Research Article

Nonisothermal Kinetic Analysis and AC Conductivity for Polyvinyl Chloride (PVC)/Zinc Oxide (ZnO) Nanocomposite

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The behavior of polyvinyl chloride (PVC)/zinc oxide (ZnO) nanoparticles was investigated. To improve the dispersion and distribution of zinc nanoparticles within the host polymer (PVC), they were treated with water before being added to the polymer. The nanocomposite samples were prepared by casting method using different weight ratios of ZnO nanoparticles. The prepared nanocomposite samples were characterized by thermogravimetric analysis (TGA). Both thermal stability and kinetic analysis of the prepared samples were investigated. The ZnO nanoparticles lower the activation energy and decrease the thermal stability of PVC. Kissinger, Flynn-Wall-Ozawa, and Kissinger-Akahira-Sunose models were used in the nonisothermal kinetic analysis of PVC/ZnO nanocomposite samples. The thermal stability behavior due to the addition of zinc oxide nanoparticles was explained and correlated with the behavior of the kinetic parameters of the samples. The AC conductivity as function of frequency and temperature was also investigated. The addition of ZnO nanoparticle increases the AC conductivity, and the temperature-independent region decreased by increasing temperature. Both S and A coefficients were predicted using the Jonscher power law and OriginLab software. The trends of S and A coefficients were discussed based on the glass transition of the host polymer.

1. Introduction

Thermoplastic polymers have physical and chemical properties that meet the requirements for many industrial applications. Among the thermoplastics, the industrial use of PVC is ranked second after polyethylene. It has been used in the manufacturing of electrical insulators, insulating floors, ceilings, medical devices, packaging, pipe industry, and many other countless applications [1]. Due to its tremendous importance in the manufacturing industry, PVC receives a lot of attention from researchers.

For example, in order to improve the thermal properties of PVC, Hajibeygi et al. [2] used a ternary nanocomposite containing PVC/chitosan-modified ZnO nanoparticles. They further investigated the thermal stability by using PVC-modified ZnO nanoparticles with imide functionalized polyethyleneimine (PEI). In both cases, they found that the ternary system possessed more thermal stability than host PVC polymer. Taha et al. [3] investigated the thermal stability of PVC/SnO₂ nanocomposite, and they found that the glass transition increased for SnO₂-doped samples. In addition, the thermal stability increased for the high-temperature decomposition stage (350-550°C). PVC reinforced by ZnO nanoparticles was investigated by Mallakpour and Darvishzadeh [4]. According to their TGA data, the thermal stability of PVC at the high-temperature stage was increased by increasing the percent of ZnO/bovine serum albumin BSA nanoparticles. The thermal stability of PVC/TiO₂ nanoparticles covered by bovine serum was also investigated by Mallakpour and Shamsaddinimotlagh [5]. Their TGA analysis showed higher thermal stability for the nanocomposite samples than the host polymer in its pure form.

Hajibeygi et al. [6] investigated the thermal stability of PVC-modified ZnO nanoparticles with imide functionalized polyethyleneimine (PEI). The thermal stability of the prepared modified nanocomposite sample was increased.

PVC loaded with 2 wt.% ZnO nanoparticles was prepared to investigate the effect of molecular weight of PVC on the thermal properties of nanocomposite [7]. The glass transition
Figure 1: (a) TGA spectra and (b) DTGA spectra for PVC and PVC/ZnO nanocomposite at 5°C/min heating rate.

Figure 2: TGA spectra for (a) pure PVC, (b) 5 wt.% ZnO, and (c) 8 wt.% ZnO nanocomposite samples at different heating rates.
of the prepared nanocomposite was increased, and it was noted that the higher the molecular weight, the greater the extent of the glass transition enhancement. Taha [8] has investigated the thermal stability for Pb₃O₄/PVC nanocomposites. The data revealed that such nanocomposites have higher thermal stability than pure PVC film.

The thermal degradation of PVC/iron oxide-modified montmorillonite (MMT) nanocomposite was investigated [9] in air atmosphere, and the activation energies were obtained using the Kissinger model. The iron-modified PVC nanocomposite samples showed higher thermal stability and higher activation energy than the pure PVC. PVC/sepiolite nanocomposite sample decreases the thermal stability of PVC and the activation energy in both decomposition stages of PVC [10]. Sánchez-Jiménez et al. [11] investigated the kinetics of PVC decomposition and revealed that there are two main different processes. The first process is represented by nucleation and growth mechanism with activation energy of about 114 kJ/mol while the second is represented by a diffusion-controlled model with an activation energy of about 202 kJ/mol. Many other researchers have investigated the thermal stability, thermal degradation, and kinetic analysis for PVC, PVC blend, and PVC nanocomposites using different kinetic models [12–20]. Several researchers investigate the conduction mechanism and the AC conductivity of such nanocomposite samples.

In the present work, we aim to investigate the kinetics of the thermal analysis of PVC/ZnO nanoparticle using different kinetic models. The effect of the addition of ZnO on the thermal stability and the AC conductivity of this type of nanocomposite will be discussed. TGA nonisothermal data at different heating rates will be used to calculate the activation energy (Eₐ) and preexponential factor (A) using the Kissinger, FWO, and KAS models. The Jonscher universal power law will be used to discuss the AC conductivity of the composite.
2. Model-Free Methods

2.1. Kissinger Method. The Kissinger model is one of the simplest models used to find the kinetic parameters of a reaction without going into the details of reaction mechanism [21]. In the Kissinger model, we rely on the relationship between $\ln \left( \frac{\beta}{T_p^2} \right)$ versus $\frac{1}{T_p}$ for a series of degradation curves at different heating rates ($\beta$) where $T_p$ is the temperature at maximum decomposition rate. For a first-order reaction, the following equation holds:

$$\ln \left( \frac{\beta}{T_p^2} \right) = \ln \left( \frac{AR}{E_a g(\alpha)} \right) - \frac{E_a}{RT_p}. \quad (1)$$

The apparent activation energy ($E_a$) can be deduced by finding the accurate slope of such relation (slope = $-E_a/R$).

2.2. Flynn-Wall-Ozawa Method. The FWO model depends on the relation between $\ln \left( \frac{\beta}{T_p^2} \right)$ versus $\frac{1}{T_p}$ for specific values of conversion at different values of $\beta$. The following equation can be used for the FWO model [22, 23]:

$$\ln \left( \frac{\beta}{T_p^2} \right) = \ln \left( \frac{A}{E_a g(\alpha)} \right) - \frac{5.331 - 1.052}{E_a R T_{\alpha_i}}, \quad (2)$$

Note that it is important to know that the function $g(\alpha)$ is constant for each given value of $\alpha$. From the above relation, one can calculate the apparent activation energy for each $\alpha$ from the slope of the linear relation (slope = $-1.052E_a/R$).

2.3. Kissinger-Akahira-Sunose. Their model can be written as follows [24–26]:

$$\ln \left( \frac{\beta}{T_p^2} \right) = \ln \left( \frac{A_{\alpha_i}}{E_a g(\alpha)} \right) - \frac{E_a}{RT_{\alpha_i}}, \quad (3)$$

by plotting $\ln \left( \frac{\beta}{T_p^2} \right)$ vs. $\frac{1}{T_{\alpha_i}}$ and from the slope $E_a$ can be obtained.

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**Figure 4:** $\ln \left( \frac{\beta}{T_p^2} \right)$ vs. $\frac{1}{T_p}$ for (a) pure PVC, (b) 5 wt.% PVC/ZnO, and (c) 8 wt.% PVC/ZnO samples, respectively.
3. Sample Preparation

Polyvinyl chloride (PVC) (Saudi Basic Industries Corporation (SABIC), MW of 30,000) and ZnO nanoparticles (Sigma-Aldrich Chemicals; <100 nm) are used for sample preparation. PVC (1 g) was dissolved in 15 mL of THF at room temperature (≈23°C) using a magnetic stirrer for 4 hours. Zinc oxide nanoparticles were mixed with 1 mL of distilled water to obtain a paste of water-saturated nanoparticles. The obtained paste was transferred to a filter paper to remove excess water and left to dry at room temperature for two hours. The paste was ultrasonicated in 3 mL of THF.

Table 1: The extracted data of the Kissinger model for pure PVC.

| Sample  | Peak | Intercept value | Preexponential $A$ (min$^{-1}$) | Slope value | Activation energy $E_a$ (kJ/mol) | Statistics $R^2$ |
|---------|------|-----------------|---------------------------------|-------------|----------------------------------|-----------------|
| PVC     | 1    | 16.47           | $2.07 \times 10^5$              | -14.59      | 121.31                           | 0.98508         |
|         | 2    | 13.20           | $7.54 \times 10^6$              | -13.88      | 115.41                           | 0.97            |
| 5 wt.% ZnO | 1    | 14.41           | $2.46 \times 10^7$              | -13.52      | 112.41                           | 0.97            |
| 8 wt.% ZnO | 1    | 15.04           | $4.68 \times 10^7$              | -13.81      | 114.82                           | 0.99            |

Figure 5: Temperature dependence of conversion $\alpha$ for (a) pure PVC, (b) 5 wt.% ZnO, and (c) 8 wt.% ZnO samples.
solvent for 15 minutes. The dispersed pretreated ZnO was added to the prepared PVC-THF solution and ultrasonicated for three hours to ensure the homogeneity of the mixture. The mixture was transferred to the magnetic stirrer and stirred overnight to ensure homogeneity of the nanoparticle's distribution within the polymer. The mixture was poured into Petri dishes at a radius of six centimeters and left to dry for three days.

4. Results and Discussion

4.1. Thermal Gravimetric Analysis. Thermal gravimetric analysis (TGA) for pure PVC and PVC-ZnO nanocomposite (5 wt.% and 8 wt.% water-treated ZnO) was carried out using TA instruments Q500 (USA). All measurements were carried out in the temperature range 25–600 °C with different scan rates with nitrogen purge at a flow rate of 60 mL/min. The sample weight was about 12 mg for all samples.

As revealed in several previous works [1, 11, 27, 28], the decomposition curve for pure PVC polymer consists of three main decomposition regions which are represented as three peaks in DTGA complex curve. The 1st main decomposition process of PVC consists of two subsequent processes. These two processes are confined in the temperature range from about 175 to 375°C. The second main decomposition is confined between 350 and 550°C. The 1st stage corresponds to the evolution of hydrogen chloride causing formation of polyene structure while the 2nd stage is attributed to the thermal cracking of the carbonaceous-conjugated polyene sequences [7].

Samples loaded with treated zinc oxide nanoparticles have the same decomposition behavior as pure PVC sample except a DTGA peak near 200°C which can possibly be attributed to the direct chlorination of ZnO by the PVC monomer [29]. It is noted that nanocomposite samples have less thermal stability during the low-temperature stage (50 to 350°C). The mass loss at 225°C was about 10%, 13%, and 16% for the pure PVC, 5 wt.% ZnO, and 8 wt.% ZnO samples, respectively. The addition of treated ZnO accelerates the initiation of HCl. The formation of HCl accelerates the formation of double bond sequences in the polymer backbone [1, 7]. The rate of formation of HCl depends strongly on the presence of oxygen [11, 28]. Decomposition of water molecules adsorbed on ZnO particles will increase the HCl

![Figure 6: ln (βα) vs. 1/Tαi for (a) pure PVC region I and (b) pure PVC region II and the dependence of activation energy on the conversion α for (c) pure PVC region I and (d) pure PVC region II.](image-url)
formation due to the production of oxygen atoms. There are several references which studied the effect of zinc oxide on the thermal stability of PVC. For example, Lewis acids (e.g., ZnCl₂ and FeCl₃) [30–34] can accelerate and lower the activation energy of PVC degradation. Also, according to Zhang et al. [29], ZnO can react with HCl or directly with the PVC monomer. ZnCl₂ can form and catalyze the dehydrochlorination of PVC [35, 36], resulting in a lower activation energy. Finally, all these factors will lead to the reduction of thermal stability for the low-temperature degradation stage.

The rate of formation of HCl depends strongly on the presence of oxygen [11, 37, 38]. Decomposition of water molecules adsorbed on ZnO particles will increase the HCl formation due to the production of oxygen atoms. This will lead to the reduction of thermal stability for the low-temperature degradation stage.

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For the high-temperature range, it is observed that the thermal stability of the samples increases by increasing the weight ratio of ZnO nanoparticles. This behavior may be attributed to the following two reasons. The first is that the number of double bond formation increases, which contributes to the thermal isolation for the remaining polymeric chains. By this way, the double bond (polyenes) structure will protect the remaining chains from degradation and increase the thermal stability. The second is that metal oxides act as adsorbents for HCl or as inhibitors of HCl formation due to their reaction with HCl, which in turn increases the thermal stability of the material [1].

### 4.2. Kinetic Thermal Analysis for Pure PVC and PVC/ZnO Nanocomposite

Kinetic thermal analysis for pure PVC and PVC/ZnO nanocomposite samples (Figures 1) was investigated using the data collected by TGA measurements. Measurements were performed at different heating rates (5, 10, 20, 30, and 40°C/min) for temperature ranging from 40 to 550°C. Using the previous equations (equations (1)–(3)) of the three models (Kissinger, Flynn-Wall-Ozawa, and Kissinger-Akahira-Sunose models), the kinetic parameters for pure PVC and PVC/ZnO were calculated.

Figures 2(a)–2(c) represent the TGA spectra for pure PVC and 5 wt.% and 8 wt.% PVC/ZnO nanocomposite at different heating rates, respectively. Figures 3(a)–3(c) illustrate the corresponding DTGA spectra for these samples.

#### 4.2.1. Kissinger Model

In the Kissinger model, the temperature corresponding to the maximum decomposition rate ($T_p$) was determined from the DTGA curves for each heating rate. By applying the Kissinger model to the 1st main decomposition processes (225 to 400°C), the relationship between $\ln(\beta/T_p^2)$ and $1/T_p$ for pure PVC and 5 wt.% and 8 wt.% PVC/ZnO was plotted and is shown in Figures 4(a)–4(c), respectively. The slope and the intercept of the straight line were determined to calculate the activation energy and the preexponential factor. The extracted data are recorded in Table 1. For nanocomposite samples, the second reaction within this temperature range was overlapped with the first reaction in a way that does not allow us to define the peak temperature for each curve, and therefore, we were unable to apply the model to this reaction region.

It is noted that the activation energies for the 1st reaction peak reduced due to the addition of ZnO nanoparticles. For pure PVC, $E_a$ was found to be about 121 kJ/mol while for nanocomposite samples it was about 112 kJ/mol for 5 wt.% ZnO and about 114 kJ/mol for 8 wt.% ZnO sample.

#### Table 2: The extracted data of the FWO model for both reaction regions of pure PVC.

| Alpha PVC | Intercept value | Preexponential $A$ (min⁻¹) | Slope value | Activation energy $E_a$ (kJ/mol) | Statistics Adj. $R^2$ | Average |
|-----------|----------------|-----------------------------|-------------|---------------------------------|-----------------------|---------|
| **PVC region 1** | | | | | | |
| 0.05      | 31.08          | $9.72 \times 10^{14}$       | -14.95      | 118.15                          | 1.00                  | 1.00    |
| 0.1       | 31.70          | $9.13 \times 10^{14}$       | -15.56      | 122.97                          | 1.00                  | 1.00    |
| 0.15      | 32.31          | $1.72 \times 10^{15}$       | -16.04      | 126.76                          | 1.00                  | 1.00    |
| 0.2       | 32.76          | $2.77 \times 10^{15}$       | -16.40      | 129.61                          | 0.99                  | 1.00    |
| 0.25      | 32.50          | $2.13 \times 10^{15}$       | -16.37      | 129.37                          | 0.99                  | 128.11  |
| 0.3       | 32.53          | $2.21 \times 10^{15}$       | -16.48      | 130.24                          | 1.00                  | 1.00    |
| 0.35      | 33.00          | $3.73 \times 10^{15}$       | -16.40      | 126.60                          | 0.98                  | 128.74  |
| 0.4       | 32.07          | $1.39 \times 10^{15}$       | -16.41      | 129.69                          | 1.00                  | 1.00    |
| 0.45      | 31.67          | $9.27 \times 10^{14}$       | -16.29      | 128.48                          | 1.00                  | 1.00    |
| **PVC region 2** | | | | | | |
| 0.6       | 33.27          | $4.96 \times 10^{15}$       | -17.60      | 139.09                          | 1.00                  | 1.00    |
| 0.65      | 34.14          | $1.23 \times 10^{16}$       | -18.29      | 144.55                          | 0.99                  | 145.16  |
| 0.7       | 34.29          | $1.44 \times 10^{16}$       | -18.57      | 146.76                          | 0.99                  | 145.16  |
| 0.75      | 33.72          | $8.11 \times 10^{15}$       | -18.42      | 145.57                          | 0.99                  | 145.16  |
| 0.8       | 33.16          | $4.62 \times 10^{15}$       | -18.27      | 144.39                          | 0.98                  | 144.39  |
| 0.85      | 33.36          | $5.70 \times 10^{15}$       | -18.58      | 146.84                          | 0.98                  | 146.84  |
| 0.9       | 33.44          | $6.29 \times 10^{15}$       | -18.84      | 148.89                          | 0.97                  | 148.89  |
4.2.2. Flynn-Wall-Ozawa Model. The Flynn-Wall-Ozawa model was used to calculate the activation energy of pure PVC and nanocomposite samples and compare it with the values calculated from the Kissinger model. By assuming that the value of $g(\alpha)$ is constant at each value of $\alpha$ and by drawing the relationship between $\ln(\beta)\alpha_i$ and $1/T\alpha_i$ at different values of $\alpha$, one can determine the activation energy $E_{\alpha}$ for each value of $\alpha$.

Figure 5 shows the conversion with temperature for pure and nanocomposite samples, considering that the range of reaction is a one-step transition. It is noted that the behavior of the conversion curve depends on the weight ratio of zinc oxide nanoparticles. In the case of the pure PVC sample, there were two regions with different rates of conversion and different reaction speeds. However, because of the inhabitation role of ZnO to HCl formation, the conversion curve became a one-step reaction form with a little deviation at the edges of the curve. These sets of curves were used to investigate the relationship between $\ln(\beta)\alpha_i$ and $1/T\alpha_i$ and determine the activation energies and preexponential factors.

Figures 6(a) and 6(b) illustrate the relation between $\ln(\beta)\alpha_i$ and $1/T\alpha_i$ of PVC for both reaction regions. The calculated values of $E_{\alpha}$ as function of conversion $\alpha$ for both reaction regions are represented in Figures 6(c) and 6(d). The activation energy for the first reaction region varies from 118 to 128 kJ/mol with an average value of 128 kJ/mol, while the activation energy for the second reaction region changed from 139 to 149 kJ/mol with an average value of 145 kJ/mol. By comparing those values with the values obtained from the Kissinger model, we find that they are higher by 5% to 20%, respectively. Table 2 shows the extracted data of the FWO model for both reaction regions of pure PVC sample.

Figures 7(a)–7(d) represent $\ln(\beta)\alpha_i$ vs. $1/T\alpha_i$ for (a) 5 wt.% PVC/ZnO and (b) 8 wt.% PVC/ZnO samples and the dependence of activation energy on the conversion ($\alpha$) for (c) 5 wt.% PVC/ZnO and (d) 8 wt.% PVC/ZnO samples.

4.2.2. Flynn-Wall-Ozawa Model. The Flynn-Wall-Ozawa model was used to calculate the activation energy of pure PVC and nanocomposite samples and compare it with the values calculated from the Kissinger model. By assuming that the value of $g(\alpha)$ is constant at each value of $\alpha$ and by drawing the relationship between $\ln(\beta)\alpha_i$ and $1/T\alpha_i$ at different values of $\alpha$, one can determine the activation energy $E_{\alpha}$ for each value of $\alpha$.

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Figures 7(a)–7(d) represent $\ln(\beta)\alpha_i$ vs. $1/T\alpha_i$ for (a) 5 wt.% PVC/ZnO and (b) 8 wt.% PVC/ZnO samples and the dependence of activation energy on the conversion ($\alpha$) for (c) 5 wt.% PVC/ZnO and (d) 8 wt.% PVC/ZnO samples.
Table 3: The extracted data of the FWO model for both 5 wt.% and 8 wt.% PVC/ZnO nanocomposite samples.

| Alpha 5 wt.% | Intercept value | Preexponential $A$ (min$^{-1}$) | Slope value | Activation energy $E_{a}$ (kJ/mol) | Statistics | Adj. $R^{2}$ | Average |
|--------------|-----------------|---------------------------------|-------------|------------------------------------|------------|-------------|---------|
| PVC/5 wt.% ZnO |                 |                                 |             |                                    |            |             |         |
| 0.1          | 29.27           | $7.3810^{13}$                  | -14.30      | 113.01                             | 0.96       |             | 99.05   |
| 0.2          | 28.75           | $4.3510^{13}$                  | -14.25      | 112.62                             | 0.98       |             | 99.05   |
| 0.3          | 27.45           | $1.1410^{13}$                  | -13.65      | 107.88                             | 0.98       |             | 99.05   |
| 0.4          | 26.49           | $4.2310^{12}$                  | -13.21      | 104.40                             | 0.98       |             | 99.05   |
| 0.5          | 25.11           | $1.0010^{12}$                  | -12.53      | 99.03                              | 0.98       |             | 99.05   |
| 0.6          | 23.16           | $1.3110^{11}$                  | -11.54      | 91.20                              | 0.97       |             | 99.05   |
| 0.7          | 21.06           | $1.4710^{10}$                  | -10.47      | 82.74                              | 0.97       |             | 99.05   |
| 0.8          | 20.46           | $7.8910^{9}$                   | -10.32      | 81.56                              | 0.96       |             | 99.05   |
| PVC/8 wt.% ZnO |                 |                                 |             |                                    |            |             |         |
| 0.3          | 27.38           | $1.04 \times 10^{13}$          | -13.4       | 105.90                             | 0.98       |             | 99.01   |
| 0.4          | 28.22           | $2.51 \times 10^{13}$          | -13.99      | 110.56                             | 0.99       |             | 99.01   |
| 0.5          | 26.91           | $6.50 \times 10^{12}$          | -13.36      | 105.58                             | 0.98       |             | 99.01   |
| 0.6          | 25.54           | $1.57 \times 10^{12}$          | -12.68      | 100.21                             | 0.98       |             | 99.01   |
| 0.7          | 23.43           | $1.74 \times 10^{11}$          | -11.60      | 91.68                              | 0.97       |             | 99.01   |
| 0.8          | 20.67           | $9.72 \times 10^{9}$           | -10.21      | 80.69                              | 0.98       |             | 99.01   |

Figure 8: $\ln (\beta/T_{\alpha}^2)$ vs. $1/T_{\alpha}$ for (a) pure PVC, (b) 5 wt.% PVC/ZnO, and (c) 8 wt.% PVC/ZnO samples.
Table 3 shows the extracted data of the FWO model for both 5 wt.% and 8 wt.% PVC/ZnO nanocomposite samples. The average activation energies for both nanocomposite samples are nearly equal to 99 kJ/mol and are less than that obtained by using the Kissinger model (≈112 and 114 kJ/mol). From the table, we observe that the average activation energy values corresponding to intermediate values of $\alpha$ (0.3 to 0.5) is the nearest to the predicted value using the Kissinger model, while small and large $\alpha$ values have activation energy less or greater than that predicted by the Kissinger model. This means that if we neglect the two edges of conversion curve we will have average values for activation energy closed to that predicted by the Kissinger model because we will reduce the errors due to the overlapping of the two decomposition processes.

**4.2.3. Kissinger-Akahira-Sunose (KAS).** The relationship between $\ln(\beta/T_{ai}^2)$ and $1/T_{ai}$ at different values of $\alpha$ are illustrated in Figure 8 for pure PVC and PVC/ZnO nanocomposites. The dependence of the calculated activation energies on conversion $\alpha$ for pure and nanocomposite samples is illustrated in Figure 9. The average activation energies for pure, 5 wt.%, and 8 wt.% ZnO nanoparticles were 116.4, 89.6, and 93.5 kJ/mol, respectively. Table 4 shows the extracted data of the KAS model for PVC and 5 wt.% and 8 wt.% PVC/ZnO nanocomposite samples.

From the obtained results, the addition of zinc nanoparticles led to a decrease in the thermal stability of the samples during the low-temperature range ($T < 350^\circ$C), which was investigated with kinetic thermal analysis models. The kinetic thermal analysis showed that the activation energy of the samples decreased by adding ZnO nanoparticles significantly through both FWO and KSA models. These results are consistent with the results of thermal stability, which were explained based on the contribution of oxygen emitted from the decomposition of adsorbed water on ZnO nanoparticle surface in accelerating the HCl formation (at low-temperature region) besides the role of ZnO chlorination in accelerating the decomposition process. At the high-temperature region, ZnO nanoparticles play an important role in inhibiting the role of HCl in the decomposition process of the polymer [29].
4.3. AC Conductivity. Figure 10 shows the variation in AC conductivity as a function of frequency at different temperatures (30 to 110°C) for pure PVC and PVC-ZnO nanocomposite films (5 wt.% and 8 wt.%). It is observed that all the prepared samples exhibit the same behavior but with different values over the whole range of measured frequency. The Jonscher universal power law (equation (4)) [39] was used to investigate the frequency dependence of conductivity for such nanocomposite. The total electrical conductivity $\sigma(\omega)$ is composed of the summation of AC ($\sigma_{ac}(\omega)$) and DC ($\sigma_{dc}(0)$) conductivities, and according to the Jonscher power law, the frequency dependence of total conductivity can be written as

$$\sigma(\omega) = \sigma_{dc}(0) + \sigma_{ac}(\omega) = \sigma_{dc} + A \omega^s.$$  (4)
The DC conductivity part is frequency independent while AC conductivity is the frequency-dependent part. Coefficient “$A$,” which represents the strength of polarizability, is a temperature-dependent constant. The power law exponent ($s$) (which generally varies between 0 and 1) is also temperature dependent. The exponent “$s$” denotes to the degree of interaction between carriers and lattice or surrounding molecules. A lower value of $s$ indicates the increase in $\sigma_{dc}$ contribution [40].

It is noted that the AC conductivity increased and the temperature-independent region decreases with temperature for all samples. Also, the AC electrical conductivity increases with increasing ZnO NPs (Figure 11). The increase of the conductivity with ZnO wt.% can be regarded to the increase in the number of charge carriers which are able to contribute in the conduction mechanism. Moreover, the presence of ZnO NPs may contribute in decreasing the chain agglomeration of the host polymer. In addition, the increase of the conductivity can be considered as an indicator to the homogenous dispersion of the filler (ZnO NPs) through the host polymer which emphasizes the absence of agglomeration of the filler (which causes reduction in conductivity and acts as trap centers for the free charge carrier) within the prepared samples.

To illustrate the behavior of samples, Figures 12–14 show the behavior of pure PVC and nanocomposite samples (5 wt.% and 8 wt.%) through five frequency bands. It is noted that for the low-frequency band there are no detectable relaxation peaks and this attributed to the rule of the DC conductivity. For both intermediate- and high-frequency bands, the AC conductivity values corresponding to the relaxation peaks increase with increasing frequency in addition to the shift to higher temperatures. The peak symmetry (for high-frequency range) indicates a single relaxation process.

The coefficients $A$ and $S$ obtained by applying the Jonscher universal power law and fitting using Origin software version 8.5 are illustrated in Figure 15. As observed from the figure, the values of coefficient $S$ lie between 1 and 0.65. Coefficient “$S$” signifies the degree of interaction between chains in pure PVC samples and represents both interactions between chains of host polymer with each other and between host polymer and filler for composite samples. The behavior of the $S$ coefficient related to the host polymer glass transition ($T_g$) about 85°C because the chain interaction of chain filler interaction depends on temperature [41]. Below $T_g$, PVC chains have less degree of freedom to contribute to AC and DC due to impurity and space charge becomes the predominant factor. During this stage, we noted that $S$ decreases with temperature up to the temperature where the chains become able to move ($T_g$) after which coefficient $S$ starts increasing with temperature. The AC conductivity above $T_g$ represents the predominant conduction mechanism. The interaction between chains and filler appears as shift in the $S$-$T$ curve to higher temperature.
temperature. The conduction above $T_g$ will be due to the segmental chain movement, and the presence of ZnO will facilitate such motion.

It is noted that the behavior of coefficient “A” is contrary to that of coefficient “S” (coefficient A increases with temperature and then decreases), and this is normal where before $T_g$
charge carriers have the ability to be polarized and to arrange themselves, while above $T_g$ the degree of randomness increases and the AC conduction due to chain motion becomes predominant. The temperature corresponding to the maximum value of coefficient “A” is slightly changed (93 to 95°C).
Polymer nanocomposite samples composed of distilled water-treated ZnO nanoparticles and PVC polymer were prepared by casting method. The thermal stability of the samples was studied, and the samples were found to undergo a decrease in thermal stability during the low-temperature range (up to 350°C). The thermal stability of the samples

5. Conclusion

Polymer nanocomposite samples composed of distilled water-treated ZnO nanoparticles and PVC polymer were
increased at temperatures higher than 350°C. The results of thermal stability interpreted taking into account the role of adsorbed water on the ZnO surface. The adsorbed water accelerates HCl formation, thus decreasing the thermal stability. At the high-temperature range, the effective role of ZnO in inhibiting HCl formation leads to increased thermal stability. The nonisothermal kinetic analysis of PVC/ZnO nanocomposite samples was investigated by the Kissinger, Flynn-Wall-Ozawa, and Kissinger-Akahira-Sunose models. Although the conditions of derivative for each model are different, the variation between the results was at the acceptable level. The deviation between the Akahira-Sunose and FWO models was less than 9%, which is close to the difference between the Kissinger model and the FWO model (11%). All results are also consistent with lower activation energy of polymer after adding the zinc oxide nanoparticles. The AC conductivity as function of frequency and temperature was also investigated. The addition of ZnO nanoparticle increased the AC conductivity, and the temperature-independent region decreased by increasing temperature. Both S and A coefficients were predicted using the Jonscher power law and OriginLab software. The trends of S and A coefficients were discussed based on the glass transition of the host polymer.

Figure 15: Temperature dependence of S and A coefficients for PVC pure and PVC/ZnO nanocomposite.
The data used to support the findings of this study are available from the corresponding author upon request.

The authors declare that they have no conflicts of interest.

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