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Molecular dynamics simulation of diffusion of O_2 and CO_2 in blends of amorphous poly(ethylene terephthalate) and related polyesters

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Abstract

The diffusion of small molecules through polymers is important in many areas of polymer science, such as gas barrier and separation membrane materials, polymeric foams, and in the processing and properties of polymers. Molecular dynamics simulation techniques have been applied to study the diffusion of oxygen and carbon dioxide as small molecule penetrants in models polyester blends of bulk amorphous poly(ethylene terephthalate) and related aromatic polyesters. A bulk amorphous configuration with periodic boundary conditions was generated into a unit cell whose dimensions were determined for each of the simulated polyester blends in the cell having the experimental density. The diffusion coefficients for O_2 and CO_2 were determined via NVE molecular dynamics simulations using the Dreiding 2.21 molecular mechanics force field over a range of temperatures (300, 500 and 600 K) using up to 40 ns simulation time. We have focussed on the influence of the temperature, polymer dynamics, density and free volume distribution on the diffusion properties. Correlation of diffusion coefficients with free volume distribution was found.

Keywords: Molecular dynamics simulation; Diffusion; Free volume

1. Introduction

The aim for this research is to explore and investigate the diffusion of gases in blends of bulk amorphous poly(ethylene terephthalate) (PET) and related alkylene and aromatic polyesters. PET is the most commercially important polyester and a widely used barrier packaging material, and therefore many authors have investigated the correlations between the structural organisation and the properties of this polymer. Polyesters and copolyesters are known to exhibit very low gas diffusion compared with most other polymers such as polyolefins, polycarbonate, polystyrene, etc. This study is therefore important from the technological point of view, since the possibility of improving the impermeability (barrier properties) of PET and related polyesters is required for many applications. The diffusion of gases through polymers is a topic of broad interest and there has been a growing interest in the understanding of migration of small molecules in polymers from a molecular point of view [1–27]. Diffusion of gases in polymers is an important, and in many cases, controlling factor in a variety of practical applications, such as protective coatings [19–21], membrane separation processes [16,22,29], food packaging [1,4,6,8,11,22,25,28,30,31], and biomedical devices [15,30–32]. The technological relevance of such behaviour has become evident in recent years through the rapidly growing demand for polymers with specified gas-transport properties. A visible trend in the area of food packaging is the increasing substitution of thermoplastics for traditional materials such as glass and metal. Plastic packaging materials offer less breakage, lighter weight (lower density) and a degree of design flexibility that glass and metal cannot provide [11,22,25,31]. However, there are no plastics that are impermeable, at the same time consumers are much more demanding and want food that is perfectly safe, nutritious and tasty. Despite this manifest increase in technological demand, however, there has been, until very recently, a considerable lack of

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fundamental understanding of a molecular-level mechanism underlying the diffusion of gases through polymeric materials and the theoretical understanding of diffusion of gases in polymers is still very limited.

In order to function as food-packaging materials, the polymers should typically be investigated at a molecular level to study the atomistic mechanism of the diffusion of gases through the walls of the container. It is a considerable challenge for polymer modelling to predict these properties.

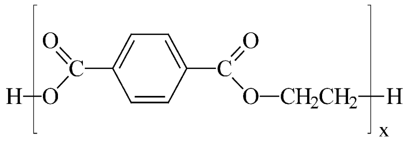
The existing methods have only recently been powerful enough to predict diffusion coefficients, permeability, and selectivity for specific polymer-penetrant systems given only their chemical structure [7–12]. There is a growing demand for better theoretical understanding of the diffusion of gaseous penetrans in polymers to achieve improvements in designing new, better membranes computer and structurally enhanced materials. With the increasing power of available systems a better insight into this phenomenon can only be gained by computer simulation and use of molecular models and simulation techniques for the study of materials at the microscopic and mesoscopic level.

It is, therefore, very desirable to use Monte Carlo (MC) and molecular dynamics (MD) simulation methods to understand and to predict the transport properties of gases in polymers. Because diffusion in a dynamic problem, the obvious approach in calculation of the diffusion coefficients is through MD simulation.

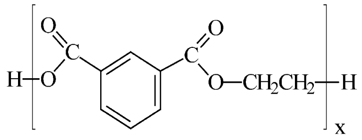
In recent years, a number of such polymers with various structural compositions have been investigated [25–32]. In particular, we are concerned with diffusion of O_2 and CO_2 through blends of bulk amorphous aromatic polyesters, such as PET, (which is one of the most widely used food packaging materials) [12,13,22,31] and related aromatic polyesters. Another reason for this research is to explore the unique properties of the studied polymers in order to gain considerable insight into the behaviour of these polymers. For the polymer blends under consideration such a study has not been previously conducted. In this study MD simulations of polymers were performed and aimed to elucidate whether a correlation exists between polymer conformation (structure), polymer dynamics, number of CH_2 groups, *ortho*-, *meta*- and *para*-isomers, density and free volume with diffusion coefficient. Until recently, free volume properties have been thought of mainly as theoretical values, however, molecular simulation technique is a novel probe to determine free volume properties.

Molecular simulation of these aromatic polyester blends is unquestionably very challenging because of the complexity of their monomeric units, which augments uncertainties in the description of intra- and inter-molecular interactions, induces the possibility of complex morphologies with large characteristic length scales, and implies the presence of molecular motions with very long characteristic times that cannot be addressed with conventional simulation techniques. Therefore, MD simulation is likely to offer explanations that are considerably far more reaching than current experimental techniques.

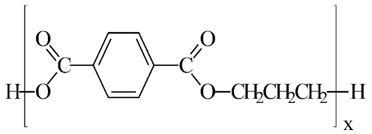
2. Polymers of the simulated blends



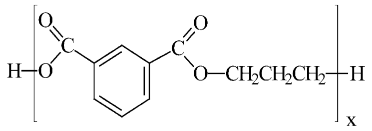
PET poly(ethylene terephthalate).



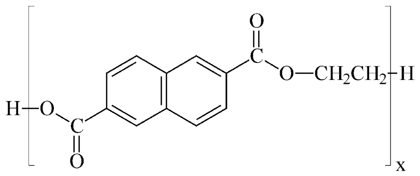
PEI poly(ethylene isophthalate).



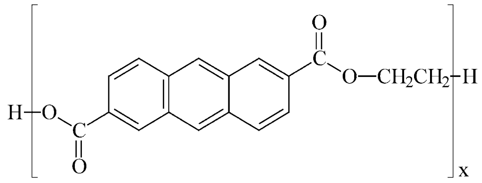
PPT poly(1,3-propylene terephthalate).



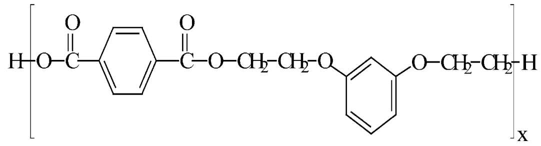
PPI poly(1,3-propylene isophthalate).



PEN-2,6 poly(ethylene 2,6-naphthalenedioate).



PEA-2,7 poly(ethylene 2,7-anthracenedioate).



PHERT-p poly(hydroxyethylresorcinol terephthalate).
The blend formulations are as following

2PET–1PEN-2,6
1PET–2PEN-2,6
2PET–1PEI

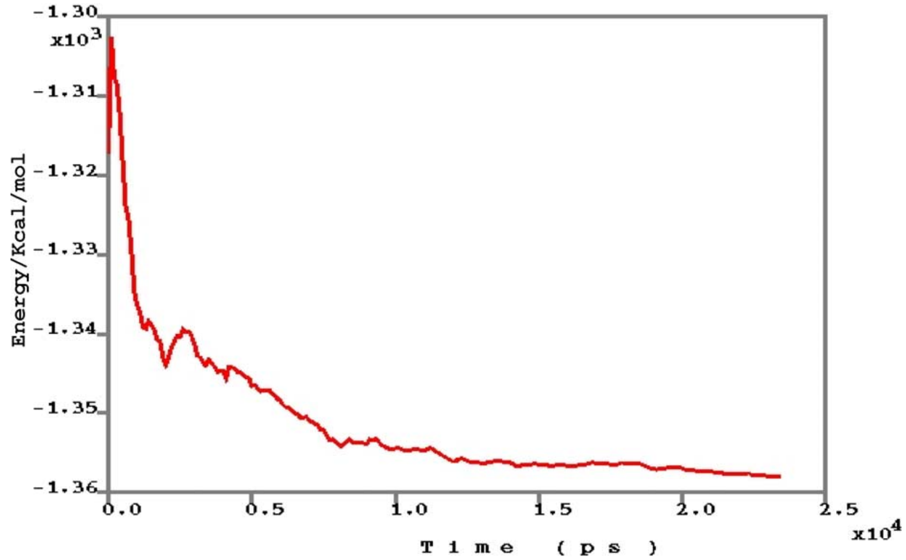


Fig. 1. MD total potential energy equilibrate vs. simulation time of the single chain of the PEI.

1PET–2PEI
2PET–1PPT
1PET–2PPT
2PET–1PPI
1PET–2PPI
2PET–1PHERT
1PET–2PHERT
2PET–1PEA-2,7
1PET–2PEA-2,7
1PET–1PEN–1PEA-2,7.

Random copolymers studied

Random-copoly-2PET/1PEA-2,7
Random-copoly-1PET/1PEN/1PEA-2,7

3. Computational methodology

The simulations were performed for amorphous unit cells of each investigated polyester blend with three polymer chains with degree of polymerization 20. Computer modelling of chemical structures of the monomers and polymers, molecular dynamics simulations, and conformational and molecular dynamics analyses were carried out using molecular simulation software for material science [36], Cerius^2 version 4.9, designed by Accelrys, Inc, San Diego, CA, USA. The Cerius^2 molecular simulation software was run on a Silicon Graphics ORIGIN 2000 workstation. The 3D-Sketcher, open force-field, charge equilibration, monomer editor, polymer, and amorphous polymer builder, energy minimiser, NVE and NPT molecular dynamics, polymer properties, and dynamic analysis modules of Cerius^2 software [36] were used in order to perform the computations and to calculate the density, diffusion coefficient, free volume and to predict the correlation between these properties.

The polymer molecule is defined using the builder (for the monomer) and the polymerizer in order to define the structure of the polymer. The open force-field (OFF) module allowed the specification of the force field to be used for these simulations. The Dreiding 2.21 force field described by Mayo et al. [37] and implemented in Cerius^2 OFF module was applied since it was found to be very suitable and reliable for the molecular simulation of aromatic polymers in accordance with previous studies [37–42]. This force field is parametized for a large class of organic molecules involving H, C, O, S, P, F, Cl and Br, allowing it to be applied to bio- and synthetic polymers [35–42]. It was found that the Dreiding 2.21 force field leads to accurate geometries for various polymeric systems and can be used to calculate and minimise the energy of a simulated polymeric system. It is then possible to calculate the forces acting on each atom of a model polymer, which can further be utilised to solve Newton's equations of motion for MD simulations.

Single chains and amorphous unit cells of the studied polyesters with degree of polymerisation 20 and 60 were used for these simulations. The initial macromolecular conformations of the simulated polymers were minimized and the value of the total potential energy and its components in the investigated polymers were obtained. The energy minimised single chain of the polymers was then used to construct the periodic unit cells of the studied polymers. The total potential energy vs. time-step of the single chain of the PEI is presented in Fig. 1 as an example and it suggests extending equilibration time.

The Dreiding 2.21 force field provides a potential energy

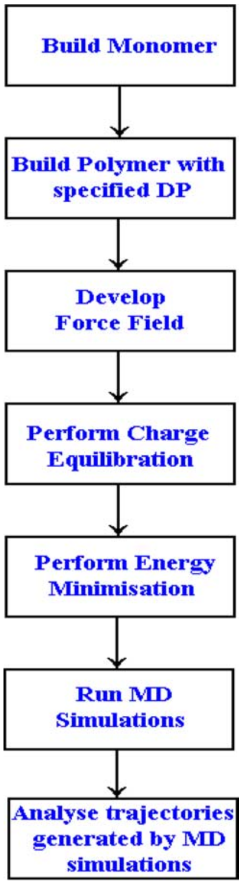


Fig. 2. Steps in the computational procedure used in this research.

interaction function (E_{total}) that accounts for both bonded (E_{b}) and non-bonded (E_{nb}) interactions: $E_{\mathrm{total}}=E_{\mathrm{b}}+E_{\mathrm{nb}}$. The bonded terms typically include harmonic bond stretching (E_{s}), harmonic angle bending (E_{a}), torsional (E_{t}), and inversion (E_{i}) energies: $E_{\mathrm{b}}=E_{\mathrm{s}}+E_{\mathrm{a}}+E_{\mathrm{t}}+E_{\mathrm{i}}$. Non-bonded terms typically contain van der Waals (E_{vdW}), electrostatic (Coulombic) (E_{q}) and hydrogen bond (10–12 potential) (E_{hb}) interactions: $E_{\mathrm{nb}}=E_{\mathrm{vdW}}+E_{\mathrm{q}}+E_{\mathrm{hb}}$.

In practice it is common to use a suitably large cut-off distance, and so for this study a cut-off distance of 150 Å was used for non-bonded interactions, so for this cut-off distance all the non-bonded interactions of the simulated polyester systems are calculated. The Mie 6–12 potential [39–44], that is often referred to in the literature as the Lennard–Jones 6–12 potential function ($u=A/r^{12}-B/r^{6}$), was used to calculate the non-bonded van der Waals interactions. A and B are parameters which determine the size of the attraction ($-B/r^{6}$) and repulsion (A/r^{12}) interactions between the atoms which are separated by a distance r equal to the sum of r_i and r_j, where r_i and r_j are van der Waals radii of the non-bonded atoms i and j.

The charge distribution in the molecule, due to Coulombic (electrostatic) interactions, of the simulated polymers was obtained with the charge equilibration method described by Rappe and Goddard [45] that is available in the Cerius^2 molecular simulation software for material science. The validity of the molecular simulation calculations depends on the suitability and accuracy of the equations used for the bonded and non-bonded potentials which are of great importance for industrial applications.

After the force field is constructed, the total potential energy is likely to be high and not representative of the actual structure. The next logical application of the total potential energy expression is to find an 'ideal' structure for the polymer molecule through energy minimisation, where the term 'ideal structure' usually is taken to mean the lowest-energy conformation.

The NPT and NVE molecular dynamics simulations were performed at 300, 500 and 600 K for each constructed and minimised polymer system. For the NVE ensemble, the number of molecules N, volume V and energy E of the system are kept constant, whereas for the NPT ensemble the number of molecules N, pressure P and the temperature T of the system are kept constant. In order to ensure that the simulations are carried out for sufficient time, which is one of the most important criteria in equilibrating the system, the number of steps of MD simulations was 40,000,000 (40 ns), and the output frequency was every 100 steps. The time step of 0.001 ps is taken to be constant for all the simulations of this study. In this study the model system exchanges energy with a heat bath in order to maintain a constant temperature. The non-canonical 'T-damping' thermostat described by Berendsen et al. [46,47] was used for isothermal-isobaric NPT-MD simulations. Molecular dynamics studies [25–32,37–43] have proven to provide a better insight into the physical phenomena exhibited by polymers. In the case of polymers, this technique can actually be used to predict physical (density, diffusion, and free volume) properties of a polymeric system.

The simulated amorphous unit cells all contained three polyester chains for each investigated polyester blend (Section 2). The energy of the polyester blend was minimized using molecular dynamics and a random conformation is produced for amorphous polymers. The unit cell was displayed and analysed. Each simulated structure was then analysed by the Amorphous_Cell module to obtain density, cohesive energy, pair correlation function (statistical analysis of relative atom positions). The density of the polyester blend unit cell was equilibrated.

Small molecules (O_2 or CO_2) were added to the amorphous cell and they move in the cell during molecular dynamics. The rate of movement can be used to calculate the diffusion coefficients for the small molecules through the polyester blend. The distribution of free volume was determined for each simulated amorphous cell. $5O_2$ or $5CO_2$ molecules were introduced in polyester blend unit cells described above.

Trajectory file data generated from MD simulation has been used in all the polymer property calculations and analyses presented in this research. The trajectory files were

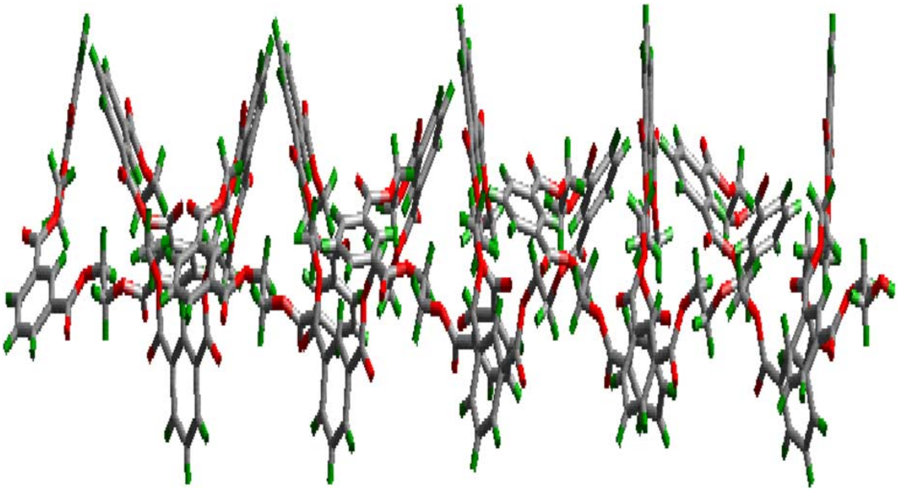


Fig. 3. Minimised structure of the polyester chain for PEI.

analysed by polymer properties and dynamics analysis modules.

The diffusion coefficient of O_2 and CO_2 in polymers was calculated from the NVE MD slope of the mean-square displacement for long times, at these times normal (Einstein) diffusion is observed, and the mean-square displacement is a linear function of time:

$$D = \frac{1}{6} \lim \frac{\mathrm{d}}{\mathrm{d}t} (\mathbf{r}(t) - \mathbf{r}(0))^2 \tag{1}$$

In Eq. (1), D is the diffusion constant, t is time, $\mathbf{r}(t)$ is the position vector of the gas molecule in space at time t, and the brackets denote an ensemble average, which in these simulations is obtained from averaging over all gas molecules in the polyester blend and all time origins $t=0$. This equation only applies in the limit of large times, times at which the simulated gas molecules have performed enough jumps for their trajectories to become a random walk in the polyester blend model.

Table 1
Predicted diffusion coefficients, free volume and density of the simulated polyester blends

Polymer code	Diffusion of O_2 (cm^2/s (10^4))			Diffusion of CO_2 (cm^2/s (10^4))			Free volume (Å^3)	Density (g/cm^3)
	300 K	500 K	600 K	300 K	500 K	600 K	500 K	300 K
2PET–1PEN-2,6	0.0959	0.1294	0.1471	0.1007	0.1364	0.1498	15.1	1.32
1PET–2PEN-2,6	0.0516	0.0632	0.0751	0.0491	0.0741	0.0952	11.7	1.31
2PET–1PEI	0.1301	0.1731	0.1853	0.1114	0.1502	0.1573	17.6	1.29
1PET–2PEI	0.1121	0.1539	0.1653	0.1094	0.1376	0.1459	17.2	1.28
2PET–1PPT	0.933	0.1098	0.1464	0.0979	0.1141	0.1369	15.7	1.31
1PET–2PPT	0.0532	0.0679	0.0859	0.0603	0.0724	0.0831	12.9	1.29
2PET–1PPI	0.1301	0.2057	0.2189	0.1161	0.1395	0.1501	18.1	1.28
1PET–2PPI	0.1153	0.1471	0.1610	0.0887	0.1053	0.1302	15.3	1.29
2PET–1PHERT	0.1301	0.1431	0.1983	0.1298	0.1402	0.1702	19.4	1.29
1PET–2PHERT	0.1202	0.1363	0.1392	0.1132	0.1262	0.1297	14.1	1.27
2PET–1PEA	0.0631	0.0751	0.0901	0.0621	0.0719	0.0781	8.4	1.26
1PET–2PEA	0.0481	0.0415	0.0732	0.0429	0.0571	0.0681	8.1	1.27
Random-copoly-2PET/1PEA	0.0269	0.0415	0.0512	0.0271	0.0413	0.0495	7.1	1.33
1PET–1PEN–1PEA	0.0501	0.0581	0.0639	0.0431	0.0561	0.0613	7.2	1.32
Random copoly-1PET/1PEN/1PEA	0.0061	0.0096	0.0156	0.0059	0.0084	0.0139	6.7	1.335

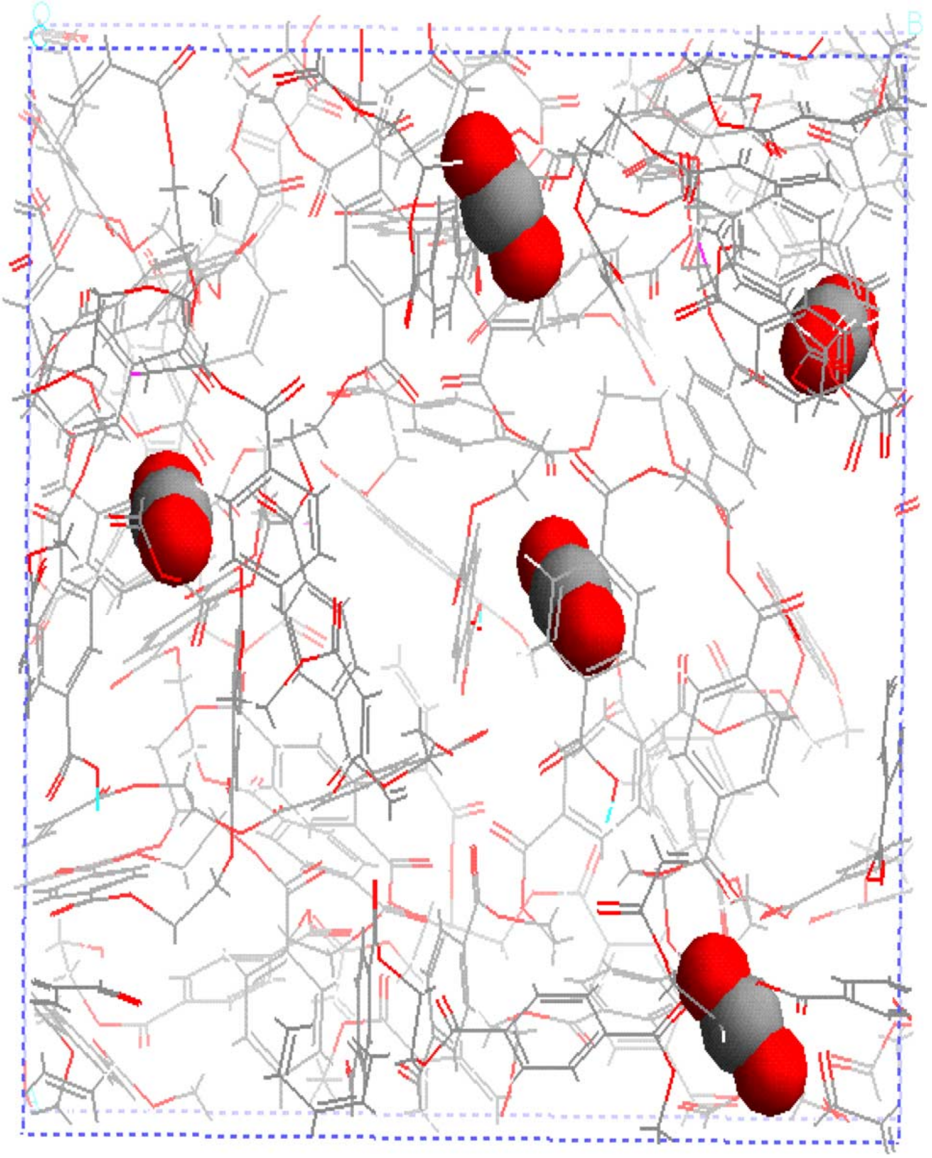


Fig. 4. Amorphous cell structure of 2PET–1PEI blend with five molecules of carbon dioxide inserted.

The computational procedure used in this research includes the following main steps shown in Fig. 2.

4. Systematic and statistical errors

As with laboratory experiments, computer simulation experiments can have both systematic and statistical errors, which however can be controlled and minimised. Applying molecular dynamics simulation, the thermophysical, structural and dynamic properties of polymeric materials can be calculated with an accuracy that strongly depends on the reliability of the potential function, in other words, on the errors arising from truncation of the intermolecular forces, and statistical errors, arising from insufficient sampling. In practice, MD simulation studies are presently limited by the speed and storage capabilities of current computers to limited polymer size and computing time scales.

For this study the reliability of the DREIDING 2.1 potential function has been proven and tested by previous molecular simulation studies of polymers [37–42]. It was found that very accurate geometries and potential barriers for various organic polymers have been obtained employing the DREIDING 2.1 force field. Consequently, similar to the initial samples of the laboratory experiments, the results of the molecular simulations will vary strongly depending on the way the system was originally prepared. One of the solutions to address this problem was to start from many, widely different conformations, and to make sure that the results obtained from them did not differ widely. For each simulated aromatic polyester blend, single chain and periodic unit cell, several cycles of potential-energy

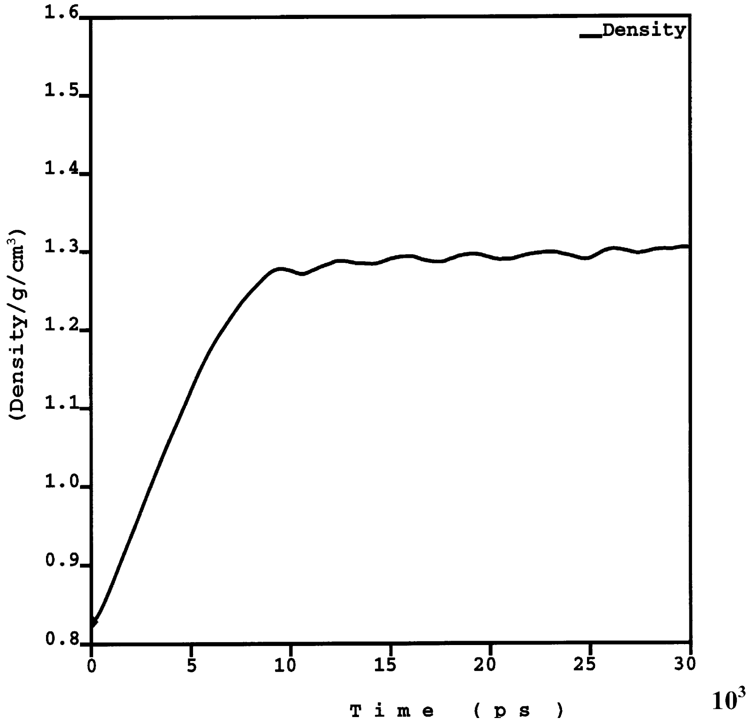


Fig. 5. Predicted NPT-MD density vs. molecular dynamics time for 2PET–1PEI.

minimisations and MD simulations were performed to create very well equilibrated polymer conformations.

5. Results and discussion

This research was performed for amorphous unit cells for each of the simulated polyester blends. Initially, for each of the investigated polyesters, a single chain was modelled and energy minimized in order to investigate the polymer conformation and the total potential energy of the polymer chain was predicted. The energy minimised conformation of the PEI polyester chain is presented in Fig. 3.

Then, an amorphous unit cell with three polymeric single chains, previously minimized, for each of the studied polyester blends was modelled in order to calculate the density by NPT MD. Density was a guide to the diffusion but the densities were very similar so other factors must be

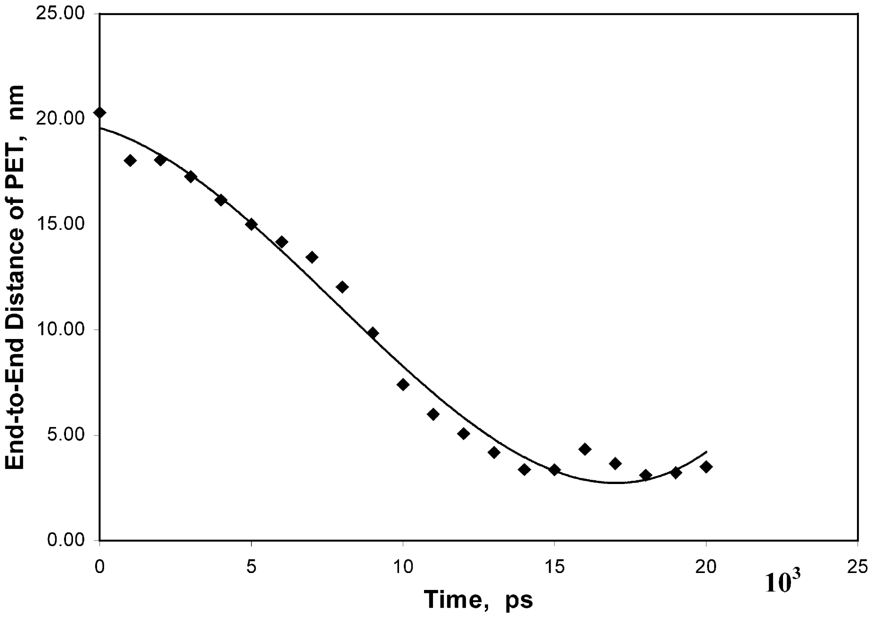


Fig. 6. End-to-end distance of PET obtained by MD simulation.

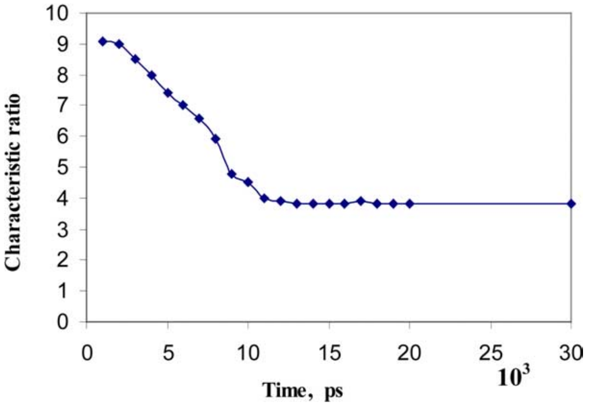


Fig. 7. Characteristic ratio of PET obtained by MD simulation.

important (Table 1). Then the predicted density for each of the studied polyester blends was used to build a new amorphous unit cell with five molecules of O_2 or CO_2 in order to calculate the diffusion coefficients and free volume at different temperature. Free volume distributions are not available from other measurements. An example of the simulated, investigated, and visually analysed unit cell for 2PET–1PEI blend with five molecules of carbon dioxide inserted is displayed in Fig. 4.

An example of the NPT MD calculated density for 2PET–1PEI blend over a wide simulation time range is presented in Fig. 5. As can be observed in Fig. 5 from the equilibration times in MD simulation the average simulated density of 2PET–1PEI blend is 1.29 g/cm^3. Fig. 5 exhibits typical density vs. time behaviour during this part of the NPT-MD simulation for 2PET–1PEI. The density fluctuations in the simulations for the investigated polymeric blend are less than 0.007 g/cm^3 (Fig. 5). The dynamics was continued until the density of the polymer blend in the amorphous cell reached a plateau.

The molecular dimensions, as expressed by the characteristic ratio and end-to-end distance are key parameters in the molecular simulations because they depend differently on the conformational characteristics of the individual bond types in the polymeric chain. These structural parameters were emphasized in testing the model and a satisfactory structure was accomplished. In order to confirm the validation of the simulated model of the studied polyesters for PET further MD simulation were performed to calculate the structural parameters, such as end-to-end distance and characteristic ratio which are presented in Figs. 6 and 7, respectively.

The predicted characteristic ratio is about 3.8 and the reported experimental values are between 3.7 and 4.1 [12–15]. The experimental values are unfortunately somewhat approximate as they are based on viscosity measurements in good solvents and corrections must be made to arrive at unperturbed dimensions.

Diffusion coefficients were obtained for each of the polymers from the mean square displacement vs. simulation time calculated according to Eq. (1). The diffusion coefficient of gas molecules of the simulated polyesters has been calculated from the slope of the penetrant mean-square

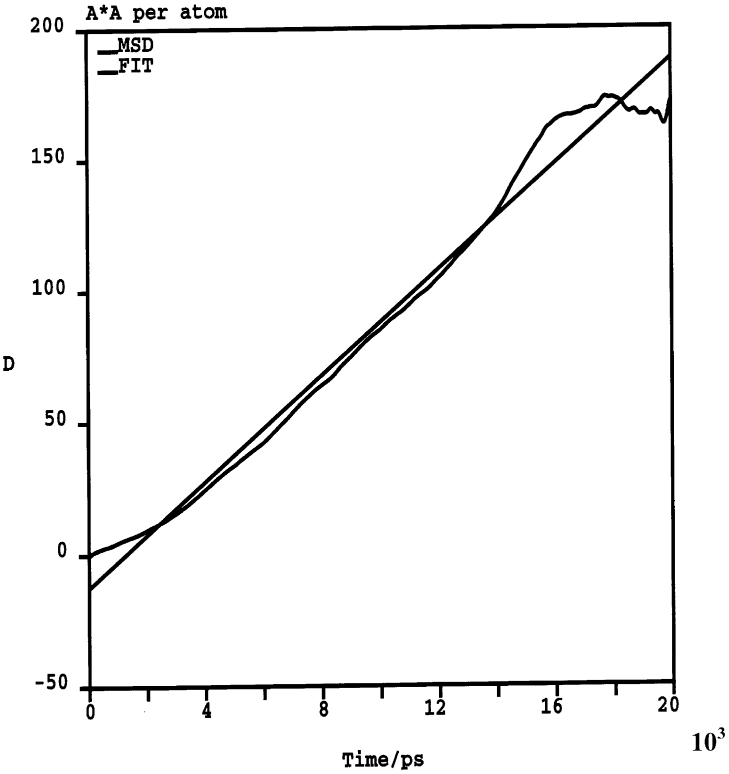


Fig. 8. Plot of mean square displacement and fit line vs. simulation time for CO_2 in amorphous 2PET–1PEI.

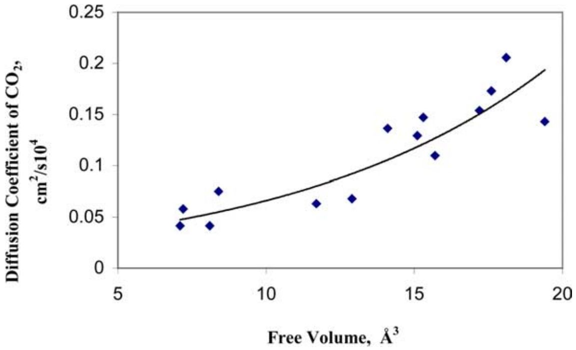


Fig. 9. Diffusion coefficient of O_2 of the studied polyester blends vs. free volume.

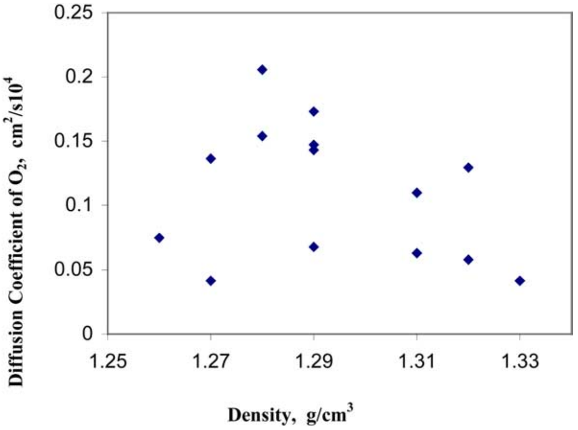


Fig. 11. Diffusion coefficient of O_2 of the studied polyester blends vs. predicted density.

displacement for long times. At these times Einstein diffusion is observed, and the mean-square displacement is a linear function of time. An example of the carbon dioxide mean square displacement at temperature of 500 K in amorphous 2PET–1PEI blend is shown in Fig. 8.

Table 1 presents the results for all the simulated polyester blends. Diffusion coefficients at 300, 500 and 600 K are listed for each of the polyester blend. In addition the free volume calculated at 500 K and the amorphous cell density calculated at 300 K are shown.

The coefficients of diffusion for both O_2 and CO_2 for the studied polyester blends increase exponentially with the increasing of the free volume. This is evidenced in Fig. 9 for diffusion of O_2 and in Fig. 10 for diffusion of CO_2. The mechanism of diffusion involves a series of random 'jumps' ('hopping diffusion') from a free volume between polymer chains to another hole or void (Fig. 4).

MD simulations performed during this study have revealed these mechanisms and dynamics, and it was shown that molecules of O_2 and CO_2 diffuse through polymer chains in a sequence of activated jumps between neighbouring locations. The gas molecule is only temporarily kept in a cavity of free volume as the thermal fluctuations of polymer atoms constantly create and destroy transient channels of free volume between neighbouring holes/cavities. When the gas molecule is at the right position at the right time having a suitable velocity it can slip through such a channel into a neighbouring hole. The size and shape of the holes available in a polymer control its rate of gas diffusion, which along with solubility determine its permeation properties. Transport of gas molecules occurs by jumps between individual sections of the free volume (holes) through temporarily open channels. The diffusion coefficient is completely determined by the jump event.

For the simulated polyester blends it was found that free volume plays an important part in the process of diffusion, compared with other factors, such as density. As it is seen in Figs. 9 and 10 the larger the free volume in a polyester blend, the greater the gas diffusion.

As it is displayed in Figs. 11 and 12 the predicted coefficients of diffusion for both O_2 and CO_2 for the simulated blends do not depend on density, therefore, in this study the calculated density was just a guide to the diffusion

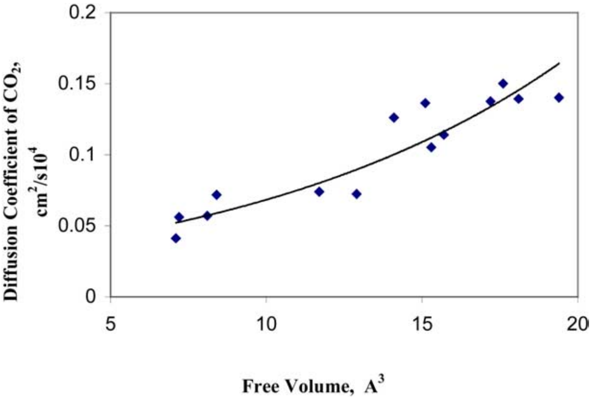


Fig. 10. Diffusion coefficient of CO_2 of the studied polyester blends vs. free volume.

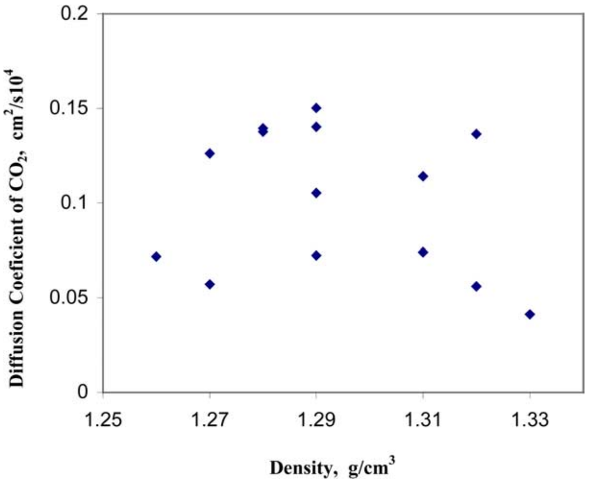


Fig. 12. Diffusion coefficient of CO_2 of the studied polyester blends vs. predicted density.

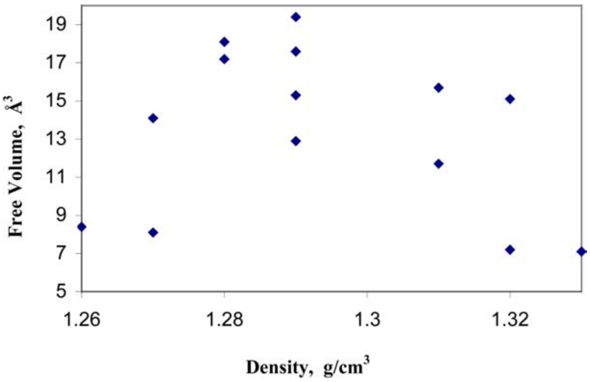


Fig. 13. Predicted densities vs. predicted free volume of the simulated polyester blends.

but the densities were very similar so other structural factors must be important. Similar to the coefficients of diffusion, the predicted free volume for the studied polyesters does not depend on density as well (Fig. 13). In Fig. 13 it can be observed that for blends with the same values, or almost the same values, of density we have obtained very different values for free volume. For four different polyester blends with the same value of density (1.29 g/cm^3) we have found four different values for the free volume, and fuor different values of the diffusion coefficients (O_2 and CO_2) as well.

It should also be noted that the diffusion of gases in the simulated blends increased with the temperature (Table 1). The O_2 diffuses somewhat slightly faster than CO_2 does, which means the diffusion coefficients correlate well with the square of the effective diameter of the diffusing gas, however, the diffusion of O_2 increases linearly with the increase of diffusion of CO_2 for the simulated polyester blends, see Fig. 14.

An example of the predicted density by NPT-MD at 300 K of the PET–PEN blends is presented in Fig. 15. The density of the PET–PEN blends decrease with the increasing the amount of PEN in PET.

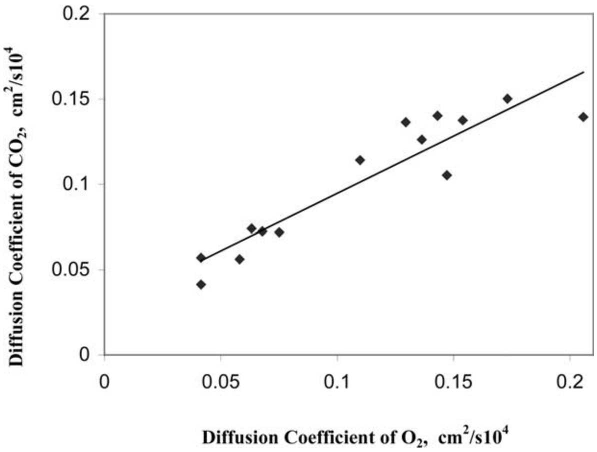


Fig. 14. Diffusion coefficient of O_2 vs. diffusion coefficient of CO_2 of the simulated polyester blends.

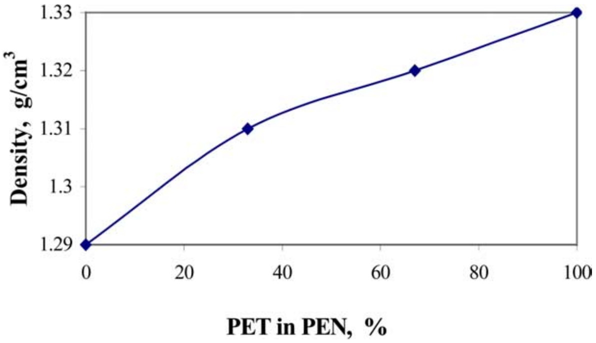


Fig. 15. Predicted density of the simulated PET–PEN blends.

The coefficient of diffusion of O_2 of the blends of PEN, PEA, PHERT, PEI, PPT and PPI in PET are shown in Fig. 16. For the simulated blends the diffusion coefficient is lower compared with pure PET, except for the blend of 33% PPI in PET. For the simulated blends the diffusion decrease linearly with the increase of the percentage of the polyesters (PEN, PHERT, PEI, PPT and PPI) in PET. The PET–PEA blends have the lowers barrier property and the coefficient of diffusion decrease exponentially with the increase of the amount of PEA in PET. PET–PEN and PET–PPT blends have almost the same barrier properties. It can be noted that for the PET–PHERT blends the diffusion coefficient is almost constant, and slightly improve the barrier properties of PET.

In general, the calculated diffusion coefficient of the simulated blends decrease from PPI, to PEI, to PHERT, to PEN, to PPT and to PEA (Fig. 16).

As it was mentioned above, the PET–PEA blends have the lowest diffusion coefficient, however, it is worth noticing that during this study it was observed that a simulated random copolymer of PET–PEA has a much lower diffusion coefficient then the blends of PET–PEA, see Table 1. This can be explained by a better packing of the copolymeric chains in amorphous phase than the packaging of the homopolymer chains of the PET and PEA into the PET–PEA blends.

A ternary blend of PET, PEN and PEA was also modelled and simulated, and analysed as well. The barrier properties of these ternary-blends are very high which are almost similar with the barrier properties of the binary blends of PET–PEA. The simulated data predict that a ternary random copolymer of PET, PEN and PEA has much lower diffusion coefficient than the ternary blends of PET, PEN and PEA, see Table 1. This can also be explained by a better packing of the ternary-copolymeric chains during the copolymerisation reaction, than the packaging of the homopolymeric chains of the PET, PEN and PEA into the PET–PEN–PEA blends.

Much more simulation work has to be done on these polyesters and especially on their blends in order to make a systematic study of the barrier properties of these polyesters and their blends and to completely analyse the diffusion

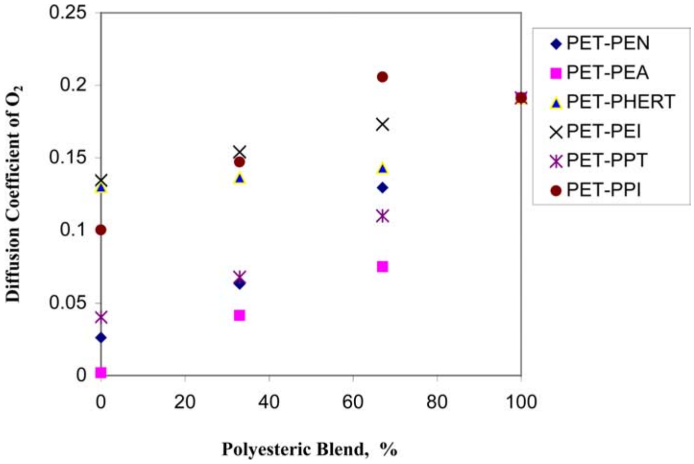


Fig. 16. Diffusion coefficient of O_2 in the simulated polyester blends.

properties and factors that affect the diffusion properties of these polyester systems.

A molecular dynamics simulation study is currently undergoing to investigate the diffusion properties of the blends of these aromatic polyester systems (homopolyesters and their blends) with thermotropic liquid crystalline aromatic polyesters. It is expected that a certain addition of thermotropic liquid crystalline polyester at these polyester systems will significantly improve the barrier properties.

5.1. Comparison of simulated data with theoretical calculated data

For the simulated blends a comparison of the simulated data with the theoretically calculated data, based on additivity, data was performed. These data are presented in Table 2. The negative values of the difference between simulated and calculated values show that the computer predicts a lower coefficient of diffusion than the theoretical calculated value for most of the studied polyester blends

Table 2
Simulated (D_s), calculated (D_c) and difference (D_s-D_c) diffusion coefficients, calculated (FV_c) and difference (FV_s-FV_c) free volume of the simulated polyester blends

Polymer code	Simulated and calculated diffusion of O_2 at 500 K cm^2/s (10^4) and its difference			Simulated and calculated diffusion of CO_2 at 500 K cm^2/s (10^4) and its difference			Calculated free vol. at 500 K, Å^3 and its difference	
	D_s	D_c	D_s-D_c	D_s	D_c	D_s-D_c	FV_c	FV_s-FV_c
2PET–1PEN-2,6	0.1294	0.1363	−0.0069	0.1364	0.1161	0.0203	15.3	−0.2
1PET–2PEN-2,6	0.0632	0.0812	−0.018	0.0741	0.069	0.0051	12.8	−1.1
2PET–1PEI	0.1731	0.1723	0.0008	0.1502	0.1508	−0.0006	17.5	0.1
1PET–2PEI	0.1539	0.1534	0.0005	0.1376	0.1385	−0.0009	17.3	−0.1
2PET–1PPT	0.1098	0.1410	−0.0312	0.1141	0.1192	−0.0051	16.0	−0.3
1PET–2PPT	0.0679	0.0906	−0.0227	0.0724	0.0751	−0.0027	14.1	−1.2
2PET–1PPI	0.2057	0.1609	0.0448	0.1395	0.1388	0.0007	16.8	1.3
1PET–2PPI	0.1471	0.1306	0.0165	0.1053	0.1144	−0.0091	15.8	−0.5
2PET–1PHERT	0.1431	0.1709	−0.0278	0.1402	0.1472	−0.007	19.7	−0.3
1PET–2PHERT	0.1363	0.1505	−0.0142	0.1262	0.1313	−0.0051	21.6	−7.5
2PET–1PEA	0.0751	0.1281	−0.053	0.0719	0.1098	−0.0379	13.6	−5.2
1PET–2PEA	0.0415	0.0650	−0.0235	0.0571	0.0751	−0.018	9.4	−1.3
Random-copoly-2PET/1PEA	0.0415	0.1281	−0.0866	0.0413	0.1098	−0.0685	13.6	−6.5
1PET–1PEN-1PEA	0.0581	0.2193	−0.1612	0.0561	0.0627	−0.0066	11.1	−3.9
Random copoly-1PET/1PEN/1PEA	0.0096	0.2193	−0.2097	0.0084	0.0627	−0.0543	11.1	−4.4

(Table 2). The simulated data are better than expected from additivity.

6. Summary and conclusions

Atomistic modelling is a useful tool for studying the microscopic structure and understanding the mechanisms of physical processes on atomic and molecular levels. Molecular simulations of polymer structure have reached the level where they are now useful in gaining insights into the molecular origins of behaviour of bulk polymers. In the present work the diffusion of O_2 and CO_2 in models of bulk amorphous polyesters have been investigated by extensive NVE MD simulation investigations in order to obtain a better insight about the gas transport mechanism. Extended equilibration procedures were necessary to obtain reasonable packing models for the simulated polyesters. A comparison between static structure and the dynamic behaviour of the free volume in the simulated polyesters have revealed qualitative differences, which are decisive for the diffusion of gas molecules in these materials. We have focused on the influence of the polymer structure, amorphous phase density, temperature and free volume distribution on the diffusion.

Molecular dynamics have been used to obtain the diffusion coefficient for oxygen and carbon dioxide in each of the studied polyester blends at different temperatures (300, 500, and 600 K).

For this group of polyester blends the density does not have a significant influence on the diffusion coefficients. However, there was a tendency of the simulated polyesters for the diffusion coefficients for both O_2 and CO_2 molecules to increase with a decrease in density.

It was found that the diffusion coefficients for both O_2 and CO_2 increased exponentially with an increase in free volume of the simulated polyester blends. Transport of gas molecules occurs by jumps between individual sections of the free volume (holes) through temporarily open channels. The diffusion coefficient is completely determined by the jump event. Direct correlations have been observed in simulated polyesters between free volume properties and gas diffusion properties. Such free volume calculation can be helpful in selecting the appropriate polymeric material for technological applications that specify/require high barrier property. The literature has shown that diffusion coefficients correlate exponentially with accessible free volume fraction.

For the simulated polyester blends the diffusion coefficient is lower compared with pure PET, except for the blend of 33% PPI in PET. For the simulated blends the diffusion decrease linearly with the increase of the percentage of the polyesters (PEN, PHERT, PEI, PPT and PPI) in PET. The PET–PEA blends have the lowers barrier property and the coefficient of diffusion decrease exponentially with the increase of the amount of PEA in PET. PET–PEN and PET–PPT blends have almost the same barrier properties. It can be noted that for the PET–PHERT blends the diffusion coefficient is almost constant, and slightly improved on the barrier properties of PET. In general, the calculated diffusion coefficient of the simulated blends decrease from PPI, to PEI, to PHERT, to PEN, to PPT and to PEA. The PEAs blends were found to have the lowest diffusion coefficient of the simulated polyester systems.

For most of the simulated polyester blends the O_2 diffuses somewhat slightly faster than CO_2 does, which means the diffusion coefficients correlate well with the square of the effective diameter of the diffusing gas. It should also be noted that the diffusion of gases in the simulated polyester blends increased with temperature.

For the simulated blends a comparison of the simulated data with the calculated, based on additivity, data was performed. The simulated data show that the computer predicts a lower coefficient of diffusion than the calculated value for most of the studied polyester blends.

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