Review

Glassy Polymers – Diffusion, Sorption, Aging, and Applications

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Abstract: For the past few decades, researchers have been intrigued with glassy polymers, which have applications ranging from gas separations to corrosion protection to drug delivery systems. The techniques employed to examine the sorption and diffusion of small molecules in glassy polymers are the subject of this review. Diffusion models in glassy polymers are regulated by Fickian and non-Fickian diffusion, with non-Fickian diffusion being more prevalent. The characteristics of glassy polymers are determined by sorption isotherms, and different models have been proposed in the literature to explain sorption in glassy polymers during the last few years. This review also includes the applications of glassy polymer. Despite having so many applications, current researchers still have difficulty in implementing coating challenges due to issues like as physical ageing, which is briefly discussed in the review.

Keywords: Glassy Polymers; Diffusion; Sorption; Physical Aging; Polymer Coatings; Gas Separation Membranes

1. Introduction

Polymers are macromolecules made up of several smaller components called monomers that are joined together. Polymers are categorised as amorphous polymers and crystalline polymers based on their morphology. Amorphous polymers are those that have amorphous areas in which molecules are randomly organised. Crystalline polymers have molecules that are evenly packed. Because all crystalline polymers have amorphous zones, no polymers are 100% crystalline.

Due to their non-uniform packed structure, amorphous polymers do not possess sharp melting point but have broader range of temperature. They are classified as glassy polymer, only when they are in glassy state at room temperature, and have high glass transition temperature (T_g) than room temperature. However, rubbery polymers and semi crystalline polymers have low T_g than room temperature [1]. Glassy polymers have non-crystalline structure and high stiffness that makes them mechanically strong to exist as hollow fibre membranes or porous flat film. The mechanical properties of coatings are important, including adhesive strength, fracture toughness, tensile and compressive strength, and wear resistance.

The atoms or molecules in glassy polymers are not arranged in a regular pattern. Bulky constituents, rigid main chains, and low cohesive energies result in a high free volume. From past a decade the study of the glass transition temperature and viscoelastic prop-

erties of glassy polymers is the subject of the research. Examples of some common amorphous glassy polymers include polystyrene, polyvinyl acetate, polymethyl methacrylate, polysulfone, poly(ether sulfone), polyimide, and polycarbonate. In comparison to rubbery polymers, glassy polymers have greater solubility coefficients and a lower diffusion coefficient. Additionally, almost all glassy polymers have permselectivity values around or at the upper bound. Rubbery polymers have a higher diffusivity selectivity than glassy polymers as a result of this [2]. These polymers can be transformed into rubbery state either raising its temperature above glass transition, addition of solvent(s), or other additives.

Films of glass polymers are prepared by using their rubbery solutions. Glassy films are initially coated from solvent solutions followed by drying in natural convection, forced convection or in industrial dryers. The choice of drying conditions such as air flow rate, air temperature, and solvent humidity control the film formation, quality and drying time. During the course of drying the rubbery solution changes to glassy as soon as the solvent level drops down the critical solvent mass fraction which is required for transition [3]. Since the polymer is dissolved in enough solvent, the coating is initially rubbery. When processing temperatures are low enough, the rubbery state transforms into a glassy transition, and during the early stages of drying, as concentration gradients grow within the film, a rubbery-glassy transition forms at the coating – gas interface, creating a glassy skin. This glassy skin grows with respect to time due more and more solvent removal from the coating. Ultimately, entire film turns into glass state.

Extensive , experimental, modelling and simulation work in the field of glassy polymers has been reported in order to explain the diffusion and drying mechanism in the glassy coating [4]. In this article, a brief overview of glassy polymer modelling as well as theories and factors that influence their properties with their limitations and applications in order to direct the future researcher to find suitable model for prediction of data. The work done over the last decade is highlighted.

2. Diffusion in Glassy Polymer System

Diffusion of small molecules in glassy polymers is essential in practise and has been widely studied. Above the glass transition temperature of the pure polymer, diffusion makes reliable predictions over a wide range of temperatures and concentrations. Free volume in the polymer is described as the volume of the total mass, which is not occupied by polymer chains so that diffusing molecules can fit in it. Solvent increases the free volume in the polymer, and diffused in the free volume polymer chains. The transport phenomenon is controlled by Diffusion. The theories based on diffusion and free volume helps in predicting and correlating the self-diffusion of solvents and polymers in the rubbery polymer-solvent systems [5, 6].

The transport phenomenon of drying is generally governed by the Fick's first law of diffusion. According to this law, the flux of a particular component at a location is equal to the diffusion coefficient times the concentration gradient. The rate of change of concentration with time is given by the Fick's second law of diffusion:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left(D \frac{\partial c}{\partial z} \right)$$

(1)

where c: concentration (g/cm³), D: mutual diffusion coefficient (cm²/s), t: time (s), z: distance (cm).

The self-diffusion coefficients are calculated using free volume theory. This theory is well-applicable for polymer – solvent coatings [7-13], and the extension of this theory to polymer – solvent – solvent systems has also been reported [14, 15]. The self-diffusion coefficient in ternary polymeric system is given by:

$$D_i = D_{0i} \exp\left(-\frac{\left(\sum_{j=1}^{3} \omega_j \hat{V}_j^* \frac{\xi_{i3}}{\xi_{j3}}\right)}{\frac{\hat{V}_{FH}}{\gamma}}\right)$$

(2)

where V^*_j: specific critical hole-free volume of a component of j, ω_j: mass fraction of the component j, D_{0i}: pre-exponential factor, γ: overlap factor, ξ: the ratio of molar volumes of the solvent and the polymer jumping units, $\dfrac{\hat{V}_{FH}}{\gamma}$: free-volume parameter.

Glassy state in the polymer solutions is referred when polymer solutions are cooled over practical time scales and the rate of cooling exceeds the rate of relaxation of the polymer. This phenomenon causes volume to be trapped in the polymer in excess of that expected at equilibrium. Free-volume theory presumes that this extra volume is available to facilitate mass transport in the glassy state.

There are two distinct points of view are given in the literature in relation to the free volume and corresponding mechanisms for diffusion and sorption in the glassy state. Both points are agreed that when a polymer reaches the glassy state, the excess free volume is incorporated, or at least temporarily frozen, into the matrix.

On the other hand, in rubbery coatings, there is no volume change on mixing, and the modelling analysis is greatly simplified by using the volume-average velocity. In glassy polymer solutions, however, addition or removal of solvent leads to structural rearrangements in the polymer matrix as it gradually moves toward a denser equilibrium liquid configuration during sorption or toward an unrelaxed glassy state during desorption/ drying.

If the polymer is a rubber, i.e., the sorption temperature is higher than the glass transition temperature of the polymer, it behaves liquid-like and the penetrant (gas) concentrations in the polymer can be described by Henry's law [16]. Cooling down a polymer from the rubbery state it undergoes a gradual change of its properties at the glass transition temperature. Additionally, to the liquid free volume, there is the unrelaxed free volume -"mimvities frozen into the matrix"- available for sorption.

Different models of diffusion in glassy polymer coatings are developed by a variety of theories. They are classed using the following formula: $M_t = kt^n$, where M_t - absorbed per unit area of polymer after an elapsed time t and k-constant. Fickian diffusion is recognised when the exponent n = 1/2; Case II diffusion is known when n = 1, and anomalous diffusion is recognised when 1/2 < n < 1 [17]. Case II diffusion and anomalous diffusion comes under non-Fickian diffusion.

The kinetics is called Fickian if the solvent transport inside the film is exclusively regulated by diffusion. Fickian diffusion models can reliably predict the drying rate for the initial drying time, while visco-elastic models can predict the solvent concentration profiles. By fitting the initial drying rate to pure Fickian diffusion, one may reliably predict

the polymer-solvent diffusion coefficient. Using systematic experimental methods such as confocal Raman spectroscopy, it has been shown in the literature that there is an increased solvent concentration region well away from the drying surface. Sharma et al. [4], a previous research group, studied the solvent evaporation from the poly(methyl methacrylate)/ethyl benzene method and developed a model for the drying of glassy polymeric coatings based on the Fickian diffusion model. By considering visco-elastic contribution to diffusion at the late stage of drying, the established model follows non-equilibrium thermodynamics principles. To solve the model equations, the author used the Galerkin finite element method [18]. For the estimation of the ethyl benzene mutual diffusion coefficient in the rubbery state (T≥T_{gm}) the author used the Alsoy and Duda model [19]:

$$D = \frac{D_1 u_1}{RT} \frac{\partial \mu_1}{\partial u_1} \; ; \text{T} < \text{T}_{gm} \tag{3}$$

Sharma et al. [20] also developed a detailed model for the drying of glassy polymeric coatings by observing the evaporation of thin films of poly(styrene)/p-xylene solutions in another paper. At high solvent concentrations, the author finds not only Fickian diffusion, but also a visco-elastic contribution to diffusion in the late stages of drying. SEM analysis of the final coating, which reveals a one-phase system with no bulk flows within the film, further validated the assumptions made in this study. A 1-D numerical experiment was used to investigate the drying of poly(styrene)-p-xylene coating.

Vrentas and Vrentas described the free volume fluctuations in glassy polymers produced by the presence of a small molecule [21]. They suggested a model based on the idea that as the penetrant concentration varies with the molecular structure of glassy polymer. The notion that the molecular structure of the glassy polymer differs at each concentration causes $\widehat{V}_{2g}^0$ to be concentration dependent. The equation gives the volume expansion that is pretty consistent with the experimental data:

$$\frac{V_m}{V_0} = \frac{\frac{\omega_1}{1-\omega_1}\widehat{V}_1^0 + \widehat{V}_{2y}^0(\omega_1)}{\widehat{V}_{2y}^0(\omega_1=0)} \tag{4}$$

$$\text{where,} \; \widehat{V}_{2g}^0(\boldsymbol{\omega_1}) = \widehat{V}_2^0(\boldsymbol{T_{gm}})\left[1 + \boldsymbol{\alpha_{2g}}(\boldsymbol{T} - \boldsymbol{T_{gm}})\right] \tag{5}$$

$\widehat{V}_{2g}^0$ is the appropriate specific volume of the glassy polymer at penetrant mass fraction $\boldsymbol{\omega_1}$ temperature T, $\widehat{V}_2^0(\boldsymbol{T_{gm}})$ is the specific volume of the equilibrium liquid polymer at $\boldsymbol{T_{gm}}$, and $\boldsymbol{\alpha_{2g}}$ is the thermal expansion coefficient calculated when pure polymer cooled below $\boldsymbol{T_{g2}}$. This relation is given by Vrentas and Duda [22]. $\boldsymbol{T_{gm}}$ (Glass transition temperature of the polymer-penetrant mixture) such that:

$$\boldsymbol{T_{gm}} = \boldsymbol{T_{g2}} - \boldsymbol{A\omega_1} \tag{6}$$

where, coefficient A is determined by the type of penetrant employed to lower a polymer's glass transition temperature $\boldsymbol{T_{g2}}$:

The authors highlighted that predicting volumetric behaviour for glassy polymer-penetrant systems is more challenging when the penetrant is a gas rather than a liquid at the temperature of interest, because a reasonable estimate for $\widehat{V}_1^0$ is often unavailable for gaseous penetrants.

Laksmana et al. [23] predicted diffusion coefficient of glassy polymer based on the method on the estimation of the polymer fractional free volume at different environmental conditions using the model of Vrentas and Duda [22]. On different hydroxypropyl methylcellulose free films with varying water activities, moisture sorption and T_g values were measured. Moisture content, storage temperature, and the molecular weight of the polymer were found to influence the fractional free volume of the films. The researcher concluded a relationship between diffusion coefficient of moisture via films and fractional free volume, allowing for the computation of diffusion coefficient of moisture via films under various environmental conditions.

The mutual diffusion coefficient for a given solvent-polymer system is frequently the most basic physical property needed to design and optimise polymer processing operations as well as other polymer products. Duda et al. [24] gave the most concise way to describe the effect of anti-plasticization and molecular diffusion on gas permeation by using free volume models. The concept of free volume is used to explain molecular motion in liquids and solids. To test the free-volume hypothesis, the author employed inverse gas chromatography technique using a capillary column coated with a polymer film to present experimental measurements of toluene diffusion in polystyrene above and below the T_g. The effect of temperature on diffusivity for a solvent-polymer system above and below the T_g was demonstrated to be compatible with the free-volume formulation provided in Eq (7). The author modified Vrentas-Duda [25] free-volume model for diffusion above the T_g to describe diffusion of low molecular weight species in glassy polymers. As solvent concentration tends to zero, the solvent self-diffusion coefficient becomes equal to the binary mutual diffusion coefficient and given by–

$$D = D_1 = D_{01} \exp\left[-y\xi \widehat{V}_2^* / \widehat{V}_{FH_2}^*\right]$$

$$\frac{\widehat{V}_{FH_2}^g}{\gamma} = \frac{K_{12}}{\gamma}\left[K_{22} + \lambda[T - T_{g2}]\right],$$

$$\lambda = 1 - \widehat{V}_2^0 (T_{g2})(\alpha_{2-}\alpha_{2g}) / K_{12} \qquad (7)$$

where K_{12} and K_{22} are related to the free-volume characteristics of the polymer; λ is related to the change in the expansion coefficient of the polymer above T_g, α_2 and the expansion coefficient of the glassy polymer, α_{2g}; $\widehat{V}_2^0 (T_{g2})$ is the volume of the polymer at T_{g2}.

Wang et al. [26] also used free volume theory to propose a model for predicting solvent self-diffusion coefficients in amorphous glassy polymers. To correctly estimate the hole-free volume variance above and below the glass-transition temperature, this new model takes into account the plasticization effects caused by small molecular solvents. To express the plasticization effect, only one parameter is added, and it can be easily calculated using thermodynamic theory about the glass-transition temperature depression. For benzene-polystyrene mixtures, the author discovered that the hole-free volume decreases as the temperature drops. The hole-free volume of a mixture with a higher solvent concentration is often greater than that of a mixture with a lower concentration, according to the findings. The estimated hole-free volume is higher than that calculated using the original and updated theories, resulting in a higher diffusion coefficient in this analysis.

Non-Fickian diffusion processes are most commonly found in glassy polymers at temperatures below T_g. The polymer chains are not sufficiently mobile at temperatures below T_g to allow the solvent to penetrate the polymer core immediately [27]. The fundamental distinction between Case II diffusion and anomalous diffusion is the rate of solvent dif-

fusion. The solvent diffusion rate is quicker than the polymer relaxation process in Case II diffusion, whereas the solvent diffusion rate and polymer relaxation rate are comparable in anomalous diffusion. In general, when solvents have high activity, Case II diffusion occurs [28].

Davis et al. [29] measured the diffusion of water in polylactide using three methods: quartz spring microbalance, quartz crystal microbalance, and time-resolved Fourier transform infrared-attenuated total reflectance – FTIR-ATR spectroscopy in polylactide at various external water vapor activities (0–0.85) and temperatures (25, 35, 45 °C). They observed non-Fickian sorption kinetic behaviour in all three which was attributed to the glassy polymer's non-equilibrium state. This non-Fickian behaviour was caused by the glassy polymer's non-equilibrium state, where two-stage sorption kinetics were observed. By regressing the early time data to a Fickian model and the data over the entire observed experimental time scale to a diffusion-relaxation model, they calculated diffusion coefficients and relaxation time constants. The observed diffusion coefficients from all three experimental methods were equivalent at all temperatures and activities studied, while the relaxation time constants vary. The variation in the relaxation time constants may be a product of the different constraints on the polymer film for the different experimental techniques. The high Deborah numbers (relaxation time/diffusion time) determined from the diffusion-relaxation model confirm the observed two-stage non-Fickian behavior.

Using confocal Raman micro-spectroscopy, Tomba et al. [30] investigated diffusion between a sequence of liquid polystyrenes and a glassy poly(phenylene oxide)-matrix. Polystyrene concentration profiles can be calculated as a function of molecular weight, diffusion temperature, and annealing time using this model. When the induced stress effectively overcomes the glassy matrix's deformation resistance, Case II diffusion occurs. The authors, on the other hand, found no indications of the linear regime that characterises Case II. The fact that a model designed for liquid–liquid polymer diffusion thoroughly explains all diffusion experiments, on the other hand, indicates a Fickian diffusion control mechanism. Based on the findings, the liquid molecular weight appears to affect diffusion rates through free volume effects, which are well accounted for by the diffusion model based on liquid dynamics.

To understand the formation of propagating sharp diffusion fronts, Gallyamov et al. [31] proposed a diffusion model by introducing the strong asymmetry of probabilities hypothesis for binding/unbinding processes. Plasticisation, unlike in standard Case II models, was not found to be the driving force for the development of sharp diffusion fronts. The diffusion front, according to the author, is not a conventional border between glassy and plasticized regions, but rather a site of efficient immobilisation of free diffusant molecules. The model appears to be very general, and it appears to apply not only to polymers but also to diffusion in microporous media. The probabilities for macromolecules to be captured by unique sites of a polymer matrix and then released are taken into account in the diffusion with change of state model.

Santos et al. [32] also used in situ pressure-contact FTIR-ATR spectroscopy to measure liquid transport in free-standing polymer films. They investigated liquid water transport in free-standing films of a rubbery polymer-poly(isobutylene), a glassy polymer-poly(methyl methacrylate) and a cross-linked polymer - epoxy/amine resin. The non-Fickian behaviour observed for rubbery polymer was found to be due to clustering behaviour in water caused by self-associating H-bonding. Due to water diffusion and water-induced polymer relaxation occurring on the same time scale, the glassy polymer

also displayed non-Fickian behaviour. The suppression of the polymer strain response was blamed for the Fickian behaviour observed in the cross-linked polymer film.

3. Sorption in Glassy Polymers

Diffusion coefficients are important, but predicting sorption isotherms of glassy polymers is also important for a variety of applications, including membrane separations, solvent extraction, volatile organic compound detection, and thin film coating. Glassy polymers vary from other polymers in that the matrix is not in equilibrium, and the normal thermodynamic effects do not apply. The sorption potential of glassy polymers is higher than that of rubbery polymers [33] . The calculation of solubility in a glassy polymer phase relies on several computational methods namely, the dual-mode sorption model; GuggenheimeAndersonede Boer (GAB) model, nonequilibrium thermodynamics of glassy polymers (NET-GP) approach, molecular dynamic simulations and many more.

Tsujita [34] interpreted gas sorption of several glassy polymers in terms of the dual-mode sorption model. The dual-mode sorption model has been widely used to describe and study the sorption of gas molecules in glassy polymers [35]. The authors' model is based on sorption sites that obey Henry's law dissolution and Langmuir-type sorption. Henry's law dissolution site is associated with dissolution of gases into rubbery polymers and low molecular weight liquids whereas the Langmuir sorption site in a glassy polymer associated with the holes which occurs due to the non-equilibrium nature of glassy polymers. The model is formulated as [36]-

$$C = C_D + C_H = k_D p + \frac{C'_H b p}{1+bp} \tag{8}$$

The author found that holes and gas sorption in glassy polymers are function of sub-T_g annealing, thermal quenching, and CO_2 pressure conditioning. The author also found that the as sub-T_g annealing period for the copolymer - vinylidene cyanide-alt-vinyl acetate decreases; C'_H also decreases. Even, with sub-T_g annealing, k_D and constant b did not improve significantly. It was also found that thermal quenching raised C'_H of polyamic acid, polyimide, poly(2,6-dimethyl-1,4-phenylene oxide), and polycarbonate significantly.

Ricci et al. [37] assessed extension dual-mode sorption model to predict the mixed-gas solubility and selectivity of glassy polymers. The authors evaluated the sorption of the mixture of CO_2/CH_4 in three glassy polymers, poly(trimethylsilyl propyne):- PTMSP, the first reported polymer of intrinsic microporosity:- PIM-1 and tetrazole-modified PIM-1:- TZ-PIM. The calculations revealed a qualitative picture of sorption under mixed-gas conditions, but with lower solubility due to competition with the second gas present in the mix, according to the researchers. The investigation also found that pure-gas data can be depicted with the least amount of uncertainty by a variety of parameter combinations, each of which yields significantly different mixed-gas predictions that, in some circumstances, only qualitatively correspond with the experimental data. Based on their findings, the authors came to the conclusion that multicomponent calculations using the dual mode sorption model produce more trustworthy results than using pure-gas data to estimate the material's solubility-selectivity.

The dual mode sorption model parameters of CO_2 in glassy polymers were predicted by Saberi et al. [38] using a group contribution technique. The group contribution approach is a method for determining the principles that regulate the link between polymer transport and thermophysical properties based on the structure of the polymer [39]. 37 structural units were examined using 82 different polymers, and dual mode sorption values for CO_2 sorption were calculated for each group by the authors. In addition, the

experimental results for CO_2 sorption in six distinct glassy polymers, which were not included in the group contribution calculation, were taken into account. The dual-mode sorption parameters were assumed as follows:

$$k_D = \sum_{i=1}^{C} \varphi_i k_{Di} \tag{9}$$

$$C'_H = \sum_{i=1}^{C} \varphi_i C'_{Hi} \tag{10}$$

$$b = \sum_{i=1}^{C} \varphi_i b_i \tag{11}$$

where $\varphi_i = \dfrac{Van\ der\ Waals\ volume\ of\ group\ i}{van\ der\ waals\ volume\ of\ polymer}$ $\qquad$ (12)

The optimization toolbox in the MATLAB software was used to solve the set of these equations. The reliability of the model was checked using two statistical indicators: root mean square error and the correlation coefficient: - R-squared. The authors concluded through this process that group contribution approach is a valuable tool to anticipate CO_2 dual mode sorption parameters in various glassy polymers.

 To explain sigmoidal isotherms, primarily water vapour sorption data, Feng [40] employed the GAB model. Based on multilayer sorption theory of GAB model, the author developed a new dual-mode sorption model for vapour sorption in glassy polymers. The famous GAB equation stated as follows: -

$$c = \frac{C_p A k a}{(1-ka)[1-ka+Aka]} \tag{13}$$

In this, k and A can be calculated as follows: -

$$k = k_0 \exp\left(\frac{H_L - H_n}{RT}\right) \tag{14}$$

$$A = A_0 \exp\left(\frac{H_m - H_n}{RT}\right) \tag{15}$$

The proposed dual-mode sorption model is based on four assumptions: (1) In a glassy polymer material, there are two types of sorption sites: one is in the matrix region of the polymer, and the other is in the micro-voids. (2) The partition functions of all the molecules in the polymer matrix region are the same. (3) It's GAB sorption in the polymer micro-void site. (4) In the micro-void region, the molecules in the layers other than the first have the same partition function as those in the matrix region. The new dual-mode sorption equation was created based on these assumptions: -

$$c = c_1 + c_2 \tag{16}$$

$$c = \overline{C_p} \frac{k'a}{1-k'_a} + \overline{C_p} \frac{(A'-1)k'a}{1+(A'-1)k'a} \tag{17}$$

The new dual-mode sorption model for vapor sorption in glassy polymers assumes that two species of the sorbed molecules contribute to the penetrant concentration in glassy polymers, one of which occurs in the matrix region of the glassy polymers and follows c_1

is a downward curve similar to that in rubbery polymers; the other happens in the micro-voids and follows c_2 which is an upward curve.

Vopicka et al. [41] also studied at the GAB model feasibility for modelling gas sorption isotherms and their temperature dependences. In contrast to the assumptions of the standard dual-mode sorption model, the GAB model assumes that molecules adsorb in multilayers on the inner surfaces of the polymer. For CO_2 sorption in cellulose acetate, polyethylene terephthalate, and PIM-1, the authors discovered that the isosteric heat of adsorption is completely reliant on relative surface coverage and showed maxima at the values around 0.8–1.2. Instead of a combination of single-layer adsorption and equilibrium dissolution, this leads in the development of adsorption multilayers. The GAB approach incorporates both pressure and temperature dependences and fits the literature data efficiently.

Carla et al. [42] used the NET-GP method to create a 1-D transport model to explain the sorption and dilation kinetics of polymeric films in supercritical CO_2. The model calculations were compared with data on mass sorption kinetics for $CO2$ in supported glassy poly(methyl methacrylate) (PMMA) films, measured in a high-pressure quartz crystal microbalance (QCM). Doghieri and Sarti [43] introduced the NET-GP approach, which is a semi-empirical approach to extending any arbitrary equation of state model for the equilibrium properties of glassy polymers to nonequilibrium states below T_g. The model is based on the assumption that an isotropic glassy mixture can be interpreted by using the partial polymer density as the order parameter to classify the nonequilibrium structure caused by the matrix prehistory. The order parameter has been treated as an internal state variable, and the associated thermodynamic relationships have been used in a systematic way.

The authors developed a sorption-diffusion-relaxation model to evaluate the solvent chemical potential under nonequilibrium conditions by combining the NET-GP model with a rheological constitutive equation.

$$\mu_s^{NE} = \mu_s^{NE}(T\omega_s\rho_p) \qquad (18)$$

Through the application of Fick's law for the diffusive flux of the penetrant species in the model, the authors represented the two-stage sorption behaviour in thin glassy polymer films.

$$j_s = -\rho_s\,D_s\,\nabla(\mu_s\,/\,RT) \qquad (19)$$

To analyse water sorption thermodynamics in polyimides, Scherillo et al. [44] employed the NETGP-NRHB model. Panayiotou et al. [45] presented the NRHB theory, which comprises of a compressible lattice model accounting for cross- and self-hydrogen bonding interactions between polymer and water molecules, based on an equation of state. The results of the analyses performed by in situ infrared spectroscopy. In the case of the NETGP−NRHB model in addition to polymer density ρ_2, two new sets of order parameters $\underline{N_{ij}}$ and $\underline{N_{rs}^{NR}}$ are incorporated as internal state variables. The generic component of the set $\underline{N_{ij}}$ represents hydrogen bonding between H^+ donor groups of type i and H^+ acceptor groups of type j, whereas the generic component of the set $\underline{N_{rs}^{NR}}$ represents the effective number of non-random contacts in the compressible lattice between kind r and kind s mers. The authors indicates that the data gives acceptable accuracy with values derived using FTIR spectroscopy analysis for self-hydrogen bonding and with values derived using a 1:2 stoichiometry in the case of cross-hydrogen bonding.

Minelli et al. [46] examined three gas-gas-polymer systems, CH_4/CO_2 in poly(2,6-dimethyl-1,4-phenylene oxide), C_2H_4/CO_2, and N_2O/CO_2 in poly(methyl methacrylate) which demonstrated considerable deviations from the ideal behaviour. The author employed the Non-Equilibrium Lattice Fluid-NELF model, which was based on the NET-GP methodology and uses the Lattice Fluid characterization of pure chemicals and mixtures[47].

The parameters of the gas-gas interaction were set to zero. Based on the partial pressure of each component in the gaseous mixture and the pure gas swelling coefficient in the polymer, the swelling induced by the gas mixture in the glassy polymer was presumed to follow an additive rule. The mixed gas solubility differed greatly from the pure gas value; in particular, the addition of a second gas lowered the equilibrium content of a gas sorbed in a polymer in all of the scenarios studied. The authors calculated pure component and binary parameters using pure gas sorption data to determine the highest discrepancy between experimental data and model predictions, which was 10%. As a result, the model appeared to be a credible method for estimating mixed gas solubility in glassy polymers.

Galizia et al. [48] compared alkane and alcohol vapour sorption and swelling in poly(trimethyl silyl norbornene) to the NELF model predictions. The following equation was used to calculate NELF parameters from infinite dilution solubility coefficients, S_0, of a wide range of n-alkane penetrants:

$$\ln(s_0) = \ln\left(\frac{T_{STP}}{p_{STP}T}\right) + r_1^0\left[\left[1 + \left(\frac{v_1^*}{v_2^*} - 1\right)\frac{\rho_2^*}{\rho_2^0}\right]\ln\left(1 - \frac{\rho_2^0}{\rho_2^*}\right) + \left(\frac{v_1^*}{v_2^*} - 1\right) + \frac{\rho_2^0}{\rho_2^*}\frac{T_1^*}{T}\frac{2}{p_1^*}(1 - k_{12})\sqrt{p_1^* p_2^*}\right]$$
(20)

The solubility isotherms of alcohols with a distinctive sigmoidal behaviour were observed to be in accordance with the NELF model prediction, as per the research. In different polymer system, the model was also successfully employed to characterize the relationship of solubility on the size of the alkane. The model appropriately predicted that the activity-based solubility coefficients in poly(trimethyl silyl propyne) increase with critical temperature, drop with critical temperature in Teflon-AF2400, and hold almost constant in poly(trimethyl silyl norbornene), according to the author. The polymers fractional free volume, cohesive energy density and their energetic interaction with the penetrant, were found to be the three key determinants impacting the level of solubility reliance on alkane size.

Vegt et al. [49] employed Iterative Widom Schemes to determine the sorption isotherms of CO_2 in glassy polyethylene while utilising molecular dynamics simulations. The author discovered that the sorption thermodynamics are driven by a hole filling process in the glassy polyethylene. This mechanism, which was predicated on the presence of energetically favourable sorption sites below T_g, manifested itself as a decrease in the number of low-energy sites as concentration increased. The configurational molar entropy of the solutes was observed to decrease as a result of this action. A finite positive CO_2 partial molar volume in the glass, in addition to hole filling, was calculated by the author, showing at least some degree of relaxation when solutes dissolve. The findings were consistent with Kirchheim's model predictions [50] in which the hole filling concept was combined with the assumption that the matrix becomes elastically distorted when a solute is dissolved. The self-intermediate scattering function of the polymer atoms was used to investigate dynamical changes at T_g. This function was also discovered to reveal the difference in dynamics between the glassy and rubbery states. Spyriouni et al. [51]

also applied Iterative Widom Schemes to determine CO2 sorption isotherms and induced polymer swelling in atactic polystyrene at temperatures ranging from 308 to 405 K. For the estimation of penetrant fugacity, the authors combined this methodology with the direct particle deletion approach [52]. The results were consistent with available experimental data, however significant variations are shown at low temperatures and high pressures. This was due to the extended relaxation durations of the polymer matrix. The linearity of the sorption curves incremented at elevated temperatures, when the polymer was in the melted state. The free volume of the polymer matrix in the CO_2- polystyrene systems reported elevated free volumes at higher temperatures attributed to polymer swelling.

4. Applications of glassy polymers

Glassy polymers are considered as the most important classes of polymers that include the matrix resin in contact lens, aerospace composites, automotive head/tail lights and many more other products. Thin films formed from glassy polymers are used in various technological applications such as liquid and gas separation, solar cells, optical materials, fuel cells, lithography [53]. Below listed are some important applications of glassy polymers which are explored by the various research groups.

4.1   Applications in Drug Delivery systems

Hydrogels are hydrophilic polymeric networks which have the ability to absorb vast volumes of water and are extremely appealing bio-compatible drug delivery devices. They significantly deliver a better efficiency of drug delivery and have a wide range of clinical applications [54]. Hydrogel polymers are unique as they have a glassy nature in the dry state and capable of immobilization of any non-uniform drug distribution introduced before the dehydration step. In the presence of water, they can absorb a substantial amount of water to turn into an elastic gel and, simultaneously, release the drug dissolved in it by diffusion through swollen region[55]. Lee et al. [56] found out a novel approach to zero-order drug delivery from glassy hydrogel beads through an immobilised sigmoidal drug distribution. The combination of controlled freeze drying and extraction process was paramount in the in-situ immobilisation of such non uniform distribution of concentration. They found out that when the extraction process was carried out on drug loaded beads in fully swollen state instead of dry glassy state, or when the drying of the film was done at a higher temperature instead of freeze-drying state, no constant release region would be observed in the cumulative drug release profiles. Seemingly, a drug concentration distribution of parabolic type was, Fickian diffusion characteristics in the rubbery state, did not lead to a zero-order release.

El-Hag Ali Said et al. [57] synthesized a pH-sensitive interpolymer polyelectrolyte complex to investigate its use as a carrier for colon-specific medication delivery. The complex was synthesized by gamma radiation-induced copolymerization of acrylic acid and dimethyl aminoethyl methacrylate- DMAEMA. At pH values ranging from 3 to 4, the pH-dependent swelling revealed distinct phase transitions depending on the copolymer composition, as well as the creation of interpolymer polyelectrolyte complexes. The Ketoprofen-loaded complex was allowed to swell in pH 1 (similar to stomach medium) and pH 7 buffer solutions (pH is similar to intestine medium). The author discovered that no appreciable drug release happens at pH 1, but that it occurs as soon as the copolymer is moved to a pH 7 buffer solution. The findings revealed that drug release is not only pH dependent, but also that the copolymer composition had an impact on the release rate and total amount of drug released. The release rate and total amount of medication released increased as the acrylic acid level in the copolymer increased.

The gamma radiation-induced copolymerization was also assessed by Taleb et al. [58] and Mazied et al. [59] in their research for the application of controlled release of Chlortetracycline HCl and flutamide respectively. Mazied et al. synthesized hydrogels based on DMAEMA and various ethylene glycol dimethacrylate ratios to demonstrate diffusion-controlled flutamide administration. The pH of the solution and the DMAEMA content of the hydrogel were the primary considerations impacting the drug release behaviour of the hydrogel, according to in vitro drug release studies in various buffer solutions. Based on 2-hydroxyethylmethacrylate and methacrylic, Taleb et al. produced multifunctional polymeric materials hydrogels. The hydrogels loaded with Chlortetracycline HCl were placed in a buffer solution of pH 1 and 7.5 to release Chlortetracycline HCl. The diffusion coefficients rose as the methacrylic content in the hydrogel increases, and the release behaviour is strongly pH dependent (low release at pH 1.0 and peak release at pH 7–8). In both the researches it was found out that the inclusion of amino groups along the macromolecular chains, which ionised at lower pH while imparting hydrophobicity to the gels at higher pH, was completely responsible for the pH-dependent releasing mechanism. It was concluded that the hydrogels developed by the authors can be used as promising carriers for drug delivery systems.

Mullarney et al. [60] studied the release of Pheniramine maleate drug using hydrophobically modified hydrogels prepared by the free-radical polymerization of N,N-dimethylacrylamide and 2-(N-ethylperfluorooctanesulfonamido) ethyl acrylate-FOSA copolymers. The authors discovered that when the amount of FOSA in the hydrogel increased, the equilibrium media content reduced and the drug release rate slowed. It was found that over the pH range of 4–8, drug diffusion was less sensitive to pH, however raising the media pH retarded permeability marginally by reducing the hydrogel's swell potential. This suggested that the mass transport mechanism for drug diffusion was investigated to demonstrate if the diffusion rate was predominantly controlled by Fickian type diffusion rather than polymer swelling.

Rudzinski et al. [61] used a solution and bulk polymerization method to create three acrylic-based methyl methacrylate copolymers with varied methacrylic acid ratios. One of the polymers was created by adding 2-hydroxy ethyl methacrylate in order to boost its hydrophilicity. Because of the presence of carboxylic acid groups, the partly crosslinked hydrogels had varied hydrophilicity, due to which they were pH-dependent. As the number of -COOH groups increased, so did the swelling. To test the controlled release functionalities of these hydrogels, Cypermethrin, a commonly used pesticide, and cupric sulfate, a micronutrient, were loaded into them. In addition to Pesticide or Micronutrient transport, their release was dependent on macromolecular chain relaxation. Farmers producing in dry terrain may benefit from the release of active substances via hydrogels, according to the findings.

Brazel and Peppa [62] studied the effect of various structural parameters of the polymers, swelling rates, water diffusion coefficients and the diffusional Deborah number on the drug release mechanism in glassy polymers. In order to transport water, two crosslinked polymer systems were used: poly(2-hydroxyethyl methacrylate-co-methyl methacrylate) and poly(vinyl alcohol). Eight types of drugs were tested to study the drug-release mechanism. Based on the size of the diffusing drug molecule and the size exclusion properties of the polymer carrier, the drug release mechanism was Fickian, anomalous, or Case II diffusion. The research showed that swelling rates were shown to be closely proportional to the mesh sizes of polymer networks. The authors also found that the in crosslinked poly(vinyl alcohol)samples, initial crosslinking ratios exhibited a significant effect on water uptake. As the molecular weight of the solute increased, the rate of release decreased. It was concluded that for each polymer studied, a molecular weight cut-off

was determined beyond which drug release was severely hampered by the hydrogel mesh size.

4.2   Applications in Coatings

4.1   Corrosion Prevention

For corrosion protection, there is a reliance on properties of glassy polymers such as mechanical, transport, and physical properties when coated on a metal substrate. The properties are affected by the presence of free volume in the polymer which in turn has an effect on coating performance. Free volume permits the diffusion of small molecules such water, oxygen and ions. It also permits local segmental movement which affects mechanical properties such as adhesion, and yield [63].

Vergara et. al. [64] studied that aliphatic amido amine crosslinkers was used in epoxy coatings to augment water barrier properties for prevention from corrosion. They found out that a critical concentration was found out where if more methylene groups were added to the pendant alkyl chain, it did not improve the water barrier properties because the solubility decreased to a lesser range than diffusivity increased beyond for the pendant alkyl chain containing more than four carbon atoms. The thermo-mechanical properties of practiced amido-amines polymers were similar to the commercial amido-amines/epoxy and had reduced T_g and higher modulus than Diglycidyl ether of bisphenol A/ Diethylenetriamine. The above-mentioned properties made the resulting Diglycidyl ether of bisphenol A - amido amine crosslinkers polymers more applicable for corrosion prevention coatings. Also, the water transport was minimised by only short alkyl modifiers containing four carbons.

Merachtsaki et al. [65] evaluated the corrosion behaviour of steel covered with epoxy-(organo) clay nanocomposite films. According to the study, both pure epoxy and epoxy nanocomposite coatings provided significant corrosion protection to steel. The nanocomposite coatings' protective qualities, including mechanical, thermomechanical, and barrier characteristics, were found to be superior to those of the pristine Epoxy Polymer. The weight loss findings as well as the optical and microscope inspection of the specimens following exposure to the corrosive environment indicated this. The electrochemical impedance experiments revealed that the coatings employed enhanced total resistance and that nanocomposites had higher total resistance values than the pure glassy epoxy polymer, implying superior protective characteristics.

Kostina et al. [66] investigated the production of a glassy metaphosphate composition-GMC from simple and easily accessible materials for comprehensive corrosion and salt deposition protection of the elements of water-heating systems. According to the findings, GMC's anticorrosion properties were due to the formation of a thin continuous phosphate film on the surface of the water-heating apparatus' elements; the thickness of the film remained constant during operation because its top layers, which could be removed as new portions of water arrive, were renewed. It was also discovered that if the composition was not fed into the water, the coating stayed protective for at least one month. GMC protected metallic surfaces from corrosion even at low concentrations when added to water. GMC reduced the volume of scale on any surface, even non-metallic surfaces, to 70 times lower levels than untreated water.

4.2   Gas Separation Membranes

Sharma et al. [67] accomplished hydrogen separation using an aligned carbon nanotubes-polymer nanocomposite. By dispersing (0.1 percent) weight fractions of single

walled carbon nanotubes and multi walled carbon nanotubes in polycarbonate matrix independently, carbon nanotubes-polymer nanocomposites were formed. In comparison to random distributed CNT/polymer nanocomposites, gas permeability had been reported in the research to be higher in aligned CNT/polymer nanocomposites because the former provided easy pathways or porosity for hydrogen penetration. It was also shown in the study that aligning carbon nanotubes in polymers can improve mass transport and electrical conduction.

Park et al. [68] evaluated how 3-D disordered mesoporous silica-DMS affected the transport of two different glassy polymer matrices, 6FDA-DAM: DABA (3:2) and polysulfone. The mixed matrix membrane permeabilities for gases like N_2, CO_2, CH_4 and NF_3 were assessed. The investigations showed that both 6FDA-DAM: DABA (3:2) and polysulfone-based membranes with a nominal DMS weight fraction of 0.2 significantly enhanced all single gas permeabilities due to enhanced diffusivity, which seemed to be the outcome of DMS particles' 3-D interconnected pore frameworks. Due to the difference in the structure (degree of rigidification) of polymer chains surrounding DMS particles, the favourable effect of DMS on permeability enhancement at relatively low DMS volume fraction was stronger for 6FDA-DAM: DABA (3:2) compared to polysulfone. Because of its potential to form H-bonding or polar–polar interactions with DMS particles, NF_3 displayed unique transport behaviours that were not observed in any of the other gases studied. According to the findings, DMS-containing mixed matrix membranes, particularly the 6FDA-DAM: DABA (3:2)/DMS (20 wt. percent) sample, had good separation performance for various gases.

Kramer et al. [69] in their invention, enhanced polymeric asymmetric membranes to improve gas separation selectivity. The researchers used ozone to oxidise an asymmetric membrane made of glassy polymer to improve its selectivity for a pair of gases when compared to the glassy polymer's intrinsic selectivity and the chemically modified glassy polymer's selectivity for the same pair of gases. The density, free volume, and close packing of the reacted polymers all had an influence on membrane selectivity, according to the authors. The degree of ordering of the polymer chains initially present in the membrane, the reactivity of the polymer with respect to ozone, and the level of reaction the polymer undergoes all contributed to the selectivity. The membranes could separate a variety of gas combinations, including He/N_2, H_2/N_2, H_2/CH_4, N_2/O_2, H_2/CO_2, He/CO_2, He/O_2, H_2O/Air, H_2O/N_2, H_2O/CH_4, H_2O/CO_2, He/CH_4.

On a porous support membrane constructed from a glassy polymer including polyethersulfone, polysulfone, polyimide, a composite of these polymers, and a blend of cellulose acetate and cellulose triacetate, a novel high flux, cross-linked, fumed silica reinforced polyorganosiloxane thin film composite membrane was designed by Liu et al. [70]. The authors demonstrated that when the operation duration was increased, the permeance and selectivity of the membrane described in this invention improved. This was mostly owing to increased membrane plasticization of condensable olefins or a drop in operating temperature. The membrane also exhibited comparable selectivities but much higher permeances of CH_4 for CH/N separation, considerably higher permeances of olefins and paraffins for olefin and LPG recovery.

Choi et al. [71] developed a gas separation membrane with a porous support layer, an aromatic poly amide layer on the porous support layer, and a coating with a glassy polymer formed on the aromatic polyamide layer for selective separation of hydrogen and helium from gas mixtures containing carbon dioxide. The glass transition temperature of glassy polymer was more than 50°C. Contacting a solution containing the glassy polymer with an aromatic polyamide layer of a composite membrane and drying the solution to create a coating of the glassy polymer on the aromatic polyamide layer could

create the gas separation membrane. Contacting a gas feed stream containing carbon dioxide with the gas separation membrane to produce a permeate stream with a concentration of helium or hydrogen that exceeds the concentration of helium or hydrogen in the gas feed stream was one method of separating hydrogen or helium from a gas stream containing CO_2.

To examine the dehydration of organic vapour mixtures by glassy polymers, Salem and Ghoreyshi [72] developed a model based on the Maxwell–Stefan formulation methodology [73]. The equilibrium and kinetic coupling of fluxes between two permeating components in the model were taken into account in the theoretical investigation of the probable transport mechanism. The dehydration of an ethanol–water vapour mixture was chosen as the system to evaluate the model. The model's results revealed that the presence of the other component has no kinetic effect on either component's mobility, but the thermodynamic interaction had a considerable impact to both components movement. The model predicted a separation factor that was quite close to the experimental value. The results further showed that the glassy PVC membrane is selective for water vapour and may be utilised to dehydrate a water–organic mixture acceptably.

Gomes at al. [74] synthesized nanocomposite membranes based on poly(1-trimethylsilyl-1-propyne)-PTMSP and silica. The membrane was prepared by sol–gel copolymerizing tetraethoxysilane with various organo-alkoxysilanes in PTMSP-tetrahydrofuran solutions. They discovered that the gas permeability characteristics of these membranes are influenced by the degree of silica conversion, the kind and concentration of organo-alkoxysilane used, and the size of the silica particle produced. When contrasted to PTMSP nanocomposite membranes produced with dispersed fillers, the marginal increase in butane permeability and butane/methane selectivity may be due to the relatively low content of silica embedded into the PTMSP membrane by sol-gel method and the role of residual silane left in the membrane.

4.3   Miscellaneous Applications of Glassy Polymer Coatings

Asai et al. [75] created a pressure-sensitive paint formulation using glassy poly [1–(trimethylsilyl)–1–propyne] as a binder for cryogenic and unstable wind-tunnel testing. The polymer has exceptionally high gas permeability. The authors showed that even at cryogenic temperatures, the created formulation-maintained oxygen sensitivity, had a quick response time, and may be sprayed on any model surface, notably stainless steel and ceramics. According to the studies, the developed coating was best suited to low-pressure applications due to its high quenching constant. A few milliseconds were the response time for a step change in pressure from vacuum to atmosphere. This coating can also be used in short-duration stress tunnel testing, according to the researchers.

Loui et al. [76] designed a microcantilever-based sensor array that can detect a variety of chemical vapour analytes while being compact and low-power. The device worked by using the static deflection of piezoresistive cantilevers caused by the expansion of glassy polyolefin coatings during chemical vapour sorption. The polymers were chosen based on their Hildebrand solubility parameters to cover a wide range of chemical characteristics in order to maximise sensor sensity to various chemical analytes. Comparison of the polymer/vapor partition coefficient to the cantilever deflection responses revealed that, while general trends may be expected, a simple linear connection did not exist, highlighting the necessity for a functional model to characterise the chemical-to-mechanical transduction. It was also found that covalent bonding of the polymer coatings to the cantilever substrate may assist avoid creep and delamination in long-term deployment applications in humid or severe environments.

Hubmann et al. [77] used cellulose nanocrystals based on glassy polymers as an adhesive to produce UV-curable coatings. The authors grafted 3-isopropenyl-α,α-dimethylbenzyl isocyanate onto polyether polyol containing Cellulose nanocrystals at loading levels of up to 1.8 wt percent. The authors discovered a 154 percent increase in adhesive strength and a 16 percent increase in tensile strength on average. The rapid transformation of a cellulose nanocrystals polyol solution into a high viscosity photocurable prepolymer suspension, followed by the creation of a hydrogen-bonded network between the nano-particles and the developing polymer matrix, was thought to be responsible for the results. They concluded that the modest filler quantity employed is promising for applications where the presence of the filler should not significantly change optical or other thermo-mechanical characteristics. The decrease of internal tensions during UV-curing is most likely to be blamed for the improved adhesive characteristics.

5. Physical Aging in Glassy polymers Coatings

For gas separations, several polymers have been investigated, but only a few membrane materials have made it to commercial usage, and this hasn't changed in decades primarily due to physical ageing. Physical ageing is prevalent in glassy materials, in which a change in a property is seen as a function of storage time with no other external influences [78]. The phenomena is caused by the fact that they are typically out of equilibrium, and it includes a wide variety of characteristics, including bulk properties like specific volume, enthalpy, mechanical, and dielectric response, as well as molecular properties like the free volume distribution [79]. According to latest research, super-glassy polymer materials age in two stages: a fast densification happens within the first few days, followed by a progressive rearranging of packed chains over longer time periods toward a theoretical equilibrium state. It is crucial to keep in mind that physical ageing only comprises reversible changes in characteristics, not structural alterations. Physical ageing distinguishes itself from other variables that can affect characteristics over time, such as chemical ageing, degradation, absorption, or contamination.

Pfromm and Koros highlighted the fact that membrane thickness affects ageing; thin films made of a fluorinated polyimide and bisphenol A Physical ageing of a polysulfone was accelerated, which was ascribed to free volume diffusion [80]. This process appeared to be more rapid as the film thickness lowers, driven by the rising segment mobility in the vicinity of a free surface [81]. Chung et al. investigated the ageing of different asymmetric and composite membranes, found that the rate of ageing was affected by spinning circumstances, such as shear rates [82].

Huang and Paul [83] examined the influence of physical ageing on gas permeability in free-standing thin polymer sheets. Thin polysulfone films with thicknesses of 400–1000 nm was obtained using both solution casting and spin coating techniques. When thin films were heated above T_g, the contraction caused by molecular chain relaxation resulted in a substantial thickness increase, according to the researchers. These films demonstrated a considerable drop in gas permeability during research as a result of a free volume decrease during storage in the glassy phase. Physical ageing occured at a pace that was orders of magnitude rapid than that found in bulk films. McCaig and Paul [84] also evaluated physical ageing on the basis of thickness   and how ageing time affected the gas permeation characteristics of films produced from bisphenol-A benzophenone dicarboxylic acid glassy polyarylate. Physical ageing was responsible for a considerable drop in gas permeability over time after quenching the polymer from above its glass transition temperature, the rate of change was faster for thinner films, according to the studies. The permeability decreased and selectivity increased with aging time. The aging process was shown to be reversed by heating above the T_g.

Kim et al. [85] measured the permeability of N_2, O_2, He, CH_4, and CO_2 in thin films of crosslinked and uncrosslinked 6FDA-based polyimides containing DABA units in the chain as a function of ageing time at 35 degrees Celsius. Physical ageing reduced the permeability of these thin films while significantly increasing their selectivity for each polymer structure. The permeability of crosslinked polyimides was substantially lower than that of uncrosslinked polyimides. Depending on the polymer structure, oxygen permeability reduced by two to thrice after roughly 2000 hours of aging. Crosslinked polyimide films appeared to have somewhat greater or similar ageing rates to uncross-linked polyimide films. The self-retarding kinetic model suggested by Struik [86] accurately described the fractional free volume findings for a given film thickness.

Xia et al. [87] investigated at the ageing of a polyimide-Matrimid in the form of thin films in both pure gas and CO_2-CH_4 (or CO_2-N_2) mixed gas permeation. The effect of pressure on pure gas permeability, according to the authors, suggested that physical ageing affects both Henry's law and the Langmuir term in the dual-mode sorption model, and that the Langmuir sorption declined considerably rapidly in thin films as compared to the thick films As the thickness of Matrimid films was lowered to the range necessary to construct high flux commercial asymmetric membranes, and as the ageing period increased, the films became more susceptible to CO_2 plasticization. For CO_2/N_2 feed mixtures, the combined effect of CO_2 plasticization and competitive sorption/permeation on thin Matrimid films appeared to be less substantial than for CO_2/CH_4 feed mixtures. In another study by Xia et al. [88] assessed the thin films composed of polyetherimide for their gas permeability and found the same ageing pattern. Thin films had a higher permeability than thick films at first, but their permeability gradually declined until it was considerably below that of the thick film.

Tiwari et al. [89] also investigated at the physical ageing of PIM-1 by measuring changes in pure gas permeability of O_2, N_2, and CH_4 at 35 °C. They discovered that thin PIM-1 films age faster than thick films, with relative permeability for thin PIM-1 films decreasing by 67 percent after 1000 hours of ageing compared to 53 percent for thick films. The influence of casting solvent (vapour pressure and boiling point) on ageing and selectivity of thin films was more evident, with initial permeability nearly two times greater for films cast with chloroform ($CHCl_3$) than for those cast with ortho-dichlorobenzene (o-DCB). For thick films, the influence of the casting solvent on the initial permeability was less pronounced. With increasing sorption temperature, the Henry's law constant increased, which was connected to the thin layer being less deep in the glassy state at higher sorption temperatures. Increased diffusivity and decreased solubility with increased CO_2 pressure at a constant ageing period supports a rise in free volume and severe plasticization in PIM-1 thin films.

Physical ageing was measured by Huang and Paul [90] by evaluating the change in refractive index of thin films made of three glassy polymers: polysulfone, polyimide, and polycarbonate (2,6-dimethyl-1,4-phenylene oxide). The Lorentz-Lorenz equation as shown was used to calculate isothermal volumetric aging rate, r and also to give the relationship between changes in refractive index and densification (or volume relaxation) over time.

$$r = \left(\frac{\partial \ln \rho}{\partial \ln t}\right)_{P,T} = \left(\frac{\partial \ln L}{\partial \ln t}\right)_{P,T} = \left(\frac{\partial \log L}{\partial \log t}\right)_{P,T} \tag{21}$$

Where, ρ is the density of the polymer, L is the Lorentz-Lorenz parameter, P and T are pressure and temperature during aging, respectively.

The volumetric ageing rate was found to be dependent on the polymer structure and film thickness, according to the author. Physical ageing caused the refractive quantities in

various forms to rise more or less linearly with log t during the densification process. The accelerated ageing of thin films than bulk polymers had been suggested in the literature to be owing to the diffusion of free volume to the film's surface, analogous to the diffusion of abnormalities, leading ageing to be thickness dependent.

Drozdov [91] created a model for the influence of physical ageing on amorphous glassy polymers' linear viscoelastic response. In tensile relaxation tests and torsional dynamic testing at various temperatures, the author used stress–strain relations to match experimental data for poly(methyl methacrylate), poly(styrene-co-acronitrile), and poly(vinyl acetate). According to the findings, increasing the annealing temperature caused an increase in rate of relaxation while decreasing the apparent rate of structural recovery. The notion of cooperative relaxation was combined with the coarsening concept for structural recovery to provide constitutive equations. The author found that for the approximation of experimental data in mechanical testing on aged specimens, the time-aging time concept of superposition was not required. It was also shown that there was great consistency between observations and numerical simulation findings when the relaxation rate was independent of waiting time, but the average energy and specific stiffness of a cooperatively rearranged regions rise with two. It was also discovered that the annealing temperature T had a significant impact on energy landscape reformation. An increase in the apparent rate of ageing was caused by an increase in the degree of supercooling. It had a far lesser influence on the development of initial elastic moduli.

Yong et al. [92] used polyhedral oligomeric silsesquioxane-POSS nanoparticles to provide a straightforward method for increasing CO_2 permeability of PIM-1 without affecting its selectivity while also suppressing ageing. At low particle loadings, the nanoparticles improved gas diffusivity, but at large particle loadings, they caused chain rigidification. The optimum gas separation characteristics may be achieved with just 2% POSS nanoparticles in PIM-1. The POSS nanoparticles disturbed chain packing at low loadings and caused chain rigidification at high loadings, according to positron annihilation lifetime spectroscopy data. The authors found that POSS nanoparticles decrease physical ageing over 120 days when compared to PIM-1. The research showed that the permeability of the PIM-1/POSS (98:2) membrane was greater, and the physical ageing rate was lower. This was owing to the fact that implanted hard POSS nanoparticles may stiffen and delay segmental motion of PIM-1 polymeric chains.

6. Conclusions

The literature on glassy polymers may be categorized as follows, all of which are crucial for future research:

- Sufficient literature is available which has explained the concept of diffusion in glassy polymers. Models of diffusion in glassy polymers are governed by Fickian and non-Fickian diffusion, out which non-Fickian is more common in glassy polymers.

- The properties of glassy polymers are dependent on sorption isotherms and to explain the sorption in glassy polymers there are various models explored in the literature from past a few years.

- As characteristics of glassy polymers are dependent on diffusion and sorption, then there a need for an extension and modification of existing models, so that they can be generalized and can be executed efficiently and easily then.

- Glassy polymers coatings have enormous applications including membrane separation, drug delivery system, corrosion prevention and many more which have been explained in this review.

- Inspite of having so many applications, yet there is still a challenge for current researchers to simulate the real-life coating problems due to problems like physical ageing which has been

briefly described in the review. There is still a scope to explore those glassy polymers which are more durable against physical aging.

Nomenclature

- D_1 - solvent self-diffusion coefficient

- μ_1 - solvent chemical potential

- $\hat{V}_2^*$ - specific hole-free volume for a diffusional step of component 2

- $\hat{V}_{FH_2}^*$ - the specific hole-free volume

- D_{01} - pre-exponential factor independent of temperature

- D_1 - equal to the mutual binary diffusion coefficient, D

- C - the total gas concentration in a glassy polymer

- C_D - the gas concentration based on Henry's law sorption

- C_H - the gas concentration based on Langmuir sorption

- k_D - the Henry's law coefficient

- b - the Langmuir hole affinity parameter

- C_H' - the capacity parameter

- φ_i - van der Waals volume fractions of the group "i" in the polymer matrix

- a - penetrant activity in a polymer in GAB model

- A - temperature-dependent constant in GAB model

- A_0- pre-exponential factor of a temperature-dependent constant in GAB model

- k - temperature-dependent constant in GAB model

- A'- temperature-dependent constant in new dual-mode sorption model

- K_0 - pre-exponential factor of a temperature-dependent constant in GAB model

- Cp - monolayer sorption capacity

- H_L - heat of condensation of a pure vapor

- H_m - heat of sorption of monolayer of a vapor

- H_n - heat of sorption of multi-molecular layers of a vapor

- R - gas constant

- T - temperature

- T_g - glass transition temperature

- j_s - out-of-plane component of the diffusive solute flux vector

- D_s - thermodynamic diffusion coefficient for solute mass flux in the solute-polymer mixture

- μ_s^{NE} - nonequilibrium solute chemical potential in the solute-polymer mixture

- ρ_s - solute mass per unit volume in the solute-polymer mixture

- ρ_p - polymer mass per unit volume in the solute-polymer mixture

- ω_s - solute mass fraction in the solute-polymer mixture

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Research Interests

      1. Diffusion and Drying of Thin Film Polymeric Coatings

2. Process Modeling & Simulation

3. Polymeric Membranes

4. Process Engineering

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