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THERMAL CURING REACTIONS OF MODIFIED CARBON-BASED NANOCOMPOSITES: THE EVALUATION BY CURE KINETICS METHODS

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Abstract

The aim is to analyze the curing behavior of MWCNT/iPE nanocomposite in suspensions containing 1.0 wt% of COOH group modified and well-dispersed via the tip-sonication method. For this purpose, various analytical techniques, TGA analysis under non-isothermal conditions in nitrogen test revealed that the stability of nanotubes sample toward high-temperature air oxidation and assaying the impact of graphitization, during thermal decomposition in nitrogen, the MWCNT as a mass-transport protective barrier can slow down the degradation of the polymer. However, released metallic derivatives from MWCNTs interphases have significant catalytic activity on thermal degradation, which causes a reduction in the thermal stability of modified MWCNTs/iPE nanocomposites compared with the cured polyester resin. The apparent activation energies of the samples were evaluated by Kissinger and Flynne-Walle-Ozawa method. DSC results indicated that a few traces of residual solvents in the composition greatly impacted the cure reaction and subsequently affected the endothermic behaviors of the modified MWCNTs/iPE nanocomposite. The Fourier transform infrared spectroscopy (FTIR) was performed for the interpretation of the result, and the fractural conversion rates of polyester resin and nanocomposite were found to be altered depending on the solvent used.

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Keywords: MWCNT, isophthalic polyester resin, melting, crystallization, thermal curing.

INTRODUCTION

Various characterization testing of polymer nanocomposite samples has shown enhancement not only in mechanical, and electrical but also in thermal properties as well. Except for the nanocomposite, a matrix is strongly dependent upon the level of dispersion and the final morphology the reinforcements also play a major role to improve properties [1]. In recent years carbon nanotubes based on the polymeric matrix become more attractive structural materials in aerospace, marine, automobile, railway, and sporting goods industries. Especially multi-walled carbon nanotubes (MWCNTs) are excellent candidates for nano-reinforcing with polymer matrices because of their strength, electrical capacity, and thermal stability [2]. In order to understand the thermal behavior of polymer nanocomposites significant to interpret the effect of reinforcements (CNT) embedded in polymer matrices on the thermal degradation mechanism of the nanomaterials. One of the most common techniques to characterize the thermal decomposition of polymeric materials is TGA analysis which gives us more evidential thermo-analytical curves for various materials [3]. The evaluation of thermal stability is one of the most important applications of TGA in the study of polymer nanocomposites.

The aim of the present research is to identify the thermal degradation of neat iPE resin, pristine MWCNTs, and F-FVD MWCNTs/iPE nanocomposites. TGA and DSC were performed to evaluate thermal performances as to the variance in the thermal property of the nanocomposite. In the crystal structure of polyester resin, the interaction between as-produced multi-walled carbon nanotubes is weak. After being chemically modified on the surface of functionalized MWCNTs plenty of carboxyl groups exist, assisting good dispersion in a polymeric matrix.

1. Experimental

1.1. Synthesis and modification of MWCNTs

Multi-walled carbon nanotubes were synthesized by the CVD method of a hydrocarbon vapor (CmHn) on catalysts powder impregnated with a ferrocene ($C_{10}H_{10}Fe$) solution. As a reactant was passed high-purity methane (CH_4) and hydrogen (H_2) gases. The synthesis process was around 30~60 mins through a tubular reactor in which a catalyst material is present at a sufficiently high temperature (600°C~800°C) to decompose the hydrocarbon [4]. MWCNTs grow on the catalyst in the reactor, which is collected upon cooling the system to room temperature. The liquid hydrocarbon (C_6H_6, alcohol, etc.) is heated in a flask and an inert gas is purged through the tube, which in turn carries the hydrocarbon vapor into the reaction zone. If a solid hydrocarbon is to be used as the CNT precursor, it can be directly kept in the low-temperature zone of the reaction tube. When the temperature at the tube of the furnace reached 800°C, the argon gas was pumped out of the chamber before methane and hydrogen gases were allowed to flow into the chamber. The flow rates of methane and hydrogen gases were kept at about 150 ml/min^{-1} ~300 ml/min^{-1}. The vacuum pressure in the reaction chamber was kept at approximately 80 kPa. Synthesized MWCNTs contained metal impurities such as carbonaceous materials and amorphous carbon which demand purification. The purification was performed by applying the acid treatment method to investigate the influence on thermal properties of MWCNTs, TEM images shown in Fig.1.

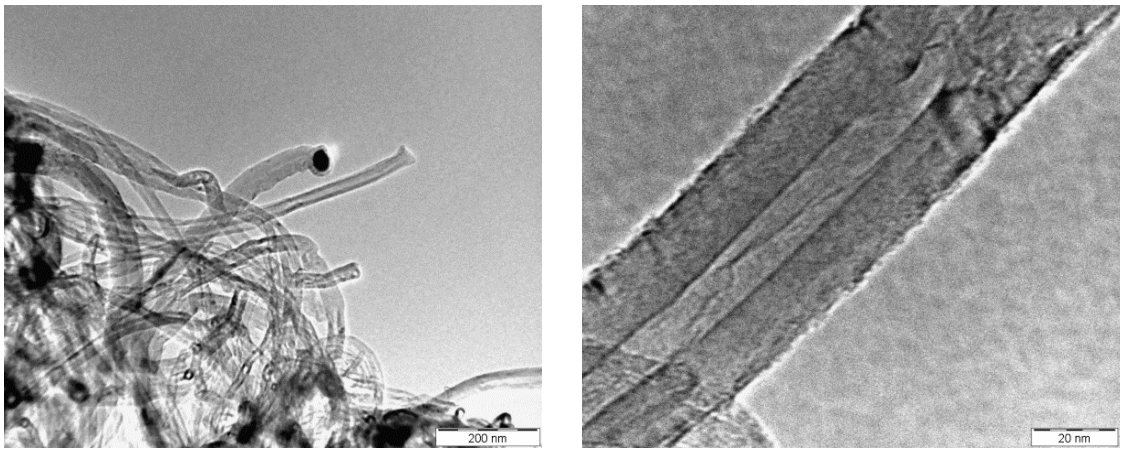

Fig.1. TEM images of synthesized, further functionalized MWCNTs (1.0 wt%) in the isophthalic polyester (iPE) matrix.

2. Results and discussion

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2.1. DSC investigation

This DSC study was to conduct a heating experiment in order to understand the sample's stability and the exothermic phenomenon of thermal decomposition reaction [5]. Fig.3 shows the nonisothermal DSC exotherms obtained at various constant heating rates (10, 20, and 30 ºC/min) for the characterization performed neat iPE resin, pristine MWCNTs, and F-VFD MWCNTs/iPE nanocomposite. The results of scanning samples showed the amorphous property of neat polyester and F-VFD MWNTs/iPE nanocomposite samples as well. By considering the initial (T_i), the peak (T_p), and the final (T_f) temperatures, and by calculating the reaction enthalpy (Q) values from each corresponding DSC exotherm, the impact of pristine MWCNTs/iPE on the cure kinetics of the entire resin system was evaluated and the data obtained were given in Table 1.

Can be seen, that the incorporation of modified MWCNTs into the polyester matrix blend increases the reaction enthalpy at each given heating rate. The resin suspensions with MWCNTs and MWCNT/iPE exhibited 3 and 10% higher enthalpy values than the polyester resin, respectively. Furthermore, the T_i value of MWCNT modified by polyester resin suspensions interestingly appeared to scatter around the same value (40°C) regardless of the heating rate. This can be considered sample evidence that carboxyl functional groups grafted onto surfaces of MWCNTs modify the interfacial interactions between nanotubes and the surrounding polyester resin.

Table 1. Experimental data obtained from the DSC test from neat polyester resin (iPE), pristine MWNCTs, and F-FVD MWCNTs/iPE

Sample	Heating Rate (ºC/min)	$T_i\,(°C)$	$T_p\,(°C)$	$T_f\,(°C)$	$Q\,(J/gr)$
polyester resin (iPE)	10	63±12	90±8	119±15	223±12
	20	79±13	94±13	125±11	245±17
	30	86±11	102±16	136±17	274±20
pristine MWNCTs	10	61±14	88±12	110±12	203±16
	20	71±16	96±10	127±18	234±19
	30	77±18	93±18	145±21	287±23
F-FVD MWCNTs/iPE	10	51±10	62±14	111±23	240±16
	20	54±11	76±10	138±18	255±23
	30	48±14	97±15	155±14	299±26

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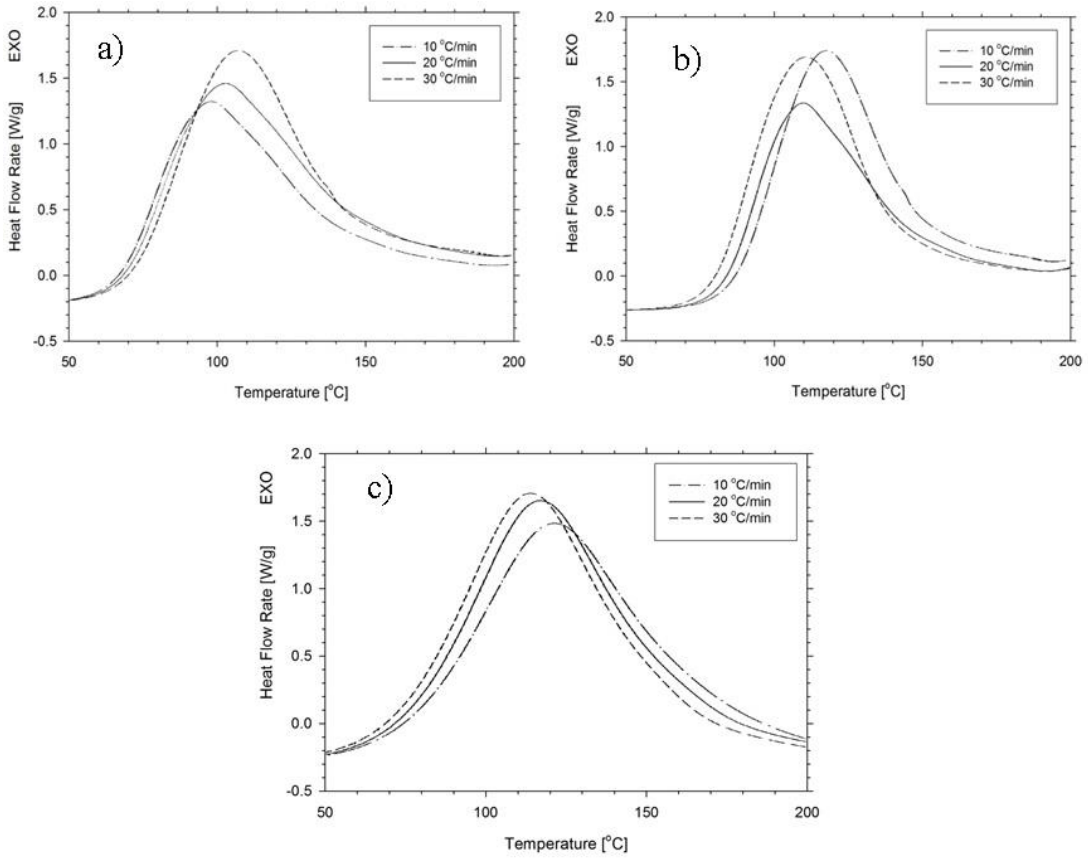

Fig.2. DSC exotherm at different heating rates: a) for polyester resin (iPE), b) pristine MWCNT/iPE
containing 1.0 wt% of CNT, c) F-VFD MWCNT/iPE containing 1.0 wt% of CNT

This lower exothermic could potentially make it easier in handling when making the composites and also possibly reduce the shrinkage of the material. As a matter of fact, exothermal reaction played an important role in the curing of polyester resin. The peak temperature depends, among other factors, on the curing system and the thickness of the samples. Therefore, the amorphous phase in polymer nanocomposites seems to be constituted by two different domains, neat polyester resin lightly cross-linked with MERK and F-VFD MWCNTs as filler that accepts a small quantity of matrix. Fig.3 gives the variation of E_a for the isophthalic polyester resin, pristine MWCNTs, and F-FVD MWCNTs/iPE nanocomposite suspensions with respect to the degree of cure.

Evidently, it was also found that the resin blends with carbon nanotubes featured moderately lower E_a values as compared to the isophthalic polyester resin blend

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at each stage of cure. This trend is more obvious for the suspensions with MWCNTs/iPE. Hence, E_a values decrease at a lower degree of cure but then gradually rise up towards the end of the curing reaction. These predictions show the consistency with our main approach that MWCNTs alter somewhat the chemical interactions within resin media during curing dependent on the functional groups grafted onto their surfaces.

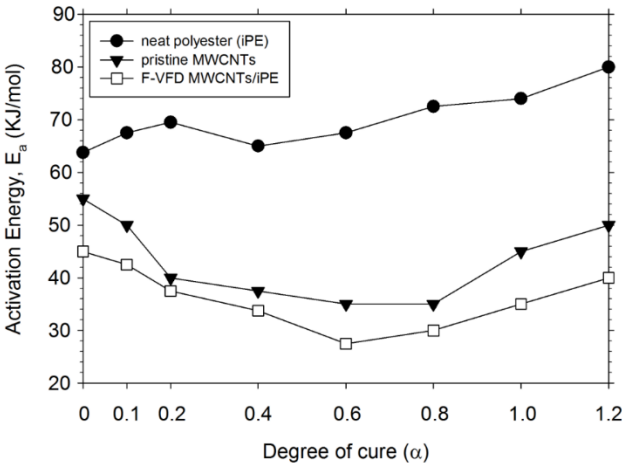

Fig.3. The plot of thermal degradation activation energy, E_a (kJ/mol) of different samples (neat polyester resin (iPE), pristine MWCNTs, and F-VFD MWCNTs/iPE).

2.2. TGA analysis

Observation of the following figures showed the thermogravimetric analysis, that surface modification of MWCNTs can alter the thermal stability of the nanocomposite materials. In Fig.4 (b), nanocomposites made with pristine MWCNTs, have only slightly affected the thermal disintegrate temperature of iPE resin whereas the functionalized MWCNTs have a great effect on the onset disintegrating temperature in Fig.4 (c). As we mentioned above TGA also was used to estimate the purity of the F-VFD MWCNTs in terms of metal and metal oxide contents. TGA graphs of the pristine MWCNTs and F-VFD MWCNTs/iPE nanocomposite specimens observed that pristine MWCNTs/iPE nanocomposite significant weight loss starts to occur at 357°C (Fig.4, b). The weight loss continued to increase rapidly with temperature increase until a stable plateau region appeared at nearly 433°C. The residual weight is 8.0% (0.88 mg), which implies that 88.1% (9.7 mg) of the mass of the pristine is carbon. The most

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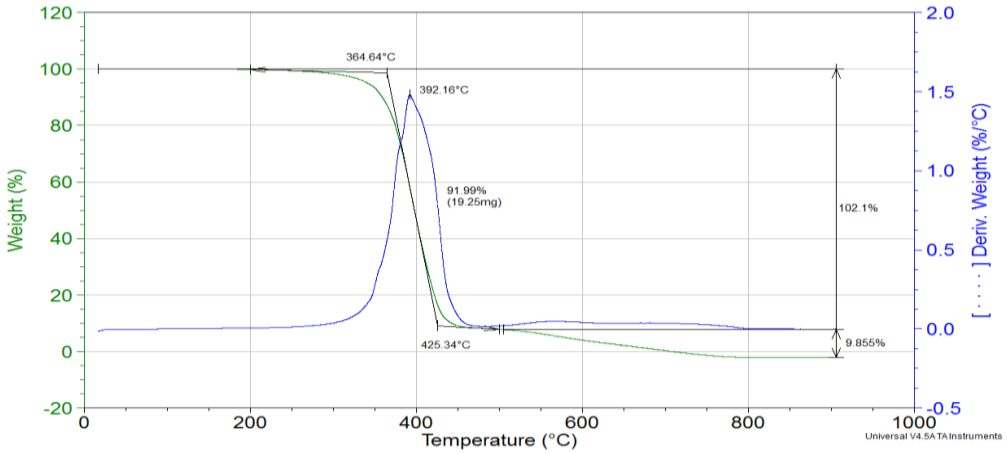
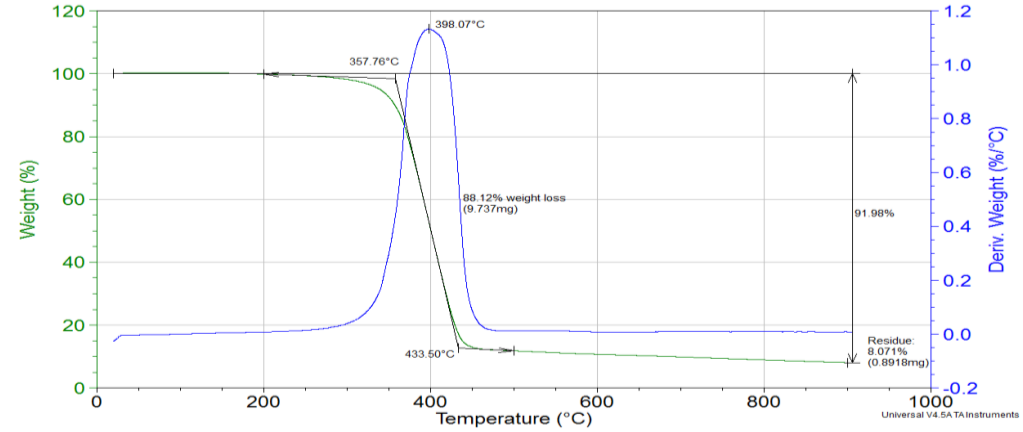
significant is that the residual weight is 0.53% (0.12 mg) appeared from 362°C to 432°C (Fig.4, c), which means that the catalyst particles were mostly removed after acid treatment as we expected. Other, the weight loss of about 90.2% (20.3 mg) while in pristine residual weight was reduced to 12% from 355°C to 434°C. There appears to be weight loss beginning around 360°C, higher than that for the pristine sample, but lower than the neat iPE sample. The results indicate that the modification of carbon nanotubes significantly enhanced the thermal stability of F-VFD MWCNTs/iPE nanocomposites in inert gas. The increase in peak temperature is also found in those systems, where a 5°C increase is reached. It's because of the interfacial interaction of carbon nanotubes with polymer matrix that may the temperature increase and could be from the barrier effect of the well-dispersed nanotubes, which blocked the transport of degradation. This lower relative stability is due to the presence of numerous defects along the walls and at the ends of the carbon nanotubes.



(a)



(b)

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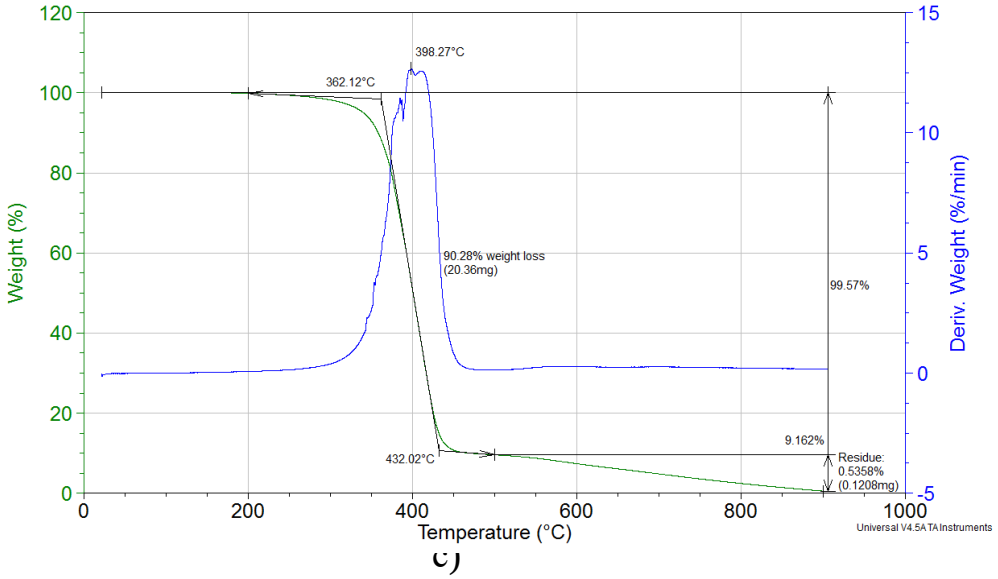

c)

Fig.4. TGA analysis of cured isophthalic polyester resin (iPE) (a), nanocomposite samples with 1.0 wt.% loaded pristine MWCNT/iPE (b) and nanocomposite samples with 1.0 wt.% loaded F-VFD MWCNT/iPE (c).

2.3. The Kinetic Analysis

The correlation of the kinetic parameters with apparent kinetic models does not allow for performing correctly the kinetic analysis using only one experimental TA curve. However, if the true activation energy is known, then the issue can be corrected. The calculation of activation energy is based on multiple scan methods where several measurements at different heating rates are required such as iso conversion methods [6]. Logically the iso conversion methods can be divided into the Ozawa-Flynn-Wall method [7], the Kissinger-Akahira-Sunose method [8], and the expended Friedman method [20]. These methods allow checking the invariance E with respect to which is one of the basic assumptions in the kinetic analysis. One of the methods known as Kissinger was used to calculate the apparent activation energy (E_a) value for the degradation, as given by the following equation [9]:

$$\ln\frac{\beta}{T_p^2} = -\frac{E_a}{R}\left(\frac{1}{T_p}\right) + \ln\frac{nAR\left(1-\alpha_m\right)^{n-1}}{E_a} \qquad (1)$$

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where A is the exponential factor, R is the universal gas constant, α_m is the ratio of weight loss at the maximum rate, and β is the heating rate. Thus, the activation energy can be calculated from the linear dependence of the $\ln\left(\frac{\beta}{T_p^2}\right)$ versus $\frac{1}{T_p}$ plot (Fig.4) for various heating rates and following the relationship of $E_a = -R \times slope$. The E_a of pure isophthalic polyester resin and pristine MWCNTs is lower than that of pure polyester resin. This result is contrary to most previous reports on nanocomposites with high thermal stability.

The activation energies of degradation calculated from TGA curves are based on mass losses in different decomposition regions during the degradation process. The multiple heating rate method proposed by Flynn-Wall-Ozawa used the following approximate equation at a constant weight loss in a thermal degradation process:

$$\log \beta = \log \frac{AE_a}{R} - \log f(\beta) - 2.315 - 0.4567 \frac{E_a}{RT} \qquad (2)$$

where β is the heating rate, $f(\beta)$ is known as the conversational functional relationship and T is the absolute temperature. This equation E_a can easily be calculated based on the slope of a plot $\log \beta$ versus $1/T$ at a fixed weight loss (α).

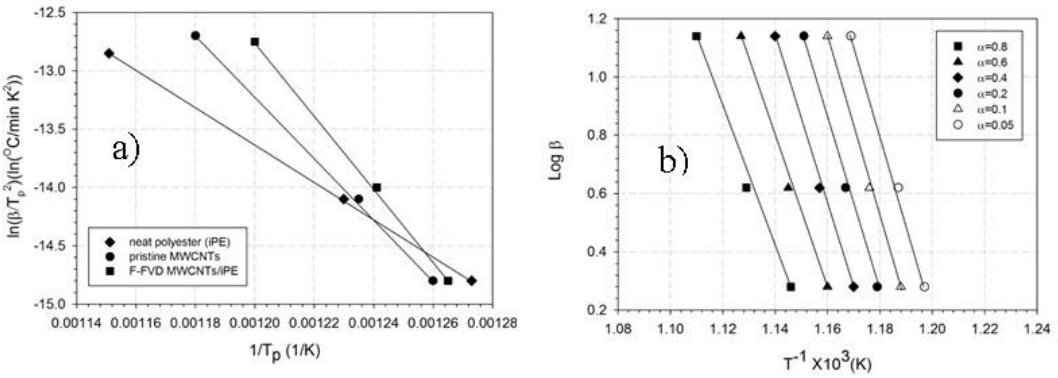

Fig.7. a) Determination of the activation energy E_a by Kissinger method, b) Flynn-Wall-Ozawa plots for the thermal degradation of F-FVD MWCNTs/iPE nanocomposite

With an increase in the conversion at the initial sections of degradation, the atmosphere temperature also increased, and then the catalysis effects enhanced significantly. Hence, at the beginning of degradation, the catalysis of dominant

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compared with a barrier effect, and the activation energies are lower than that of pure polyester and lessen gradually with the further development of decomposition after that the activation energy increased at the last degree of conversion.

4. Conclusion

Nonisothermal DSC analysis at different heating rates (10ºC, 20ºC, and 30ºC) revealed that the presence of MWCNTs within the iPE resin system alters the polymerization reaction by increasing the heat of cure while decreasing the activation energies (E_a). It was emphasized that the relatively low aspect ratio of carboxyl functionalized nanotubes may play a crucial role in the alteration of the interfacial chemical interactions during polymerization. The predicted DSC curves via the autocatalytic kinetic model were in good agreement with those experimentally obtained.

The thermal curing behavior of neat polyester, pristine MWCNTs, and F-VFD MWCNTs nanocomposites was investigated by TGA with heating rates (10°C/min) in air. It revealed unique and excellent features regarding morphology and structure. Enhancement observation of the thermal stability of iPE resin by the loading (1.0 wt%) with F-VFD MWCNTs has shown an improvement in the existence of an interfacial interaction. TGA test demonstrated the stability of nanotube samples toward high-temperature air oxidation and assaying the impact of graphitization. The apparent thermal degradation energies E_a of the above three samples have been evaluated using the Kissinger and Flynn-Wall-Ozawa method, and the E_a data of pristine MWCNTs and F-FVD MWCNTs/iPE nanocomposite were lower than those of neat iPE resin. The clay acts as a protective mass and thermal transport barrier in the polymer matrix, slows down the polyester chain decomposition rate, and assists to increase the thermal stability of nanocomposites.

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