# Thermogravimetry technical to study the stability of membrane

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Abstract - This work admits two essential objectives: preparation of three types of polymer-based membrane either PP, HDPE, LDPE with the addition of a suitable solvent non-toxic on the environment or Betyl Acetate (AB) with addition alumina (AL) as a pyrogen. These results were followed analytically by themogravimetry (TG, DTG, DTA) to know the stability of the membrane as revealed by nonlinear Arrhenius plots and / or the in the second step used to calcul activation energy  $E_a$ , entropy  $\Delta S$  and enthalpy  $\Delta H$ . this results gives a satisfactory idea on the choice of suitable membranes. While the polymer solution volume fraction decreased due to solvent and non-solvent removal from polymer solution and blend membrane formation. The predicted results from model of heat treatment process on blend membrane were indicated that increasing in membrane thickness and formation of dense layer in blend membrane. Kinetics the parameters obtained were found to be very close to the values reported in the literature. It makes it possible to use single DTG curve to determine the kinetic parameters

Key words - Thermogravimetry (TG, DTG, DTA), Stability, Activited energy, Enthalpy, Entropy

## I. Introduction

A membrane is a permselective material that allows the transfer of objects from one phase to another action of a driving force. The difference between pressures, concentrations, and electric potentials or temperatures actives transport membranes. Membrane filtration for potabilization is a method of purifying water by applying the pressure difference between the feed and the permeate. Membranes made from synthetic or biomass-based polymers account for more than 80% (Wei Shang et al 2019) of the membrane filtration market. They have a production cost approximately 10 times lower than that of an inorganic membrane (Haiqing Chang et al 2019) and their implementation is easier than mineral membrane. Many polymers are used to make membranes, among which cellulose acetate (CA), poly (sulfone) (PSu), poly (ether sulfone) (PES), poly (acrylonitrile) (PAN), poly (ethylene) (PE), poly (propylene) (PP), poly (tetrafluoroethylene) (PTFE), polyvinylidene fluoride (PvDF) and polyvinyl chloride (PVC) (Chang, H et al 2019). This wide variety of polymers, which define the chemical nature of the membrane, combined with multiple membrane geometries, makes it possible to manufacture membranes with different properties and able to cover varied needs in many areas of use. The membranes are thus classified by filtration domains according to their average pore size. Microfiltration membranes (MF) filter objects of size between about 0.05 µm and 2 µm (Munirasu, S et al 2016). Ultrafiltration membranes (UF), used in potabilization of water because they retain viruses and bacteria, filter objects with a size between 0.005 microns and 0.1 microns. Finally, nanofiltration (NF) membranes filter nanometric objects. The conducted research demonstrated that different membrane manufacturers using the TIPS method could produce the PP membranes with a similar morphology and properties. All the tested commercial capillary membranes, with inner and outer diameters equal to 1.8 and 2.6 mm, respectively, exhibited a good resistance to wetting during 1000 h of MD process operation (El-Bourawi, M et al 2006). The long-term studies of water desalination confirmed that a low surface porosity and smaller size of pores on the capillary surfaces enhances the membrane resistance for wetting. However, the wall of capillary membranes should have a sponge-like structure, with the nominal diameter of pore cells in the range of 1 to 3mm, and the dimensions of "chambers" connecting these cells should not exceed. The first aim of this mini review was (Shaffer, D. L. et al 2013) PET and modified PET membrane fabrication with different methods for water treatment application. The second intention was probable application of VFD as a new device for synthesis of PET membrane as a first idea. The new VFD (Mahamed M.A et al 2017) application idea can optimize the production of a commercial membrane with more probable homogenous and higher quality nanofibers. Further, we can also apply VFD for recycled PET

(rPET) (Song YK et al 2015) solution production to fabricate low cost high quality membrane .Lower energy consumption and faster reaction with smaller effective volume of reactants during membrane fabrication are other positive results of VFD usage too. At the end the final purpose of recycled bottle grade (Schultz, Cantow 1986, Bonnet, M. et al 1998). To analyze the stability of organic-based compounds (polymer), thermogravimetric it one of the most suitable methods which has been used in several works. The term thermal stability is commonly used for endothermic reactions and essentially belongs to thermodynamics (Scott C et al 1994, Seadan M et al 1993). The term energy activation belongs to chemical kinetics. If the activation energy for the exothermic process is high, the initial compounds are kinetically stable. Thermogravimetric (DTG) analysis under non-isothermal conditions in a nitrogen atmosphere at multiple heating rates. The TG - DTA study made it possible to deduce the presence of network water in the external sphere of all polymers. The decomposition was carried out in three to four well separated steps where involved the loss of water molecules in the first step followed by an organic ligand, therefore, it was concluded that these compounds can be called as thermally stable materials. The thermodynamic-kinetic triplet obtained for each step of the decomposition reaction reflects the mechanism linked to a defined characteristic of the system under study. Activation energies were obtained assuming the order of reaction under Coats - Redfern Method using TG / DTG and DTA data, where Cd (II) shows the highest values of activation energy per compared to others. Derivation of a detailed theoretical proof of kinetic compensation relations between enthalpy and entropy (Alok dhauundiyal et al 2018, Ratiram Gomaji Chaudhary et al 2019) (or pre-exponential factor and activation energy) should include consideration of influence of vibrational energy (Zwbvbpcrbq BR et al 1976) and the effects of distribution of media molecules around diffusing, subliming, and reacting species as well as energy of intermolecular interaction (Ivanov AI et al 1986, Vadim V Krongauz 2019, Sergey Vyazovkin 2020). The Arrhenius treatment it means that one should generally expect the respective Arrhenius plots to be nonlinear and, therefore, the activation energy to vary with temperature. The considered models aord an understanding of the origins, the experimentally observed nonlinear plots and variations in the Arrhenius activation energy. Furthermore, fitting the theoretical temperature dependencies to the experimental ones may permit the evaluation of important intrinsic parameters of the process. J. Yang et al 2001 illustrate this new method, so-called the "DTG curve fitting" method, by determining the kinetic parameters of six important plastics found in the municipal solid waste stream: highdensity polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS), polypropylene (PP), poly (vinyl chloride) (PVC), and polyethylene terephthalate) (PET). This method involves first measuring the weight loss behaviour obtained by using thermogravimetry (TG) and then using the Arrhenius equation to fit the DTG curves obtained from the TG measurement The purpose of this study is to investigate the kinetics of thermal decomposition of memebrane that will used at water distillation. Devolatization was done with the help of TGA/DTG curves obtained at different heating rates implemented to estimate activation energy (Ea) and frequency factor (A). The effect of heating rate on the

II. Methods

# **Preparation method**

The experimental preparation of the membranes was made by mixed polymer. To prepare the membrane, polymers (PE, PP) and by adding alumina powder with different quantities the mixture is dissolved in a solvent (butyl acetate, paraffin oil) at a temperature of 130  $^{\circ}$  C with stirring for 5 hours until complete dissolution of the polymer (Fig. 1). Once the collodion is prepared, we spread it out on a glass plate using a manual spreading knife.



Fig.1. Preparation of memebrane at 130°C for 5 hours

The resulting film is exposed to atmospheric conditions for 5 minutes (Fig.2) then immersed in hexane (fig 3) then ethanol to extract the solvent from the membrane after it has been dried in an oven at 70°C. Finally, the membrane is left 24 hours at ambient temperature (Fig.4)



Fig.2. Membrane exposed to ambient temperature for 5 minutes



Fig.3 . Membrane immersed in hexane



Fig. 4. Real experimental membrane for different percent of Alumina and PP

During our preparation for the membranes we kept quantities AB, LP, HDPE, PHBD the same all we vary the quantities of PP from 0 to 3 g, and a quantity of AL which increases from zero to 1 g. The following table 1 gives the mass of different products used during our work.

The work was carried out under the same conditions to be able to compare the membranes obtained. The real photos of these membranes it given by Fig.4.

## III. Resultat analysis

Thermogravimetric analyzes (TG / DTG / DTA) were carried out under a nitrogen atmosphere at heating rates different from 20°C, 30°C, 50°C / min<sup>-1</sup> in the range of 0°C to 1000 ° C on using an  $AL_2O_3$  crucible (100µL). These results were carried out at the Environment, Catalysis and Process Analysis laboratory at the National School of Gabes Engineering (ENIG). The thermal curves of the samples were recorded on the Perkin Elmer STA 6000 integrated thermal analyzer with a computer. Kinetic parameters were evaluated using thermal data using TG / DTG / DTA curves.

## Effect of heat flow rate

• Mass losses (m/m<sub>0</sub>)

Thermogravimetric graphs for the polymers are obtained at different heating rates, which are illustrated in Fig 5. The thermo-analytical data show that the decomposition process for  $E_1$ , its around 499.28°K at heat flow rates 30°C minu<sup>-1</sup> and 50°C minut<sup>-1</sup> wile for 20°Cminu<sup>-1</sup> it is equal 200°C. The decomposition for  $E_2$  memebrane its equal to 381.61°C for the three hot flow rates stadied, and atteined 389.34°C for  $E_3$  for differents heat flow rates and continued to decrease until the temperature reached 531°C decabonisation step for all memebranes preparation.

# • DTG results

Derived thermogravimetric curves (DTG) for the three membranes at three differents heating rates of  $20^{\circ}$ C.min<sup>-1</sup>,  $30^{\circ}$ C.min<sup>-1</sup> and  $50^{\circ}$ C.min<sup>-1</sup> under inert nitrogen atmosphere are shown in Fig. 6. For E1 membrane we notice that there is only one peak for the three heat flow rates and that the peaks increase and become more and more important as we increase the speeds 20, 30, 50 ° C min<sup>-1</sup>. Regarding the E2 and E3 membranes, we found the appearance of two peaks for differents heat flow rate study with an intense increase in these peaks when the speed increases with a shift of these two peaks regardless of the E2 and E3 membrane towards the right.

The three different stages showed the temperature range at which dehydration, pyrolysis took place. At the initial stage of pyrolysis, is aimed at drying or removing moisture. Primary pyrolysis reactions decrease between the ranges from 100°C to 380°C at low heating rate ; whereas in the event of high heating rates, the same phenomena took place at a slightly elevated temperature ranging from 350°C to 405°C at 20°Cminu<sup>-1</sup>. In addition, the two peaks ( $E_2$  and  $E_3$ ) (Strezov V et al 2003) give information on the degradation of the constituent components of the membranes. The variation in the heating rate dramatically affects the locations of the maximum decomposition rate and the maximum temperature deflection in the derived thermogravimetric plot (DTG). As the heating rate increases, the degradation temperature shifted to the right (Fig. 6)



Fig.5. Effect of differents heat flow rates at  $E_1$ ,  $E_2$  and  $E_3$ 



Fig.6. Variation of DTG for E1 E2 and E3 at different heat flow rates

IV. Experimental study

## • Kinetic theory

The solid-state decomposition process can be expressed by the rate Eq. (1) (Alok dhauundiyal et al 2013)  $\frac{dx}{dt} = k(T)f(X)$ (1)

Where k(T) it's the rate constant, X represents conversion ; it can be derived from mass loss data of decomposed sample. It can be stated as :

$$X = \frac{m_0 - m_t}{m_0 - m_r} \tag{2}$$

Where,  $m_0$  is the initial mass in,  $m_t$  is mass recorded at specific instant of time t, and  $m_r$  is the residual mass at the end of heating process.

Temperature dependence of rate constant k is obtained from Arrhenius Eq. (3)

$$k = Ae^{-\frac{La}{RT}}$$
(3)

The passage to logarithm

$$Ln(k) = Ln(A) - \frac{E_a}{RT}$$
(4)

Where  $E_a$  it's the apparent activation energy, kJmol<sup>-1</sup>is activation energy or minimum energy required to initiate the reaction. The equation was elegantly simple; however, the physicochemical significance of the equation is still debated. T it's the absolute temperature °K. R it's the gas constant, 8.314 JK<sup>-1</sup>mol<sup>-1</sup>. A it's the frequency factor, min<sup>-1</sup>. We obtained the basic expression of analytical method by putting the value of rate constant k in Eq. (3). Piloyan et al. 1966 suggested the kinetic analysis that follows Eq. (4).

$$\frac{\mathrm{dX}}{\mathrm{dt}} = \mathrm{Af}(\mathrm{X})\mathrm{e}^{-\frac{\mathrm{E}_{\mathrm{a}}}{\mathrm{RT}}} \tag{5}$$

Taking the natural logarithm of Eq. (5), we obtained Eq. (6)

$$\operatorname{Ln}\left(\frac{\mathrm{dX}}{\mathrm{dt}}\right) = -\frac{\mathrm{E}_{\mathrm{a}}}{\mathrm{RT}} + \operatorname{LN}(\mathrm{A}) + \operatorname{Ln}(\mathrm{f}(\mathrm{X})) \tag{6}$$

Piloyan et al 1966 suggested that the term  $\ln (f(X))$  could be neglected and thus the value of  $E_a$  and  $\ln (A)$  are estimated by plotting  $\ln \left(\frac{da}{dt}\right)$  versus $\frac{1}{T}$ . It has been reported that the error rate encountered while estimating  $E_a$  values is around 15% to 20%. However, later on, this method has kept with group of methods, which evaluates the kinetic triplet at the single heating rate. Similarly, Criado et al 1994 have also made conclusions on the drawbacks in their study and reported the detail calculation of the error in  $E_a$  occurred due to this assumption. Flynn et al 1966 stated that f(X) follows a reaction model in which it varies according to the power of remaining mass fraction :

$$f(X) = (1 - X)^n \tag{7}$$

Where n it is reaction order.

Temperature increase, dT/dt = b (b its the heating rate in K/min), the integration Eq. (8) leads to various differential or integral methods for n= 1 and n not equal to zero or unity. Out of several methods available to allow kinetic analysis of thermogravimetric data, the integral method developed by Coats–Redfern (CR) 1964 has been widely accepted as a reliable method. By using thermogravimetric data (TG/DTG/DTA) different steps of decomposition curve were subjected to find out kinetic analysis under non-isothermal condition by Coats–Redfern method. According to this method above expression can be expressed in logarithmic form where n= 1 and n #1

$$Ln\left(\frac{-Ln(1-\alpha)}{T^2}\right) = Ln\frac{AR}{\beta E_a}\left(1 - \frac{2RT}{E_a}\right) - \frac{E_a}{RT} \quad n = 1$$
(8)

$$Ln\left(\frac{-Ln(1-(1-\alpha)^{1-n})}{T^2}\right) = Ln\frac{AR}{\beta E_a}\left(1-\frac{2RT}{E_a}\right) - \frac{E_a}{RT} \quad n \neq 1$$
(9)

The E<sub>a</sub> can be estimated from the slope of a line established from fitting the TG data  $Ln\left(\frac{g(\alpha)}{T^2}\right)$  versus  $\frac{1}{T}$  the plot will give a traight line (Rocco AM, 2012). Since the order of reaction is usually not known beforehand, it is first necessary to fit the TG data with an assumed value of n. If the assumed reaction order adequately represents the reaction, the line becomes straight. If not, another reaction rate is assumed and the fitted line is examined for straightness (Tonbul Y et al 2001). By using data obtained from Eq. (9), change in entropy ( $\Delta$ S),

change in enthalpy ( $\Delta$ H), change in free energy ( $\Delta$ G) and frequency factors were calculated by standard thermodynamic equations (Mahfouz RM, et al 2002)

#### V. Discussion

The thermal degradation behavior of polymer-based membranes was strongly interpreted and discussed. The thermal degradation curves (TG / DTG / DTA) of the different sample (E1 E2 E3) were plotted The initial, semi and final decomposition temperatures and total mass losses for each step of the thermal decomposition of the polymer compounds were studied using TG analysis at a heating rate of 50  $^{\circ}$  C min<sup>-1</sup> under a nitrogen atmosphere was chosen to calculate the thermodynamic quantities. TG analyzes of polymeric compounds were performed for milligram weight loss of compounds versus increase in temperature. Peak temperatures, initial and final decomposition temperatures of all polymeric compounds were identified by DTG analysis, while the DTA method was used to assess endothermic or exothermic weight loss. The thermographs of all polymer compounds are shown in Fig7.8.9 The thermal stability properties of the polymer compounds were evaluated using TG / DTG and the DTA data and results revealed good thermal stabilities for all of the polymer compounds



Fig.7 m/m0/DTG TG/DTA of membrane E1





Fig.8. m/m0/DTG TG/DTA of membrane E2



Fig .9 .m/m0/DTG TG/DTA of E3 membrane

Peaks in  $T_{DTG}$  were observed for E1, E2, and E3 at 138.08, 136.68, and 131.71 °C respectively, which may be due to network water loss. Additionally,  $T_{DTG}$  peaks were seen in the second peak at 504.3; 394.78 and 400.08 °C, respectively, which may be associated with the removal of water. The third peak E2 504.81 and 503.36 for E3. The DTG curves of the polymer compounds observed at temperatures below 1000 °C, indicate the decomposition of the fragment (Fig10)



Fig.10 .m/m<sub>0</sub>(TG), DTG for E1 E2 E3 for  $50^{\circ}$ Cmin<sup>-1</sup>

Polymers have a higher heat capacity above of the glass transition temperature. This change in heat capacity taking place at the glass transition, use to measure the glass transition temperature  $T_g$  of a polymer. We notice that the change does not happen instantly, but takes place on a beach temperatures. This makes the exact determination of Tg rather difficult, but we use the well-known tangent method to determine Tg. The temperature at the highest point is called the polymer crystallization temperature  $T_c$  It is also possible to measure the area of the "peak", which is the value of the latent heat crystallization of the polymer. This increase tells us that the polymer can crystallize. Heat can allow crystals to form in a polymer, but too much heat can lead to their dismantling. If we continue to heat our polymer after its crystallization point Tc, we may reach another thermal transition called fusion  $T_f$  (Fig11)

Table 2 gives the value of temperaure of critallisation T<sub>c</sub>, fusionT<sub>f</sub> and transitionT<sub>g</sub>

The following table 3 gives the different temperature results for the different study curves

The thermal stabilities of all samples were measured using thermodynamic-kinetic parameters, as the performance of the kinetic study under non-isothermal conditions supported the current facts. Non-isothermal methods have been widely used for the evaluation of the kinetics and mechanism of condensed phase reactions.

# • Interpretation of stabilities by thermodynamic kinetic studies

The thermal stability of the polymers was measured on the basis of the performance values of the coals. The higher the value of the residue, the more the thermal stability will be. The most interesting and reliable parameters in physical chemistry are the thermodynamic and kinetic parameters. The triplet parameter i.e. activation energy, reaction order and pre-exponential factor with thermodynamic parameters such as entropy, enthalpy and Gibbs free energy were complete and valuable, which help to decide on the stability of the polymer compounds. Here, the kinetics and thermodynamics parameters were calculated for each degradation step by the method at a heating rate equal to 50  $^{\circ}$  C min<sup>-1</sup> under nitrogenous conditions and summarized in Table 1.

The thermal degradation linearization curves of all the chelated polymers were elucidated by plotting  $Ln(g(a)/T^2)$  against 1/T, which gives a line of slope equal to Ea/R and the activation energies were calculated from the slope obtained (Fig12) for each reaction step. Also, correlation obtained coefficients (R<sup>2</sup>) of the linearized curves were found approximately in the range of 0.98 to 0.99 and displayed in Table 4.



Fig.11. Tc, Tf and Tg for three polymer compound



Fig.12. Plot of E<sub>a</sub> for E1, E2, E3 for 50°C minu<sup>-1</sup> heat flow rate



The thermal data and the thermodynamic parameters were significantly inferred by the presence of the thermal stability of the polymer compounds. The order of thermal stability of the polymer compounds on the basis of the degradation of the organic groups, can give an idea on the stability of the compounds (the initial degradation temperature Ti, the decomposition half-temperature (Th), the final decomposition temperature (Tf)) gives the following stability classification for our study membranes, namely:  $E_1 > E_2 > E_3$ .

Based on studies of kinetic and thermodynamic parameters ((Ea,  $\Delta S$ ,  $\Delta H$  and  $\Delta G$ )) we did not obtain the same order of thermal stabilities for us three polymer compounds the order becomes  $E_3 > E_2 > E_1$ (Ea3>Ea2>Ea1) (Eathis result is explained by the fact that the activation energy which is none other than the minimum energy required to break the bond or the molecules obtained, i.e. the highest DTG peaks with a maximum mass loss percentage means that it requires a lower activation energy Ea. A high DTG peak with a lower percentage mass loss means that it takes too much energy to remove the molecules. A double bond / triple bond or a strong functional group requires high energy to remove the bond / groups.

In our experimental study we further explains this results because the addition of PP on the thermogravimetric curves of the first sample shows a remarkable drop in mass at 499.28  $^{\circ}$  C, on the other

hand the third sample shows two levels the first corresponds to  $389.34 \degree C$  and the second peak at  $531.78 \degree C$  which shows that the third sample is more thermally stable due to the addition of the high amount of PP compared to the first sample and the second samples.

In addition, the addition of alumina on the thermogravimetric curves for the first sample E1 shows a remarkable drop in mass to 499.28 ° C for the second sample  $E_2$  shows two stages the first corresponds to 381.61 ° C and the second peak at 490.35 ° C which shows that the second sample more thermally stable thanks to the addition of alumina compared to the first sample, a larger quantity was added at the third  $E_3$  shows an even important stability compared to  $E_1$  and  $E_2$  it can therefore be concluded that alumina increases the thermal resistance of the membrane studied. However, changing negative entropy values indicate that the dehydrated coordination polymers have more ordered structure and that the reactions are slower than normal.

VI. Correlation between apparent emission activation energy and enthalpy of vaporization

# • Effect of Polymer Solution Temperature :

Pour the mixture of material on an analysis over the temperature rang (408 436 445 455 460, and 473 K). In corn to know the appropriate temperature of the PP/ HDPE and PP/LDPE solution mixture and to indicate their effect so many correlation it be used

The solubility of the two polymers in solvent is determined by their chemical structure. Polymers will dissolve in solvent whose solubility parameters ( $\delta$ ) are not too different from their dissolution of an amorphous polymer in a solvent which is governed by the free energy of mixing(Mahfouz RM, et al 2002, Miller-Chou B.A.et al 2000)

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

When the value of Gibbs free energy change of mixing is negative the mixture is stable over a certaine composition range and the mixing process will occur spontaneously. Enthalpy change on mixing and entropy change can affect on the Gibbs free energy change signe (Miller-Chou B.A.et al 2000). The Flory–Huggins solution theory uses solubility parameters ( $\delta$ ) of each component in polymer solution to determine miscibility of polymers by Eq. (11):

$$\chi_{ij} = \frac{V_{m}(\delta i - \delta j)^2}{RT}$$
(11)

The Flory–Huggins interaction parameter *x*ij is a function of temperature; the mole fraction of each polymer, and the degree of polymerization. In this equation,  $V_m$  is an appropriately chosen 'reference volume', often taken to be  $100 \text{ cm}^3/\text{mol}$ . The blend miscibility is assumed to decrease with increasing xij. The heat of mixing for any component can be calculated using equation (12):

$$\Delta H_{\rm m} = RT \chi_{ij} \phi_i (1 - \phi_i) \tag{12}$$

¢i Volume fraction of component i

As previously mentioned, the basic idea in this approachis to split the total cohesion energy density (CED) into different parts (Hansen C.M 2000) that originate from separate molecular interactions. The dispersive energy ( $E_d$ ) stems from atomic non-polar forces i.e. dispersive Van der Waals interactions, whereas forces between molecules of permanent dipoles constitute a polar energy contribution ( $E_p$ ). Due to the specific nature of hydrogen bonding, this energy contribution is considered separately ( $E_h$ ). These partial cohesion energies  $E_d$ ,  $E_p$ , and  $E_h$  are divided by molar volume to result in the corresponding total and partial solubility parameters according to equation 1 :

$$CED = \frac{E}{V} = \frac{(E_d + E_p + E_h)}{V} = \frac{(\Delta H_v - RT)}{V}$$
(13)

The Cohesive Energy Density (CED) was in turn defined as the energy needed to break all attractive interactions  $\delta_t$  in one mole of solvent divided by the molar volume according to Equation 14

$$\delta_{t}^{2} = (CED) = \left(\frac{\Delta E_{v}}{V_{m}}\right) = \left(\frac{\Delta H_{v} - RT}{V_{m}}\right) = \frac{\Delta H_{v} - RT}{\frac{1}{\rho_{sol}}} = \rho_{sol}(\Delta H_{v} - RT)$$
(14)

Where

 $\Delta E_v$  is the latent energy of evaporation and

 $V_m$  is the molar volume of the solvent.

 $\Delta H_v$  latent heat of vaporisation (in case of solvents)

T is the absolute temperatureT.

 $\rho_{sol}$  is the density of solvent in theSI system.

## VII. Estimation of solubility parameters

For low molecular weight substances (solvents),  $\Delta H_v$  can be calculated by a number of methods. Experimental values of  $\Delta H_v$  (Fig13) can be obtained using vapor pressure–temperature data or from heat capacity-temperature measurements. Numerical values for most solvents can be found in the literature. Therefore, estimating values of  $\delta$  for low molecular weight solvents can be made (Yip Y et al 2006). When values of  $\Delta H_v$  are known at one temperature, they can be converted to the appropriate  $\Delta H_v$  values at any other temperature using. Hildebrand developed method to calculate  $\Delta H_v$  based on an empirical relationship which relates  $\Delta H_v$  at 25°C to the normal boiling point, Tb; of non-polar liquids(Lee H et al 2010).

$$\Delta H_{\rm v} = T_{\rm b}^2 + 23.7T_{\rm b} - 2950 \tag{15}$$

Where

$$\frac{T_b}{T_c} = 0.567 + \sum \Delta_T - (\sum \Delta_T)^2$$
(16)

If reliable experimental values cannot be found, techniques are available for estimating the critical constants with sufficient accuracy for most design purposes. For organic compounds Lydersen's method is normally used (Chein-Hsiun Tu 1995)

$$T_c = \frac{T_b}{0.567 + \sum \Delta T - \left(\sum \Delta T\right)^2} \tag{17}$$

$$P_{c} = \frac{M}{(0.34 + \sum \Delta T)^{2}}$$

$$V_{c} = 0.04 + \sum \Delta V$$
(18)

Where Tc = critical temperature, K, Pc = critical pressure, atm (1.0133 bar), Vc = molar volume at the critical conditions, m3/kmol, Tb = normal boiling point, K, M = relative molecular mass,  $\Delta T$  = critical temperature increments,  $\Delta P$  = critical pressure increments,  $\Delta V$  molar volume (Table 5).

This problem can be overcome by an alternate means of estimating the heat of vaporization at room temperature from data at different temperatures. At low pressures below atmospheric pressure the latent heat of vaporization follows the relationship:

$$\log\Delta H_{\rm v} = -(\frac{\rm m}{2.303})t + \log\Delta {\rm H^{\circ}}_{\rm v} \tag{19}$$

Where  $\Delta H^{\circ}_{\nu}$  is the heat of vaporization at some standard temperature and m is a constant. Using this relationship it is possible to estimate  $\Delta H_{\nu}$  vapor at 298°K by calculating the heat of vaporization in the temperature range in which the Antoine constants are valid and fitting these values into Equation 18 to determine the slope m and  $\Delta H^{\circ}_{\nu}$  (Table6)

The investigated vaporization time of the casted membrane was at (0, 10, 20, 30 min) for the finest blend polymer solution. The  $\Delta$ Hv was calculated according to equations (17) and (18), where log  $\Delta$ Hv0 was 5.0061 as shown in Fig 13 Table 7 illustrates calculated heat of vaporization; cohesive energy and cohesive energy density, where the results indicated that increasing in all these parameters were observed with increasing in vaporization time.

# VIII. Conclusions

In this work, thermogravimetric parameters were used to determine the kinetic parameters of three main membranes constructed from polymer base such as HDPE, LDPE, AB and AL The kinetics the parameters obtained were found to be very close to the values reported in the literature. It makes it possible to use single DTG curve to determine the kinetic parameters

Some other correlation be used to evaluted the enthalpy of vaporisation and give good value us compaired with our work

Abbreviations

E<sub>1</sub> membrane 1
E2 membrane 2
E3 membrane 3
Highdensity polyethylene (HDPE)
Low-density polyethylene (LDPE)
Polypropylene (PP)
CED Cohesive energy density [J cm-3]
E Cohesive energy [J]
Tc Critical temperature [K]
Tb Normal boiling temperature[K]
ΣΔT Lyderson constant
ΔG Gibbs free energy change on mixing [J mole-1]
ΔS Entropy change on mixing [J mole-1 K-1]

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