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Thermal degradation behavior and determination of activation energy for degradation of polyvinylidine fluoride-hexafluoro polypropylene nanocomposites containing graphene oxide nanoparticles with Flaneen-Wall-Ozawa (FLW) and Kissinger models

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Abstract: The purpose of this study was to investigate thermal degradation and determination of activation energy for degradation of polyvinylidine fluoride-hexafluoro polypropylene nanocomposites containing graphene oxide nanoparticles with FLW and Kissinger. In this regard, polyvinylidine fluoride-hexafluoro-polypropylene nanocomposites containing different amounts (1.3, 5%) of graphene nanoparticles were prepared by melt mixing in microcomponent. An electron microscope (TEM) was used to detect graphene nanoparticles in a nanocomposite mixture. Thermal degradation behavior of nanocomposite specimens was investigated by Thermometry Analyzer (TGA). Determination of degradation energy by using the FWO method in non-homogeneous state at several different heating rates indicated that the polyvinylidene fluoride-hexafluoro-polypropylene sample containing 5% graphene nanoparticles contains the highest degradation energy. The activation energy values calculated by the Flaneen-Wall-Ozawa (FLW) model in the oxygen medium showed that the energy of activation increased with increasing conversion. Studies have shown that polyvinylidine fluoride-hexafluoro-polypropylene nanocomposites have the highest degradation energy. Also, based on the results, in a constant time, for the PVDF-HFP sample, conversion percent is higher than nanocomposite samples. But, for example, PVDF-HFP contains 5% graphene oxide during a constant time, the less the substance is degraded, resulting conversion percentage is less.

Keywords: Thermal Degradation, Activation Energy, Nanocomposite, Flane-Wall-Ozawa Model (FLW), Kissinger Model.

Introduction

Today, the use of plastic materials has been used extensively in various aspects of human life, and this material can be seen everywhere. But the high applicability of polymers in different industries creates the question of how the selection criteria for polymers are determined in different applications. Accordingly, one of the main concerns of scientists is the clarification of properties for different applications. One of the most widely used polymer material is the polyvinylidine fluoride which is very important in electrical applications.

Polyvinylidene fluoride has pyro, follower, and ferroelectric properties, due to the presence of a dipole moment due to the positive charge of hydrogen and the negative charge of fluorine per CF2CH unit. Various factors affect these properties, including these nanoscale agents, which, in addition to their effect on the properties of crystallinity, affect the properties of thermal degradation (Liu et al., 2016).

Polyvinylidine fluoride-trifluoroethylene copolymers have been widely studied not only in terms of ferroelectricity, pyro and piezoelectricity properties, but also in significant applications in applications such as sensors and transducers. The structural properties of these copolymers, by varying the composition of the percentage of monomer trifluoroacetylene, have provided an unbelievable application platform, providing a broad field of research for researchers that is characterized by numerous mechanical and dynamic tests to identify structural properties . Therefore, most of the research focuses on films made with thicknesses greater than 10 micrometers.

In recent years, these couplers have been used to improve the properties of polymer piezoelectricity, and this research has responded well to the structural uncertainties and their properties. Hence, almost all functional branches of these copolymers can be understood to this day. For example, these composites, despite all the problems, can today be used as a dielectric layer in less interactive microelectronic devices, which has created a huge transformation in this industry. In addition, the use of these thin-film composite materials with ferroelectric properties not only has the general advantages of weight loss and size, but also the ability of these films to uniquely produce low-voltage applications is unimportant. Hence, the study of structural properties is of great importance (Goodarzi et al., 2010).

Many researches have been done to reduce the α phase and increase the phase β in different ways. Recently, nanoparticles have been considered. Here are some of these studies.Carbon nanotubes are a suitable substrate for making piezoelectric nanocomposites (Sangtabi et al., 2017). Nandy et al. Made a nanosized composite composed of PVDF as a polymer matrix and 3-aminoethyl imidazolim bromide-MWCNT ionic liquid as nanofill. In addition, to a significant increase in β phase, there was a significant increase in the electrical conductivity of the nanocomposite (Datta et al., 2014).

Davend has also been studying the design and identification of PVA / PVAc nanocomposite with nanocarbon particles and graphene oxide (surface-modified) and solvent solutions. His results indicated that the addition of graphene oxide and carbon nanotubes would alter the crystalline structure of α to β. Also, the presence of polyvinyl acetate caused the smoothness and softness of the nanocomposite films and greatly altered the film's stretch. The presence of PVAc has another important effect, which has significantly improved the diffusion of carbon nanotubes. Graphene oxide has been able to significantly increase the mechanical properties of nano-composites, but carbon nanotubes do not have a significant effect (da Silva & Soares, 2017).

In another study, Nandi et al. Developed a hybridization of the functionalized graphene with polyethylmethacrylate and PVDF by using graphene oxide (GO) in the vicinity of hydrazine (as a reducing agent). IR and DSC evaluations showed a significant increase in the β-phase in the nanocomposite produced compared to pure PVDF. In this work, by using the functionalization of the graphene plates with polyethylmethacrylate, the polarity of these plates increased, which led to an increase in the interaction and stability of the β-polar phase (Kolařík et al., 2003).

Clarkakes et al. evaluated the effect of clay nanoparticles on PVDF / EVAc alloy. The results of the tensile test for EVAc32, which showed a higher percentage of the Vac group, showed that each dopantin composite exhibited a remarkable mechanical performance compared to the non-alloyed alloy. The 1331T nano-composite showed a significant increase in the Young's modulus (up to approximately 2 times) and increased toughness by up to 80%, while its long elongation did not differ significantly from the filler alloy.

On the other hand, the B30-based nano-composite increased both the Young's modulus and longitudinal elongation and increased toughness by up to 200%. However, the increase in Young's modulus in the sample containing T 1.31 was more pronounced. In this study, it was also observed that better nanoparticle nanoparticle nanocomposites based on an alloying matrix with a higher content of the polar group resulted in a significant increase in toughness and viscosity. While in nanocomposites with a less polar matrix (less content of Vac), the hydrophobic nanoparticle has led to a significant increase in Young's modulus and viscosity (Goodarzi et al., 2014).

Hako et al. evaluated and compared the effects of SWCNT and MWCNT on PVDF nanosized composites made by injection molding. The results show that MWCNT has a greater effect on mechanical properties than SWCNT, which is due to the fact that the MWCNT network and the bond have formed a better interconnection period and will be more effective than the SWCNT (Pedrazzoli & Pegoretti, 2014).

Casalini and roland evaluated the density of crosslinkings in order to improve the electrical properties of composite P (VDF-co-TrFE) by combining 65% polyvinylidine fluoride in a randomized copolymer structure to improve the polymeric network by using two crystal grade parameters and increasing the configuration Form β can gain acceptable results. Therefore, increasing the density of transverse joints in the polymer composite network results from the induction of the electric field in the direction of the longitudinal strain of the sample.

The dielectric measurements in low electric fields indicate the presence of a region with a relaxed frequency of tension, which was previously not seen in a copolymer without transverse joints, and the properties of this region are directly related to the copolymer crystalline phase. This process plays a vital role in increasing the electrical activity of the polymer. However, the constant dielectric reduction with frequency implies a reduction in the strain at higher frequencies. In this regard, the determination of the frequency dependent electrostatic strain can certainly be useful and increase the electrical properties of these polymers (Starkova et al., 2014).

Weimin Xia showed various properties using different process methods such as fast-cool, slow-acting, and annealing, by studying the association between the electrical properties of copolymer P (VDF-co-TrFE) and its crystalline structure. Their observations focused on the amount of crystallization and the size of the crystals, and the results showed that the copolymer prepared by the anode method has the highest piezoelectric constant. Also, with the physical modification of the monomers and the composition of their percentages, it is possible to achieve more piezoelectric properties and ferroelectricity (Pérez et al., 2008).

The purpose of this research is to investigate the thermal degradation and determination of activation energy of degradation of polyvinylidine fluoride-hexafluoro polypropylene nanocomposites containing graphene oxide nanoparticles with Flain-Wall-Ozawa (FLW) and Kissinger models.

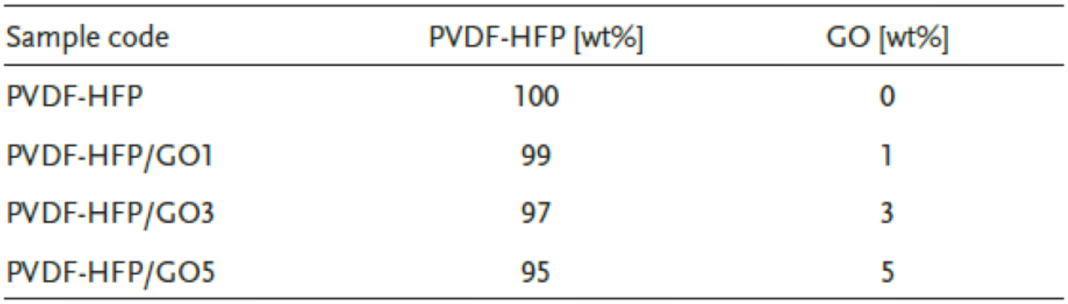
Materials and methods

Raw materials and method of preparation

Polyvinylidene fluoride-hexafluoro polypropylene with a molecular weight of 53,400 g / mol was prepared from Sigma Aldrich Company. Graphene oxide nanoparticles with a molecular weight of 4240 g / mol and a purity of 99.9% and an average diameter of less than 100 nm were prepared from Sigma Aldrich.

Melt mixing was used to prepare nanocomposites. Polyvinylidine fluoride-hexafluoro polypropylene nanocomposites with different percentages of graphene oxide were prepared by microcomponent in two spirals. Before the melt was mixed, the material was dried under vacuum oven at 80 ° C for two hours. In Table 1, the composition of the percentages of the prepared samples is shown.

Table 1. Naming the prepared samples



Sample code	PVDF-HFP [wt%]	GO [wt%]
PVDF-HFP	100	0
PVDF-HFP/GO1	99	1
PVDF-HFP/GO3	97	3
PVDF-HFP/GO5	95	5

A microdermabber has been used for the preparation of polymeric mixtures with the brand name DACA. This machine is in fact a Co-rotating extruder, which is capable of installing both types of both-directional and non-directional screws. Figure 3-2 shows the overall device with an identical spiral .

The main difference between this extruder and commercial co-rotating extruders is that the material is returned to the feed site through the return channel to the feed site after passing through the tip of the spiral. This action helps to mix up the material as much as possible. Meanwhile, the enclosure is closed and materials are under nitrogen gas that prevents their destruction. Meanwhile, the maximum amount of material needed to mix 10 to 12 g depending on the density of matter.

The feed is fed into the compartment by using a cylinder and piston that works under pressure. Sampling was carried out at microcamprant at 100 rpm according to Table 1.

Tests: In order to evaluate the behavior of the final product, various tests of properties determination are necessary. The following evaluations were carried out to control the properties: structural and morphological evaluation, crystallinity and melting behavior, and thermal degradation behavior evaluation.

Transmition Electron Microscopy (TEM) is like a slide display device that emits an electron beam from the sample and then an image of its microstructure is formed on the curtain, by using interactions between matter and electrons. The collision of electrons with matter includes various mechanisms like create x-rays, then scatter and pre-dispersion, and so on. The electron beam used in this microscope is made up of various methods, such as field emission and thermodynamic emission. In this device, electrons are accelerated at high voltage (kV100-1000), which speeds from about 0.9 to 0.8 times the speed of light. Energetic electrons pass through the object and, depending on the density of the substrate, an image of the microstructure is formed on the screen, the lower the electron density, the brighter the image. In this research, we used electron microscopic transducer images (Carl Zeiss) LEO 910 TEM with a voltage of 120 kV to study the morphology and distribution of silica nanoparticles in each of the phases. A thin layer of 100 nm thick pieces was prepared by using the EM UC / FC6 microtome and 120 ° C. Also, due to differences in the electron density of the components (existence of sufficient discretion), the staining method was not used.

Thermal decomposition test: A heat-decomposition test was performed by Perkin Elmer's Pyris1 TGA model at a temperature range of 30 to 650 ° C with a different heating rate of 5, 10 and 20 deg / min. Destruction of samples in oxygen and nitrogen environments was evaluated.

Results

Evaluation of morphological results by using transmitted electron microscope

Graphene oxide dispersion in polyvinylidene fluoride-hexafluoro-polypropylene matrix in two magnifications for samples containing 1 and 3 percent graphene oxide has been given in Figures 1 and 2.

Evaluating the results of these two forms shows that particles of graphene oxide have been well distributed in the polymer matrix and have good dispensation. However, in some places hunchbacking is observed.

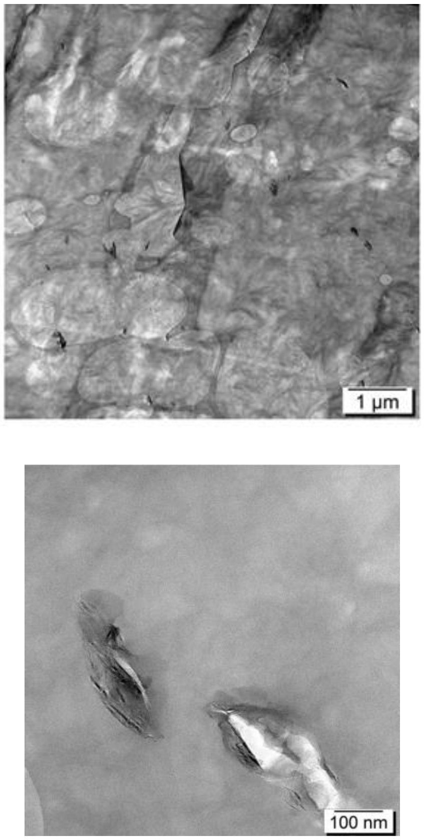


Figure 1. Transmission electron microscopic results for PVDF-HFP / GO1 samples in two different magnifications

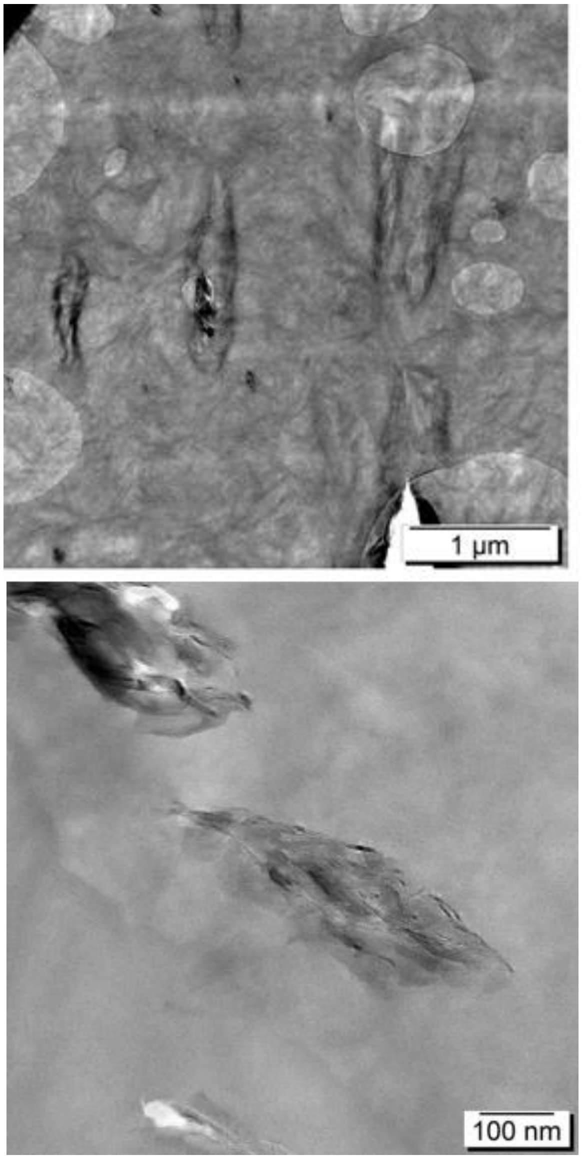


Figure 2. Transmission electron microscopic results for PVDF-HFP / GO3 samples in two different magnifications

Results of the test of heat dissipation

In this research, a heat dissipation test was conducted for different samples under the two oxygen and nitrogen atmospheres, and tried to evaluate all samples from a sustainability point in each of the test environments. The curve of sample mass changes as a function of temperature for polyvinylidine fluoride-hexafluoro-polypropylene, in both oxygen and nitrogen, is shown in Fig. 3.

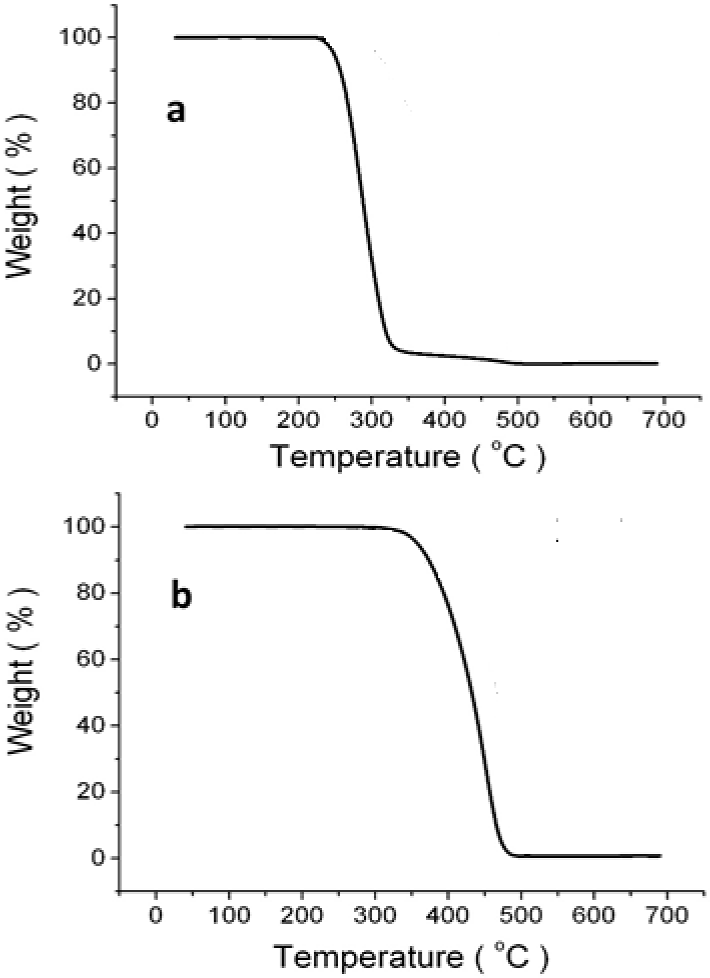


Figure 3. Heat dissipation diagram of polyvinylidine fluoride-hexafluoro-polypropylene graphite in (a) oxygen and (b) nitrogen

As shown in Fig- 3, the weight loss of the samples begins in the nitrogen atmosphere later. This reflects the effective effect of oxygen on increasing the rate of mass reduction in the first stage of degradation, and in this atmosphere, radical is rapidly combined with oxygen and the degradation process is followed up more rapidly. But in the nitrogen environment, this radical remains stable. The presence of oxygen and heat are among the factors contributing to the increased rate of degradation of polyvinylidine fluoride-hexafluoro polypropylene.

Evaluation of kinetics of oxidation and thermal degradation

Evaluation of the process of polymer degradation is one of the most important points in discussing the use of polymer materials in the industry or everyday life. Understanding the factors affecting the mechanism of destruction and knowing the energy needed for the destruction of polymer materials is one of the most useful points in discussing the destruction of these materials. Various methods, such as Kissinger and Flein-Wal-Ozawa, have been proposed to calculate the energy required for destruction.

Kissinger presented an approximate method for calculating energy of degradation activation; the formula has been given below.

$$\ln\left(\frac{\beta}{T^{2}}\right)=-\frac{E_{a}}{RT}+\left(\ln\left(\frac{AR}{E_{a}}\right)-\ln F(\alpha)\right)$$

n this case, $\beta = \frac{dT}{dt}$ is the constant heating temperature, Ea, is the activation energy, T is the absolute value in Kelvin, α is the conversion value ($a = \frac{m_0 - m(t)}{m_0 - m_f}$) and R is the gas constant, and A is a constant value. In this regard, the plot of the graph $\ln\left(\frac{\beta}{T^2}\right)$ in $1/T$ is obtained in terms of a constant conversion value of a straight line that the amount of energy activation is obtained from the line gradient.

In Fleine et al method, another formulation is used to calculate the energy of activation, which can be used to obtain the amount of degeneracy activation energy at a constant conversion value at different heating rates based on equation (2).

$$\log \beta = -0.4567\left(\frac{E_a}{RT}\right) + \left[\log\left(\frac{AE_a}{R}\right) - \log F(a) - 2.315\right]$$

The amount of activation energy from the gradient of the chart line is calculated in terms of value at a constant value of conversion percentage. In this research, we used heat dissipation analysis for different samples with different heating rates of 5, 10 and 20 ° C / min in two oxygen and nitrogen environments.

In Figures 4 and 5, heat dissipation and derived heat dissipation diagrams in oxygen environment are two PVDF-HFP samples containing 3 percent and 5 percent graphene oxide from the studied samples. In these diagrams, it is observed that with increasing the heating rate, the weight loss values are transmitted to higher temperatures, which is due to a reduction in the time of destruction. In this research, Flein et al method was used to kinetics evaluation of degradation.

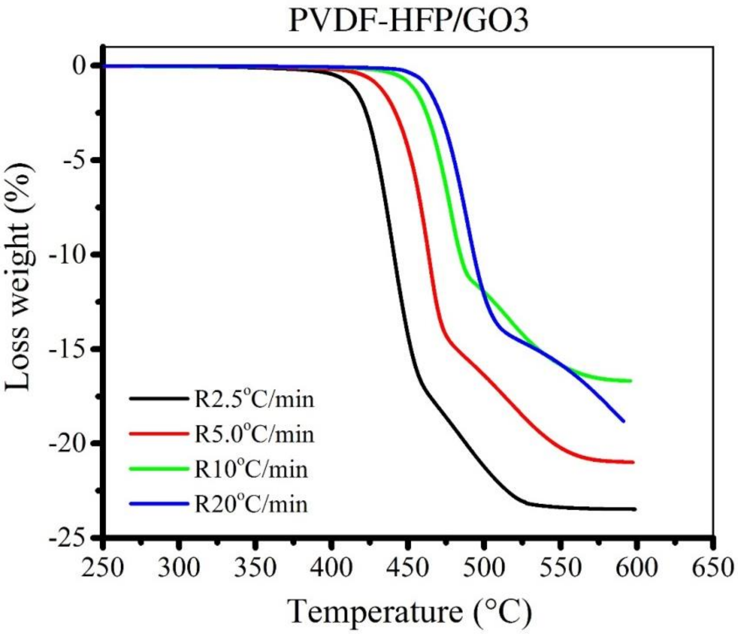


Figure 4. Heat dissipation and derived heat dissipation diagram in non-homogeneous conditions for PVDF-HFP / GO3 sample

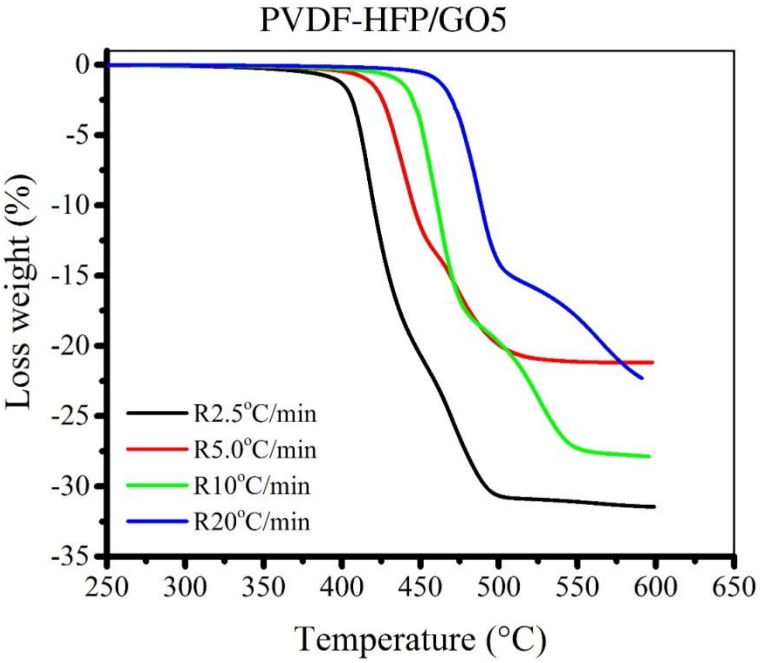


Figure 5. Heat dissipation and derived heat dissipation diagram in non-homogeneous conditions for PVDF-HFP / GO5 sample

By using equation (1), the amounts of activation energy for the samples were calculated in two atmospheres of nitrogen and oxygen. By using equation (2), the diagram is shown in Figures 6 and 7, based on the percentage conversion of 10 to 90 for PVDF-HFP and PVDF-HFP / GO5 samples. As a result, the amount of energy of degradation activation in any conversion value can be obtained and reported from the gradient of these lines.

Figure 8 shows the activation energy diagram according to the conversion rate for the samples studied in the oxygen environment based on the FLW model. Figure 8 shows that for all samples in two media (nitrogen is not reported here), increasing the conversion rate increases the activation energy. As the percentage of conversion in the degradation test decreases the amount of material available for degradation, that this increases the amount of activation energy.

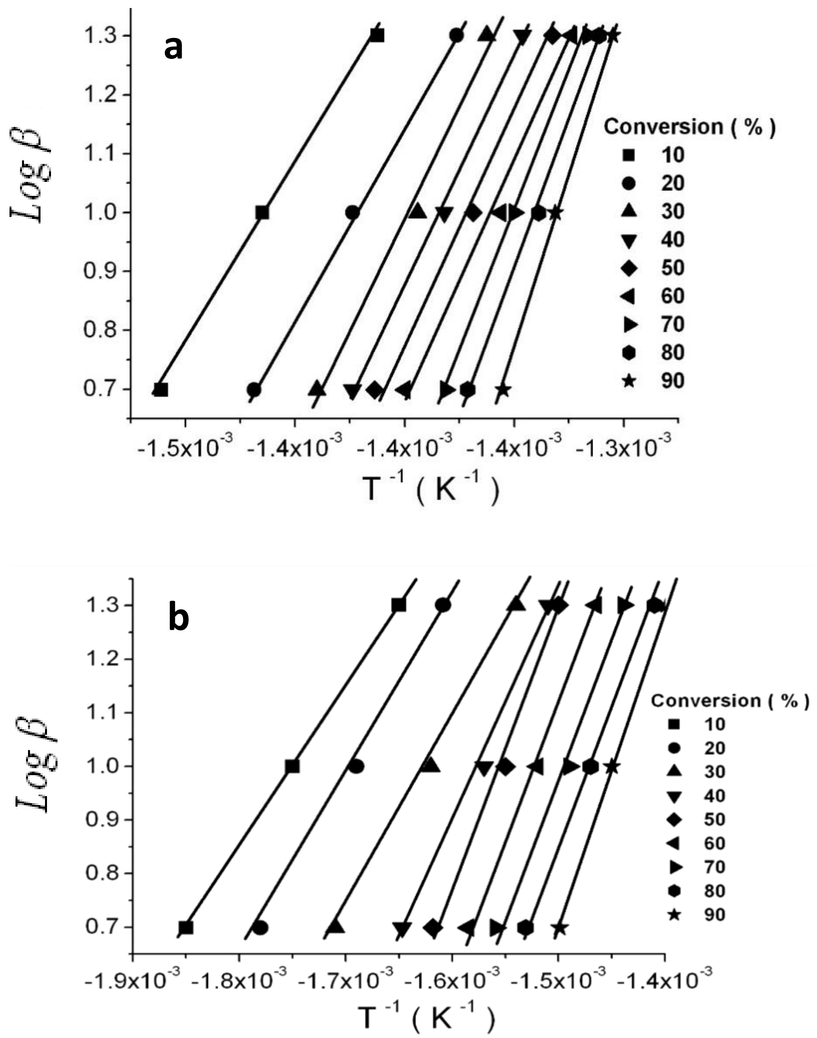


Figure 6. $Log\,\beta$ diagrams of T^{-1} for PVDF-HFP sample in (a) nitrogen and (b) oxygen

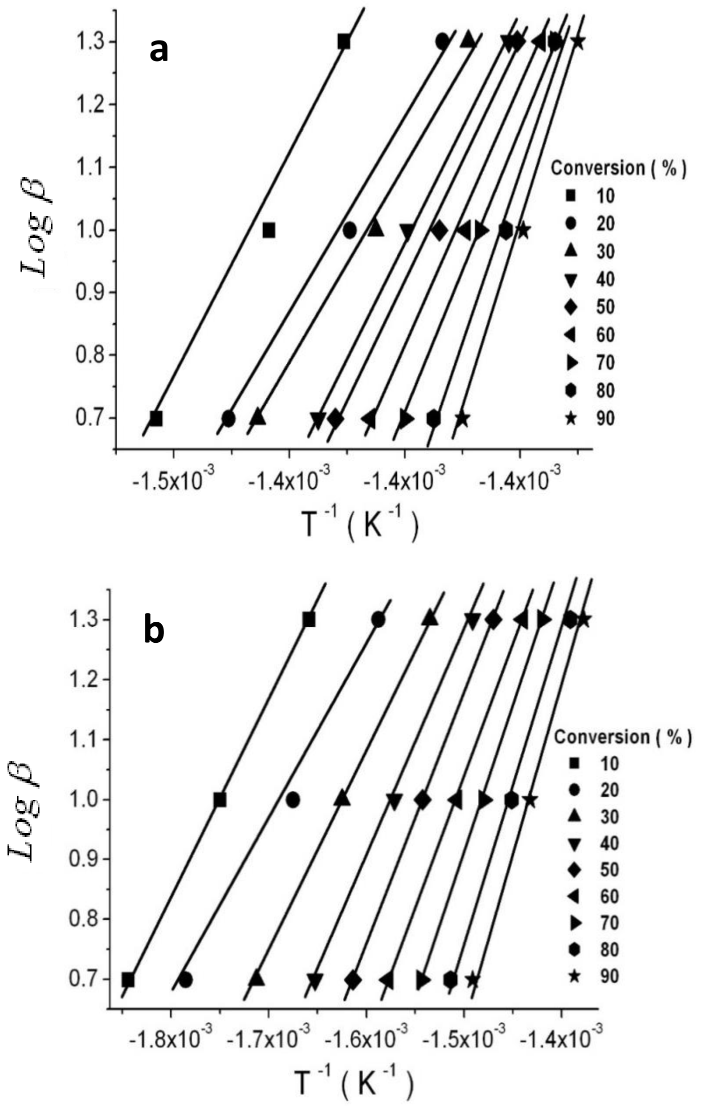


Figure 7. The $Log\,\beta$ diagram of T^{-1} for PVDF-HFP / GO5 sample in (a) nitrogen and (b) oxygen

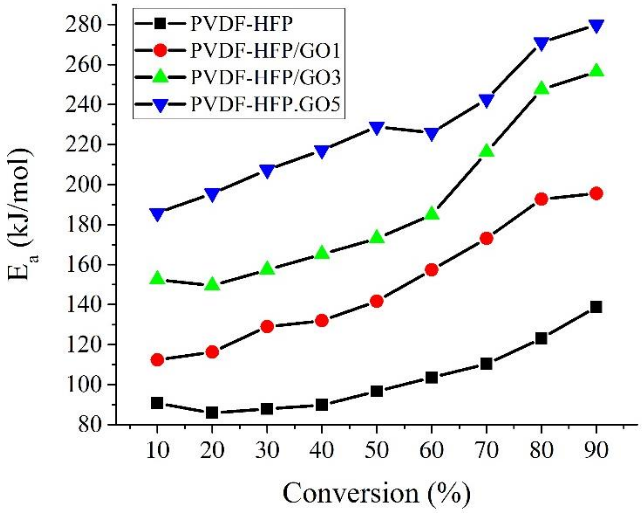


Figure 8. Activation energy diagram in terms of conversion rate for the samples in the oxygen atmosphere based on the FLW model

It is seen in this figure that nanocomposites have the highest degradation energy.

Estimation of constant temperature conditions by using non-homogeneous data

One of the methods used to evaluate the degradation process in polymer materials is the use of constant temperature conditions. In this case, the sample is placed under a constant temperature and measures the time to lose weight. There are also methods that can be used to test the constant temperature test conditions by using non-heuristic tests. Consequently, using the data obtained in non-homogeneous state, the constant temperature conditions can be approximated so that the following equation is considered for the evaluation of the degradation in polymer materials.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A\exp\left(\frac{-E}{RT}\right)f(\alpha) \qquad \mathbf{b}$$

In the above relation t is the time, α is the conversion rate, $k(T)$ is the arenyoid constant, A and E parameters of Arrhenius, and R is the gas constant. By using the method of the separation of variables in the solution of differential equations, the above equation is obtained as follows:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = A\int_0^{t\alpha} \exp\left(\frac{-E}{RT(t)}\right)dt \qquad \mathbf{b}$$
$$= AJ[E, T(t_\alpha)]$$

In the above equation, $g(\alpha)$ is the integral form of the function of the reaction model and $T(t)$ is the thermal function with time. In the above equation, we can define the J functions, which depend on the temperature and energy of the activation in each degradation percentage. Consequently, by using the above-mentioned equation and the integral taken at any time, the equation can be obtained for a constant temperature state as shown below.

$$t_\alpha = \frac{J(E_\alpha, T(t))}{Exp\left(\frac{-E_\alpha}{RT_0}\right)}$$

In these equations, by inserting the required values, it is possible to obtain the time for each percentage and at any desired temperature T_0 and approximate the constant temperature conditions using it. These equations are independent of the destructive reaction model and do not have any relationship to how the reaction is degraded, so this is called a free model of prediction. For the evaluation of constant temperature conditions, the temperature of 400 ° C was considered and the calculations were carried out. In these evaluations, numerical integrals were calculated by using the Simpson 3/8 method, which was considered to be the appropriate accuracy. As a result, the data were presented in Fig- 9. In this figure, for a fixed time in the PVDF-HFP sample, the percentage of conversion is higher than the other samples. For the PVDF-HFP / GO5 sample in a constant time, the less amount of matter is degraded and the conversion percentage is less.

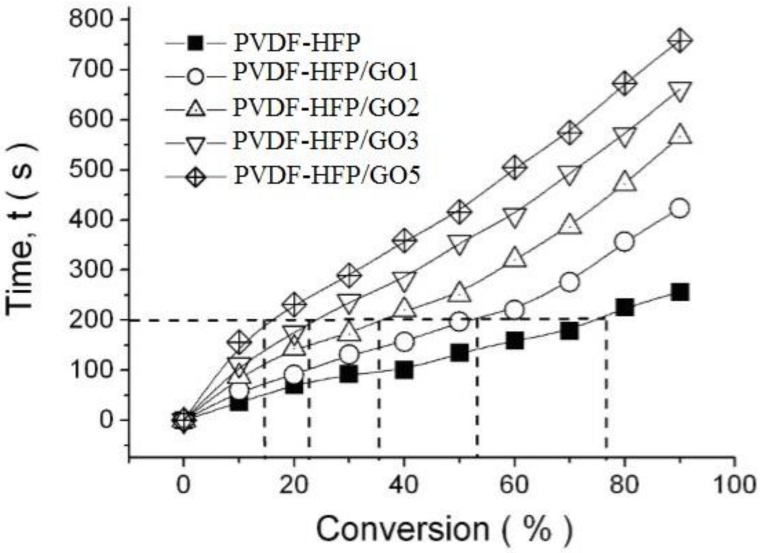


Figure 9. Heat degradation prediction for the studied samples at 400 ° C

Discussion and Conclusion

In this research, polyvinylidine fluoride-hexafluoro-polypropylene nanocomposite samples containing different percentages of graphene oxide were prepared by melt mixing method. Then, the behavior of thermal degradation and activation energy of polyvinylidine fluoride-hexafluoro-polypropylene nanocomposites containing graphene oxide nanoparticles were evaluated with FLW and Kissinger models. An evaluation of the polyvinylidine fluoride-hexafluoro-polypropylene nanocomposite morphology showed that graphene particles were well distributed in the polymer matrix, although there were also hunchbacking particles in some places. The results of heat dissipation analysis showed that the weight loss of the samples begins in the nitrogen environment later. This reflects the effective effect of oxygen in increasing the rate of mass reduction in the first stage of degradation, and in this radical atmosphere, it is rapidly combined with oxygen and the degradation process is followed up more rapidly. But in the nitrogen environment, this radical remains stable. The presence of oxygen and heat is one of the effective factors in increasing the rate of degradation of polyvinylidine fluoride-hexafluoro polypropylene.

The results of heat dissipation in the oxygen environment showed that with increasing the heating rate, the weight loss values are transported to higher temperatures, which is due to the reduction of the degradation time.

The activation energy values evaluated by the Flaneen-Wall-Ozawa (FLW) model in the oxygen environment showed that increasing the conversion rate increased the activation energy. As the percentage of conversion in the degradation test increases, the amount of material available for degradation decreases, which causes increase the amount of activation energy. The results of the research showed that polyvinylidine fluoride-hexafluoro-polypropylene nanocomposites have the highest degradation energy.

In this figure, for a constant time in the PVDF-HFP sample, the percent conversion is higher than the other samples. For example PVDF-HFP / GO5 in a constant time, less amount of matter degrades and conversion percentage is less.

Research suggestions

Despite the efforts made to carry out this project, the device, cost and time problems caused all aspects of it not to be evaluated, therefore, it is recommended to complete this project:

- Evaluation of thermal degradation kinetics of polyvinylidine fluoride-hexafluoro polypropylene nanocomposites containing graphene nanoparticles and evaluation of degradation products by spectroscopy
- Use of other copolymers of polyvinylidine fluoride and compare their destruction process in pure state and in the presence of nanoparticle material.
- Evaluation of thermal degradation kinetics of polyvinylidine fluoride-hexafluoro polypropylene nanocomposites with other nanoscale materials
- Using two nano-particles with different geometric shapes and comparing their degradation behavior with polyvinylidine fluoride-hexafluoro-polypropylene / graphene oxide nanocomposites

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