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Characterisation of polyimide membranes using thermochemical data

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It was found that polyimides exhibit excellent thermal and mechanical properties for gas separation applications as they have an overall hydrolytic stability and good resistance to wear, radiation and inertness to solvents [1, 2, 3]. The polyimides membranes are most likely to be used in new installations made to transport gases through dense homogeneous membranes of polyimides as they combine a high permeability with a high selectivity when they are supposed to be at least as good as the competitive techniques. The work described herein aims to relate physicochemical polymer properties to various gases transport across polymeric membrane. Applying Askadskii [3] method to determine the packing density of the polymer used there was obtained a packing coefficient K equal by 0.67. Hence 33% of the polymeric matrix consists of free volume. The distribution of the free volume over smaller and larger holes is also very important in determining the rate of the gas diffusion. As below the glass transition point the structure may contain more free volume than could be expected from the difference in thermal expansion coefficient, we determined the T_g value applying DSC analysis. Also, there were performed thermal analyses of the polyimides studied in order to determine the pre-exponential factor A which is related to the amount of free volume. It could be considered a scaling factor to account for the total unoccupied volume of the system in its ground state.

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1. Introduction

As stated in previous studies, a membrane is an interphase and its special properties derive from the fact that it can communicate simultaneously with its two adjacent phases; this permits the establishment and maintenance of gradients across the membrane and allows exchange occur at both surfaces [5]. Membranes for the separation of gases can be considered as a first approach to act as molecular sieves. The permeability of a gas through a polymer is controlled by the product of two distinctly different parameters, the solubility, S and the diffusivity, D.

This study aims to relate some physicochemical polymer properties to transport gases through dense homogeneous membranes of a particular series of polyimides obtained from pyromellitic dianhydride precursors [2, 3]. Polymers should combine a high permeability with a high selectivity. From literature it is known that polymers are needed with high chain rigidity. This kind of stiff polymers has high mobility - diffusivity – selectivity [6]. The general objective when working on developing new materials to be used for gas separations is to calibrate the packing density to generate a polymer matrix presenting a narrow distribution in the free volume, comparable to molecular sieves. The free volume model proposed to explain the diffusion of small molecules in polymers, is relating the fractional free volume present in the polymer matrix, and the size and the shape of the small molecules are the rate-determining parameters [7]. The study performed herein used polyimides because it is known that these polymers exhibit excellent thermal, chemical and mechanical properties, combined with good gas separation abilities and good processability [8]. An amorphous polymer matrix is built up by a random organization of the chains. One of the major causes for the anomalous behavior of glassy polymers, as polyimides, is the free volume's excess, the result of the inability of the matrix to pack most efficiently, hence the existence of voids. A chemical species can move more or less freely within a domain given by some free volume element, if this is large enough to accommodate the respective molecule. The movement if the molecules in the holes took place very fast, therefore this movement will certainly not be the rate-limiting step [9]. The molecule moves from hole to hole through tunnels that open up in a glassy polymer in the direct neighborhood of it. The opening of the tunnel is accomplished by thermal motion of some polymer segments. In glassy polymers the translational motion of polymer segments is restricted. The chain rigidity is one of the most important properties of a polymer which is responsible for many of its bulk properties. The overall effect of stiffer polymer chains will often be an enhanced diffusivity due to a greater free volume and thus the permeability will be higher. The glass transition temperature is an indication for a presence of a highly rigid polymer chain.

The packing density of the polymeric matrix is currently a very important parameter determining the permeability of a gas: lower the packing density more easily gases will diffuse [3]. The packing density of a polymer could be accurately determined following the procedure presented by Askadskii [4]. This method is applying in fact a refined group contribution method. By adding the volume increments of each atom, which depends on its direct surroundings, the total volume of a polymeric repeat unit could be calculated. The total amount of empty space in the polymer can thus be taken up largely by small holes, or can be spread over a wider range of holes sizes. The consequences for the movement of a molecule are considerable: a wider distribution in hole sizes will allow a molecule of a certain size to use a larger part of a free volume for the diffusion process.

2. Experimental

The polyimide used to obtain the membranes was synthesized as described in our previous works [2, 3] starting from polyamic acid (pre-imidized polyimide) from Aldrich. The actual imidization was a cyclo-dehydration reaction. The typical procedure supposed to cast on a glass slide a 25% solution of polyamic acid in dimethyl formamide (DMF) prepared under nitrogen stream, and then to heat up the homogeneous film obtained. All chemicals used were analytical grade (Aldrich). In the imidization reaction the water has to be removed, therefore the thermal procedure was applied. The FT-IR data recorded for cured polymer showed that the imidization was complete: the absorption of amide bonds (2865 – 3100, approx. 1655 and approx. 1540 cm^{-1}) were below detection limit, while the imide absorptions (approx. 1785 and 1720 cm^{-1}) are strongly present.

The density was measured in a calibrated gradient column, ranging from $\rho = 1.2$ to 1.6 (a mixture of hexanol and tetra chloromethane). The used solvents prevent the swelling of the polymer samples.

It is important to know the crystallinity degree of the polymers. Therefore, X – ray diffraction analysis (WAXD) was performed on a Philips PW 1710, using Cu Kα radiation. The inter-chain distances from the reflection angles were calculated applying the Bragg’s law:

$$n\lambda = 2\, d \sin\theta \qquad (1)$$

where: n is the order of the reflection, λ is the wavelength X-rays, d stands for the distance between reflective planes and θ is the reflection angle.

The thermal cyclo dehydration reaction has been studied using non-isothermal thermogravimetry (TG). The TG measurements of the samples are less time-consuming than the conventional isothermal procedures. The kinetic parameters were calculated from thermogravimetric data according to the Coats-Redfern method applying an updated software than the previous presented [10], namely Versatil [11] program. The kinetics of a system undergoing thermochemical change is governed by a general mathematical model as:

$$d\alpha / dt = f(\alpha) \cdot k(T) \qquad (2)$$

where α is the degree of conversion and t is the time.

It can be noticed that the rate of conversion is both a function of the degree of conversion, given by f(α), and a function of temperature, given by k(T). when a constant heating rate is used, $\beta = dT / dt$, equation (1) becomes:

$$d\alpha / dT = f(\alpha) \cdot k(T) / \beta \qquad (3)$$

The conversion function f(α), generally is complicated for heterogeneous reactions. Like most kinetic studies the Arrhenius equation is used for expressing the temperature dependence of k(T). The previous equation becomes:

$$d\alpha / dT = f(\alpha) . (A / \beta) . \exp(-E / RT) \qquad (4)$$

where A is the pre-exponential factor, E is the energy of activation, R is the gas constant and T is the absolute temperature. Further mathematical works on the above mentioned equation allows to evaluate A, n – the reaction order and the activation energy.

For TG experiments was used a Perkin Elmer 7 Series Thermal Analyzer, applying heating rates of: 2.5 K/min, 5 K/min and 10 K/min, in the temperature range 25^0C - 1000^0C. During the experiments N_2 was purged – a continuous gas flow of 50 cm^3/min.

The differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer DSC 4 calorimeter at a heating rate of 10^0 C / minute. Samples were heated initially 30-40^0 C above T_g in order to eliminate sample history, quenched and re-run.

3. Results and discussion

The thermogravimetric curve (TG) of the synthesized polyimide obtained in the above mentioned conditions, at a heating rate of 10^0 C / min. This curve is presented in Fig. 1. A small increase in weight, of approximately 0.35%, due to water adsorption, can be observed, up to 98^0C. Three distinct stages of weight loss are observed. These phases could be assigned to the loss of the absorbed water, the second one represents the loss of water caused by the cyclodehydration reaction of polyamic acid and then the third stage of weight loss represents the loss of volatiles occurring as the degradation of the in situ formed polyimide takes place.

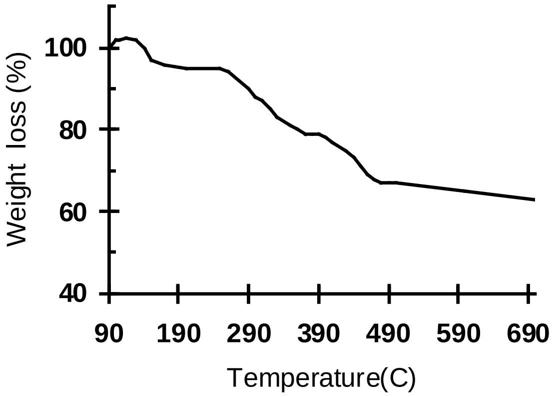

Fig. 1. Thermogravimetric curve for polyamic acid recorded at a heating rate of 10^0 C/min in nitrogen atmosphere.

The sample shows a slight decrease in weight after the cycling weight loss. This makes difficult to distinguish between the end of the cycling reaction and the beginning of the degradation process. Over 498^{0}C the residual sample was black in color and kept its weight. The third stage visible in the TG curve recorded at 10^{0}C, was possible to be detailed (split) in two other decomposition processes by running the sample at a lower heating rate, 5^0 C/min. The weight losses at various temperatures are listed in Table I.

Taking into account the weight loss – due to the absorbed water, as previously shown [2], for each monomer unit there were lost 1.6 water molecules during the second step of adsorbed water release (step II), supporting the assumption that an important amount of adsorbed water exist within the polymer's structure. In this sense, the density determinations on the polymer by help of a gradient calibrated column using a mixture of hexanol and tetrachlormethane as specified in the Experimental section, allowed to calculate for density a value of 1.41 g/cm^3.

Table I. Weight loss (20^{0}C - 1000^{0}C); sample weight 2.741 mg, heating rate 10 K/min.

Temperature range (^{0}C)	Weight loss (mg)	Assigned process
20 - 98	+ 0.009	adsorption H_2O
98 - 130	- 0.017	loss of: adsorbed H_2O (step I)
130 -270	- 0.029	Loss of: H_2O; dehydrocyclisation (step II)
270 - 365	- 0.031	loss of: CO; CO_2 (step III)
365 - 498	- 1.015	loss of: CO; CO_2; H_2 (step IV)

Considering a molecular mass of the polymer repeat unit of 394 g and the Van der Waals volume of the polymer molecules [4] the packing coefficient K (the part of the volume which is occupied) was determined, being equal to 0.67. As consequence, a large quantity of water could be accommodated within the 33 % of polyimide matrix free volume. The result in sustained by the thermogravimetric data obtained which put in evidence an important amount of water absorbed.

In Table II the calculated values of the activation energy as well as of the preexponential factor for the thermal decomposition of the polyimide film are presented.

The values obtained are in accordance with those reported in literature, although for the third step the preexponential factor value in the order of 10^{16}s^{-1} is considerably higher than our value. This value was determined using the same model function f(α), but for a reaction order equal to unity.

Table II. Kinetic parameters for the kinetically workable steps of the thermal decomposition of polyimide membrane at a heating rate of 5 K/min.

	Kinetic parameters			
Step	Reaction order	Activation energy (kj/mol)	Pre exponential factor (s^{-1})	Correlation coefficient (r)
I	1.0	134.5	7.2×10^8	0.9995
II	1.4	181.1	6.0×10^{14}	0.9997
III	0.66	300.3	5.3×10^{12}	0.9989
IV	0.8	142.0	6.9×10^6	0.9977

Our reaction order of 2/3 could be assigned to contracting sphere kinetics. Also, it has to be underlined that our values were calculated applying an integral method, while the literature data are reported on the differential form of the rate equation [12].

It was difficult to distinguish between different reaction orders mainly in the first part of the curves. The best fit using the theoretical master curve seems to be at a first order reaction for the first decomposition step. For the following stages of the thermolysis there is a significant deviation from a first order reaction curve. The determination of the order of the process applies to all methods where a model relationship is tested for linearity, because of the small differences between the values of individual model functions [13]. Furthermore it has to be taken into consideration that the function f (α) is a very simple and limited function because it cannot describe in general the kinetics of diffusion or nucleation and nuclei growth. Especially for heterogeneous reactions, as these reactions we are studying here, several processes can occur at same time, therefore the factor n has only an empirical meaning.

The glass transition temperature is high, 376^{0}C. This indicates the presence of highly rigid polymer chain. The glass transition temperatures of the plasticized polymers are always significantly lower than the corresponding polymeric matrix [14]. This effect is very important, because higher chain flexibility may result in a more efficient polymer packing of the polymer matrix. As a consequence a narrower free volume distribution may directly affect the permeability of small molecules (as gases) in negative way.

The polyimide matrix studied is completely amorphous. The value of the "d-spacing" (that position of the maximum intensity) was determined as 5.7 Å. This high value could be considered as an indication of the open polymeric matrix. The crystallinity in the polymer is a factor that influences the diffusion coefficient and the heat capacity jump accompanying the glass transition temperature, but the X-ray diffraction did not put in evidence any crystallinity in the polyimides. The jump in heat capacity at T_g is in the order of what is usually found for the amorphous state, so the polymer is still expected to be amorphous after annealing.

4. Conclusions

The evaluation of the kinetic parameters at different conversion degrees allowed the follow up the changes occurring in the decomposition processes. Thus, there parallel processes besides the cyclo dehydration were observed, one at the beginning probably representing simultaneously loss of solvent residues, and one at the end of the conversion process which could represent a decomposition or degradation reaction. Applying an integral method the kinetic parameters were calculated. For the rate determining step in the conversion process, although the reaction order suggest a contracting sphere mechanism, another mechanism could be proposed, namely a rotation of segments in polyimide chain. Further investigations are needed in order to establish the mechanism. The determination of the pre-exponential factor and the order of the reaction could be still improved as it needs a model describing the dependency of the reaction rate upon the composition of the sample. The determined energies of activation for polyimide have a considerable higher pre-exponential factor indicating a dependency of the kinetics on the morphological form or the history of the polymer sample.

The polyimide is an amorphous polymer. The investigated polyimide polymer combines good thermal stability with processability. This polymer seems to be a promising polymer for gas separations, not only at ambient temperatures but also at elevated temperatures. A further study dedicated to the gas permeability at high temperatures has to be performed.

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