mol)*	*A(s^{-1})*	*E (kJ/mol)*
FSS+10%PS	34-160 1st step	26.7	-238.8	130.1	3.03	30.31
	360-500 2nd step	17.16	-269.8	225.7	0.13	23.59
FSS+20%PS	46-205 1st step	28.20	-242.0	143.9	2.26	32.18
	374-500 2nd step	26.23	-254.2	222.8	0.85	32.66
FSS+30%PS	45-152 1st step	48.21	-185.33	126.9	$1.85\ 10^{3}$	51.73
	381-460 2nd step	45.55	-210.6	199.9	152.7	51.65
FSS+40%PS	31-150 1st step	36.88	-216.88	128.6	41.42	40.40
	383-460 2nd step	61.70	-184.4	196.9	$3.55\ 10^{3}$	67.80

The thermal behavior process is generally well understood when kinetic parameters such as activation energy *E*, and frequency factor *A* are known. The basic equation for the fraction of conversion at a constant temperature,

$$\alpha = \frac{(m_o - m)}{(m_o - m_f)} \tag{1}$$

where *m* is the weight of composite, m_o is the weight at the beginning of the decomposition and m_f is the end of weight loss event of interest. The basic equation for the rate of conversion can be expressed by the following relationship,

$$\frac{d\alpha}{dt} = f(\alpha)K(T) \tag{2}$$

where *K(T)* is the rate of weight loss and $f(\alpha)$ is the function of conversion and *K(T)* is defined by an Arrhenius relationship,

$$K(T) = A exp(-E/RT) \tag{3}$$

where *A* is the Arrhenius frequency factor, *E* is the activation energy and *R* is the gas constant (R=8.315 J/mol.K). A combination of Eq(2) and Eq(3) gives

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = f(\alpha)A exp(-E/RT) \tag{4}$$

where β is the heating rate $\beta=dT/dt$. This method is so-called Friedman-Reich-Levi method which is a differential method [7]. If conversion function is taken as $f(\alpha)=(1-\alpha)^n$, combining of Eq(3) and Eq(4) gives the complete rate equation for nth-order reactions,

$$\frac{d\alpha}{dt} = A exp(-E/RT)(1-\alpha)^n \tag{5}$$

In logarithmic form, the equation can be written as,

$$ln(\frac{d\alpha}{dt}) = ln A - E/RT + n ln(1-\alpha) \tag{6}$$

If $ln(d\alpha/dt)$ is plotted as a function of *1/T*, *A* and *E* values can be obtained from the intercept and slope of the regression line.

The kinetic parameters can be also calculated using Coats-Redfren method [8-11]:

$$ln\left[\frac{g(\alpha)}{T^2}\right] = ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{7}$$

where α is the fraction decomposed at temperature T. The kinetic parameters such as activation energy and Arrhenius factor for the composites can be calculated graphically from this equation by selecting a $g(\alpha)$ function listed in Table 1. On the other hand, thermodynamic parameters for decomposition such as such enthalpy $\Delta H^{\#}$ change, entropy change $\Delta S^{\#}$ and Gibbs free energy change $\Delta G^{\#}$ of the composites can be calculated using the following relations:

$$\Delta S^{\#} = ln(\frac{Ah}{kT})R \tag{8}$$

$$\Delta H^{\#} = E - RT \tag{9}$$

$$\Delta G^{\#} = \Delta H - T\Delta S^{\#} \tag{10}$$

where h is the Planck constant and T is the temperature involved in the calculations selected as the temperature at the end of the decomposition step, *A* is the Arrhenius constant. The entropy and activation energy were calculated using intercept and slope of the plot of $ln[g(\alpha)/T^2]$ vs. *1000/T* using [12-15],

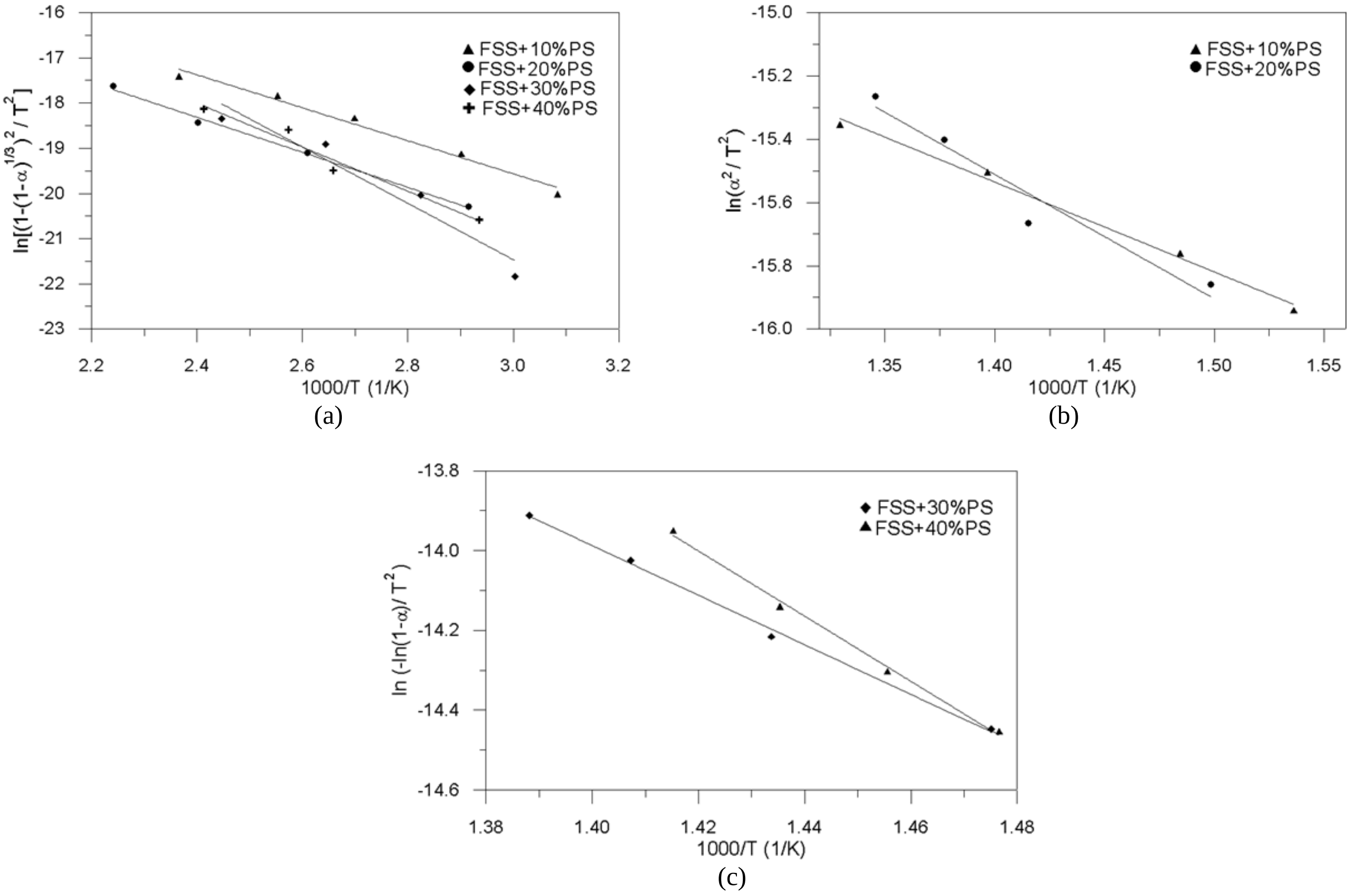
$$int\,ercept = ln(\frac{AR}{\beta E}) \tag{11}$$

and

$$E = -slopex8.315(\,kJ\,/\,mol\,) \tag{12}$$

Eight $g(\alpha)$ functions were used to evaluate the kinetic parameters. The goodness of fit is checked by calculating the correlation coefficient. The correlation coefficients for each function were calculated and the correlation coefficient having maximum value is chosen as the mechanism of decomposition. The highest value of correlation coefficient is obtained for $[1-(1-\alpha)^{1/3}]^2$ in the first decomposition step of the composites. On the other hand, α^2 and $-ln(1-\alpha)$ functions were ,respectively, obtained for the second steps of FSS+10%PS, FSS+20%PS and FSS+30%PS, FSS+40%PS composites. Hence in the first step of the composites, the mechanism of decomposition is D3 type which is the three-dimensional diffusion mechanism. But, in the second step, the decomposition mechanism is from one-dimensional diffusion (D1) to the random nucleation mechanism (F1). (see Table 2). The other models gave less satisfactory fit of data [16,17].

The plots for decomposition mechanisms of the composites were given in Figs. 2(a-c). A computer program was written to calculate the data analysis using different models. All the calculations for the decomposition mechanisms were done with the help of this computer program and the best fit for the results was calculated by the least square method. The activation energies *E* for first and second steps of the thermal decomposition of the composites are respectively in the range of 30.31-51.73 and 23.59-67.80 kJ/mol. It is observed that while the values of E for 2nd decomposition step are showing a definite trend along the compositions, they do not a definite trend for 1st step. The entropy values also indicated negative value. This means that the activated composite has a more ordered structure than the reactants.



(a)

(b)

(c)

Fig. 2 Plots of ln[g(α)/T2] vs 1000/T for the composites a) 1st step for composites b)2nd step for FSS+10%PS and FSS+20%PS c)3rd step for FSS+30%PS and FSS+40%PS

The low thermal stability of the composites is reflected in the calculated values of activation energy as shown in Table 2. It is observed that in the first and second decomposition steps, the activation energies changed with PS content. Activation energies calculated from the first step indicated that the decomposition started from the soft segment has the bond FSS groups. On comparing the activation energies of the second steps, FSS+30%PS and FSS+40%PS composites show a higher value. None of the kinetic parameters for the second decomposition step show a definite trend. But, in the first step, all the kinetic parameters show a definite trend.

Table 2 The kinetic and thermodynamic parameters for the composites (TG)

No	*g(α)*	Correlation coefficient (R)							
		FSS+10%PS		FSS+20%PS		FSS+30%PS		FSS+40%PS	
		Step I	Step II	Step I	Step II	Step I	Step II	Step I	Step II
1	$-\ln(1-\alpha)$	0.9698	0.9884	0.9935	0.8992	0.9193	0.9971	0.9534	0.9889
2	$[-\ln(1-\alpha)]^{1/2}$	0.8699	0.7066	0.9796	0.8939	0.8535	0.9720	0.8940	0.9316
3	α^2	0.9777	0.9974	0.9964	0.9793	0.9330	0.9647	*.9659	0.9429
4	$\alpha+(1-\alpha)\ln(1-\alpha)$	0.9794	0.9972	0.9961	0.9793	0.9345	0.9668	0.9660	0.9412
5	$[1-(1-\alpha)^{1/3}]^2$	0.9809	0.9969	0.9987	0.9793	0.9361	0.9690	0.9662	0.9393
6	$[1-(2/3)\alpha]-(1-\alpha)^{2/3}$	0.9799	0.9971	0.9959	0.9791	0.9351	0.9676	0.9660	0.9405
7	$1-(1-\alpha)^{1/2}$	0.9655	0.9949	0.9942	0.9426	0.9161	0.9680	0.9530	0.9387
8	$1-(1-\alpha)^{1/3}$	0.9670	0.9959	0.9940	0.9450	0.9172	0.9692	0.9531	0.9381

4. Conclusions and Recommendations

The TG measurements show that the composites studied decomposed in two steps. The kinetic parameters in non isothermal conditions are investigated and thermodynamic parameters such as enthalpy and entropy of the composites were calculated. The results show that in the first decomposition step of the composites, the decomposition mechanism is D3 type. But, in the second step, D1 type decomposition mechanism was changed to F1 mechanism when the PSS content was increased.

4. Acknowledge

The author thanks to Prof.Dr. Fahrettin YAKUPHANOĞLU for his supporting.

References

1 M. Zayed and F.A. Nour El-dien, Thermochem. Acta, 114(1987) 359

2 A.A. Salman, J. Therm. Anal. Cal., 63 (2001) 22

3 L. Nunez, F. Fraga, M.R. Nunez, M.T Villanueva, Polymer 41 (2000) 4635.

4 X. Wang, K. Yang, Y. Wang, B. Wu, Y. Liu, B. Yang, Polymer Degradation and Stability, 81 (2003) 415.

5. M.I. Nad-Elrahman, M.O. ahmed, S.M. Ahmed, T. Aboul-Fadl, A. El-Shorbagi, Biophysical Chemistry, 97 (2000) 113.

6 N. Bmanaragan, N.S. Saxena, D. Bhandari, M.M. Imran and D.D. Paudyal, Bull. Mater. Sci., 23(5) (2000) 369

7 H.L. Friedman, J. Poly. Sci. Polym. Symp., 41 (1964) 183

8 H.H. Horowitz, A. Metzger, Anal. Chem, 35 (1963) 1464.

9 A.W. Coats, J.P. Redfren, Nature 201 (1964) 68.

10 R.M. Mahfouz, K.A. Al-Farhan, G.Y. Hassen, A.I. Al-Wassil, S.M. Alshehri, A.A. Al-Wallan, Synth. React. Inorg. Met-Org. Chem. 32(3) (2002) 489.

11 Wenhan Cao, Jun Li, Leo Lue, Energy Procedia, 142 (2017) 136.

12 Fahrettin Yakuphanoglu, J. mater. electron. Device, 1 (2017) 21.

13 M Sekerci, F. Yakuphanoglu, Journal of Thermal Analysis and Calorimetry, 75 (2004) 189.

14 Fahrettin Yakuphanoglu, Mehmet Sekerci, Ertan Evin, Physica B 382 (2006) 21.

15 Jing Ma, Hainan Luo, Yi Li, Zhengang Liu, Dong Li, Chao Gai, WentaoJiao, Bioresource Technology, Accepred 2019.

16 F.Yakuphanoglu, A.O.Gorgulu, A.Cukurovali, Physica B: Condensed Matter, 353 (2004) 223.

17 F. Yakuphanoglu,Y. Aydogdu, U. Schatzschneider, E. Rentschler, Physica B 334 (2003) 443.