Molecular Dynamics Simulation of Diffusion Behavior of Cyclohexane in Natural Rubber During Reclamation

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ABSTRACT: Reclaiming oil is a common additive involved in many physical rubber reclamation processes. In this work, molecular dynamics simulation is used to investigate the diffusion of oil in natural rubber (NR) under different temperatures and pressures. The structures of polyisoprene and cyclohexane molecules are constructed. The diffusion coefficients (Ds) of cyclohexane molecules in polyisoprene under different temperatures and pressures are calculated. The free volumes are also obtained to better understand the change in microstructure. The diffusion experiments of oil in NR samples under different temperatures and pressures are also conducted. The simulation results show that D increases as the temperature rises, especially at temperatures above 400 K, while the pressure does not affect D significantly. The fractional free volume calculated from the free volume and occupied volume exhibits a similar trend to that of D. Furthermore, the calculated Ds agree well with the experimental results. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40347.

INTRODUCTION

Because of its stable cross-linked three-dimensional network structure, vulcanized rubber is difficult to degrade naturally, creating serious ecological and environmental problems. Reclamation of waste rubber has long been investigated with great efforts. Through reclamation, the three-dimensional network of waste rubber is broken down at the cross-link sites or in the main chain bonds.[1] There are various methods to break down the network of the waste rubber, including chemical,[2] physical,[3] and biological[4] means. In a physical reclaiming process, the three-dimensional network of cross-linked rubber is broken down with the help of external energy. Thus, the plasticity of the rubber is improved.[5]

Reclaiming oil plays an important role in many physical reclaiming procedures. Under appropriate conditions, the oil molecules permeate into the cross-linked network of the rubber and weaken the intermolecular interaction between the macromolecules, thereby increasing the plasticity of the reclaimed rubber. Besides, addition of oil facilitates the impregnation and dispersion of the reclaiming agents into the vulcanized rubber matrix, resulting in a continuous uniform structure for the reclaimed rubber.[1,6]

Factors such as temperature, pressure, and shear force are important in physical rubber reclamation. There have been some previous studies on the effects of these factors on the reclaiming process.[1,3] The objective of the present study is to evaluate the effects of temperature and pressure on the diffusion behavior of reclaiming oil in rubber.

However, it is a daunting task to experimentally investigate the diffusion behavior of oil molecules in a rubber matrix under various temperatures and pressures. In addition, it is difficult to precisely control the pressure. Therefore, it is more convenient to investigate the diffusion behavior theoretically.

Recently, computer modeling of molecular systems at a detailed atomistic level has become a standard tool in the study of sorption and diffusion of small molecules in polymeric media.[7–9] Molecular dynamics (MD) simulation is a computer modeling method that is used to model the trajectory of an ensemble of atoms subjected to mechanical or thermodynamic boundary conditions. The trajectory of the atoms is usually determined by solving Newton's equations of motion for a system of interacting particles. MD simulation is valuable for the investigation of the equilibrium and dynamic properties of polymeric microstructures at the molecular scale. It has been extensively used for the investigation of the diffusion mechanism of small penetrant molecules in amorphous polymer matrices and polymer composites, as well as for the estimation of diffusion coefficient
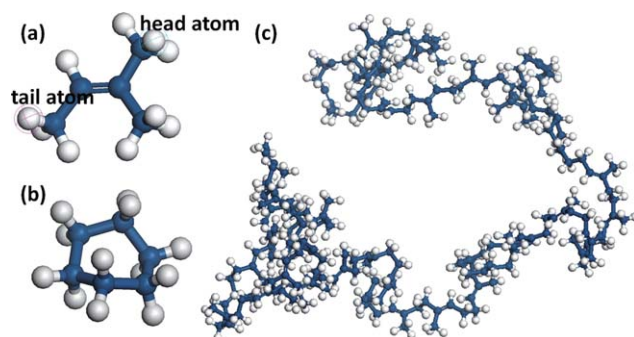
Figure 1. Models for (a) isoprene repeat unit, (b) cyclohexane molecule, and (c) polyisoprene chain in MD simulation (white spheres stand for H atoms, and dark blue spheres stand for C atoms). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(D).[10,11] Kucukpinar and Doruker calculated the diffusion and solubility coefficients of small diffusants in nitrile rubber and styrene butadiene rubber (SBR) matrices by MD simulations. The calculated diffusion and solubility coefficients indicated reasonable agreement with experimental results. Aggregation of water molecules was observed in the hydrophobic matrix SBR.[12] MD simulation was also performed by Mozaffari et al. to investigate the diffusion and permeation of gases, including argon, nitrogen, methane, carbon dioxide, and propane, in polystyrene over a wide range of temperatures. They found that the Arrhenius plot of ln(D) versus $1/T$ were different for different diffusants and the relationship between D and the molecular diameter was confirmed.[13] Generally speaking, MD simulation is of practical importance in predicting D and understanding the mechanism of diffusion.

In this study, MD simulation was used to investigate the effects of temperature and pressure on the diffusion behavior of cyclohexane molecules in a polyisoprene matrix. The diffusion coefficients of cyclohexane molecules were calculated by the Einstein relation.[10] The free volume characteristics of the polyisoprene-cyclohexane system were also investigated. Furthermore, the calculated Ds were compared with the experimental results of pine tar (primarily made of guaiacol, cresol, and phenol) and naphthenic oils (primarily made of cycloalkanes) permeating in natural rubber (NR). The basic structure of these two reclaiming oils is carboatomic ring, similar to the structure of cyclohexane.

SIMULATION DETAILS

For the MD simulations, the Visualizer, Discover, and Amorphous Cell modules of the Material Studio software developed by Accelrys Software were used.

The condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field was used for all the theoretical calculations. The COMPASS is an *ab initio* force field and has proved to be a powerful force field supporting the optimization and prediction of the structural, conformational, and thermophysical condensed phase properties of molecules including macromolecules. A force field refers to the form and parameters of mathematical functions used to describe the potential energy of a system consisting of molecules and atoms. In the

COMPASS force field, the total energy of the system is the combination of bonding and nonbonding interactions. The bonding terms include bond stretching, bond angle bending, and torsion angle rotation energy along with the diagonal and off-diagonal cross-coupling terms. The nonbonding term consists of the van der Waals and electrostatic force interactions.[14,15]

An "all-atom" model consisting of polyisoprene and cyclohexane was built first in this study. Cyclohexane was chosen as the diffusant because it has the representative structure of commonly used reclaiming oil. Besides, the solubility parameter of cyclohexane (16.7 $MPa^{0.5}$) is similar to that of polyisoprene (16.5 $MPa^{0.5}$), indicating good compatibility between them.[16] Figure 1(a,b) shows the structures of isoprene repeat unit and cyclohexane molecule constructed with the Visualizer module, respectively. The polyisoprene polymer chain consisting of 50 repeat units, as shown in Figure 1(c), was built with homopolymer building tools. Energy minimization was applied after each building step by using the smart minimization method until the energy convergence was <0.01 kcal mol^{-1} nm^{-1}. As shown in Figure 2, the periodic cell containing two polyisoprene chains and four cyclohexane molecules was constructed with the Amorphous Cell module.

After a 5000-step minimization of the cell structure, a 150 ps MD equilibration run on the system was performed in the constant pressure and temperature (NPT) ensemble to obtain the equilibrium density. In the NPT ensemble, the number of atoms, the pressure, and the temperature of the space were kept constant. The temperature was controlled by the Andersen method,[17] while the pressure was controlled by the Berendsen method.[18] Afterward, the microcanonical (NVE) ensemble was used for the dynamics calculation. In the NVE ensemble, the number of atoms, the volume of the space, and the total energy (Hamiltonian) of the system were kept constant. The NVE dynamics was performed on the end point of the NPT run to obtain equilibrium molecular structures and the atomic trajectory was recorded every 0.25 ps for the subsequent analyses.
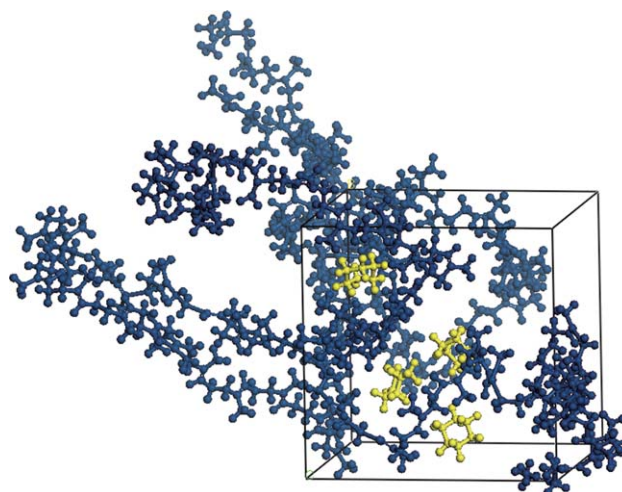

Figure 2. Periodic cell with two polyisoprene chains (dark blue) and four cyclohexane molecules (yellow). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
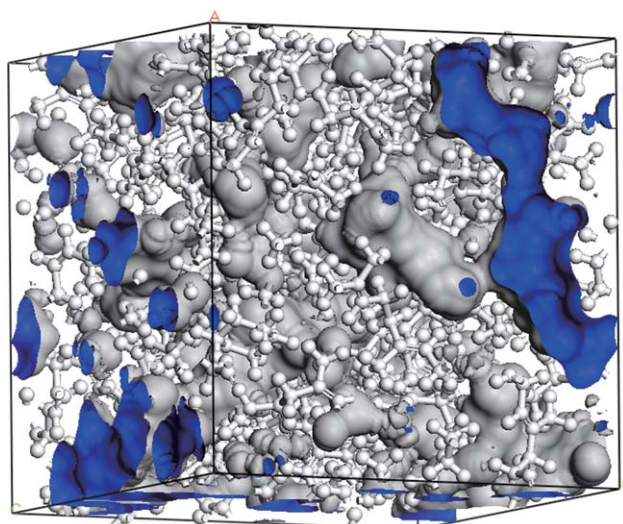
Figure 3. Model for free volume analysis of cell (the blue space represents the free volume, whereas the gray space represents the occupied volume). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The four cyclohexane molecules in the cell were defined as a set to analyze the trajectory of the diffusing molecules, which means the mean square displacement (MSD) of the molecules during the NVE run. The MSD can be calculated from the following equation:

$$MSD = \langle (r_i(t) - r_i(0))^2 \rangle \tag{1}$$

In eq. (1), $r_i(0)$ is the initial position coordinate of the diffusant atom i in the polymer microstructure, and $r_i(t)$ is the position coordinate of this atom after a time t. $(r_i(t) - r_i(0))$ represents the displacement of atom i during time t. The angle brackets denote averaging over all diffusant atoms as well as over all time origins.

Fick's first law [eq. (2)] is a commonly used macroscopic law to describe diffusion behavior[19]:

$$J = -D\nabla c \tag{2}$$

In eq. (2), J is the diffusion flux, which is the amount of substance that will flow through a small area during a small time interval. D stands for the diffusion coefficient, which depends on experimental conditions, such as time, temperature, and pressure, as well as the properties of both the diffusant molecules and the polymer bulk. D reflects the dynamics of the diffusant-polymer system. ∇c refers to the concentration gradient of the diffusant molecules.

Ds of the cyclohexane molecules in polyisoprene can be easily obtained by analyzing the correlation between MSDs and the time under different simulation conditions. The effects of temperature and pressure on the diffusion behavior of cyclohexane in polyisoprene were studied separately. First, the NPT runs were carried out from 293 to 533 K in steps of 20 K under the pressure of 1 MPa to investigate the temperature dependence of D. Second, the NPT runs were carried out under 1, 2, 3, 4, and 5 MPa at the constant temperature of 293 K to evaluate the effect of pressure.

Free volume[13,20,21] plays an important role in the transport behavior of diffusant molecules in the polymer bulk because it provides paths for the diffusants. At present, positron annihilation lifetime spectroscopy is the common experimental approach to probe the interior cavities in the amorphous region of polymers directly.[22,23] However, this technique is laborious and can hardly provide details on the morphology of the free volume voids. MD simulation allows a quick and accurate determination of the free volume amount as well as its distribution. The fractional free volumes (FFVs) of the cell under different simulation conditions were calculated with the free volumes and occupied volumes (as shown in Figure 3) obtained by a hard spherical probe.[24,25]

EXPERIMENTAL

The experiment of oil mixture permeating NR was conducted to observe the permeation of oil in a rubber matrix. The basic structure of the main components in pine tar and naphthenic oils is similar to the structure of cyclohexane. And these two oils are generally used reclaiming oils in the rubber industry. So the mixture of them in the mass ratio of 1 : 1 was chosen as diffusant in the experiment. Vulcanized NR was made into 53.5 mm × 10.5 mm × 2.0 mm cubic samples. Each sample was weighed before the diffusion tests. Then the samples were kept immersed in the oil mixture under different temperatures and pressures in a high-temperature, high-pressure tank for 1 h.

After the 1-h diffusion process, the oil on the surface of the samples was wiped away, and the samples were weighed. The weight diffusion parameter P_w, which is actually the weight increase per unit weight, is defined by the following expression:

$$P_w = \frac{M_2 - M_1}{M_1} \tag{3}$$

In eq. (3), M_1 and M_2 are the sample weights before and after the diffusion process, respectively.

Moreover, an optical microscope (transmitted light, 30 times magnification) was used to observe the degree of diffusion of
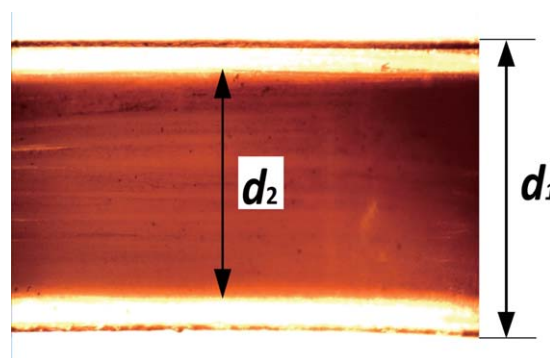

Figure 4. Optical micrograph of cross-section of NR sample after diffusion (d_1 is the thickness of the sample before the diffusion process, and d_2 is the thickness of the section unreached by the oil). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
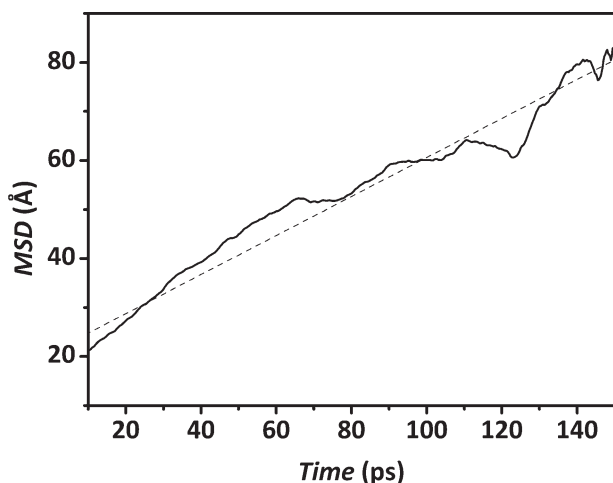
Figure 5. Mean square displacement (MSD) for cyclohexane at 493 K and 1 MPa. The dashed line shows the least-squares fit to the curve.

Figure 7. Values of FFV of cyclohexane in polyisoprene as a function of temperature at 1 MPa calculated by MD simulation. A hard spherical probe with a radius close to zero was used to measure the free volume.

the oil in the rubber sample. Another diffusion parameter P_d was used and is defined by the following equation:

$$P_d = \frac{d_1 - d_2}{2} \tag{4}$$

In eq. (4), d_1 is the thickness of the sample before the diffusion process, and d_2 is the thickness of the section unreached by the oil, as shown in Figure 4.

RESULTS AND DISCUSSION

Effect of Temperature on Diffusion

MD Simulation of Diffusion Coefficients and FFV at Different Temperatures. To calculate the diffusion coefficient, D, of the cyclohexane molecules in polyisoprene, MSD of cyclohexane molecules is plotted against time in Figure 5. The MSD of cyclohexane molecules increases linearly with time.

D can be calculated by both the Einstein relation and the Green-Kubo relation.[26] They give essentially the same result. In this work, D was calculated by the Einstein relation[10]:
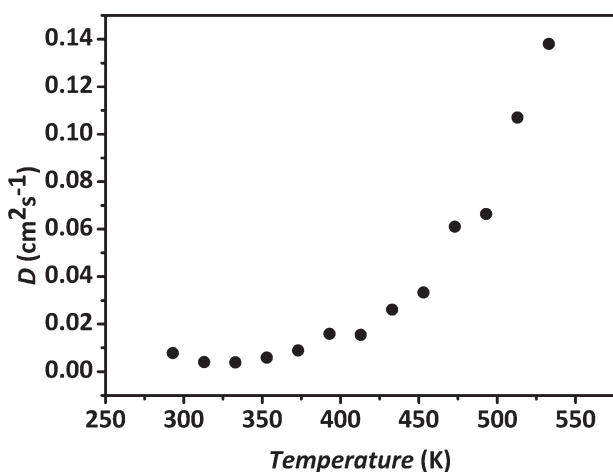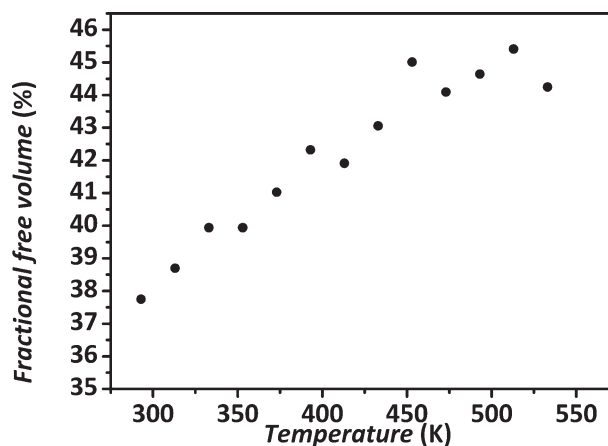

Figure 6. Calculated diffusion coefficient of cyclohexane in polyisoprene as a function of temperature at 1 MPa.

$$D = \frac{1}{6N} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N} \langle (r_i(t) - r_i(0))^2 \rangle \tag{5}$$

where N is the number of diffusive atoms in the system. The above differential is approximated by the ratio of MSD to the time difference, i.e., the slope of the plot of MSD against time. Since the value of MSD is already averaged over the number of atoms, eq. (5) can be simplified to

$$D = a/6 \tag{6}$$

where a is the slope of the MSD versus time curve.

The MSDs of the cyclohexane molecules were calculated over a wide range of temperatures, 293–533 K, in 20 K intervals. The simulated results of Ds at different temperatures under the constant pressure of 1 MPa are shown in Figure 6, which shows that the diffusion coefficient generally increases as the temperature increases. Below 400 K, the increase is not obvious. But the increase becomes significant above 400 K. It is believed that the rate of increase in D increases with increasing temperature because of the enhanced movement of the diffusant molecules. That is, at higher temperatures, the diffusant molecules have higher energy to overcome the activation energy required to enter the new free volume voids.[12] Furthermore, at higher temperatures the mobility of the polymer chains increases, with more chains and segments activated. The increase in mobility also contributes to the increase in D. There are also more free volumes between the chains. In other words, the FFV of the cell enlarged as shown in Figure 7. The free volume was obtained by a hard spherical probe with a radius R_p approaching zero to determine the overall FFV of the model. The overall FFV encompasses all volume unoccupied by polymer molecules. FFV is commonly used to characterize the efficiency of chain packing and the amount of free space in a polymer matrix. A common definition of FFV is given in the following equation:

$$\text{FFV} = \frac{V_{\text{un}}}{V_{\text{un}} + V^*} \tag{7}$$

where V_{un} is the so-called unoccupied volume, which is the free volume in the periodic cell, and V^* is the occupied volume.
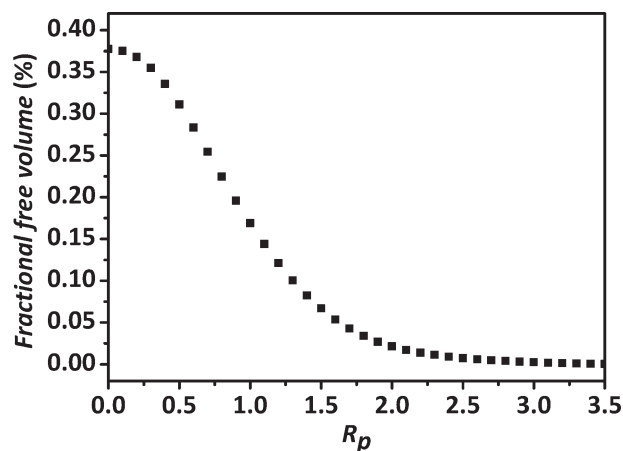
Figure 8. Calculated values of FFV of cyclohexane in polyisoprene as a function of probe radius R_p at 1 MPa and 293 K.

Figure 9. Experimental values of diffusion parameters at different temperatures. The pressure was 1 MPa, and the test time was 1 h.

Usually, V^* is determined from tabulated values of van der Waals volumes (V_w) and $V^* = 1.3V_w$.[27] Figure 7 shows that the FFV increases as the temperature increases. At higher temperatures the chains move and rearrange more easily, so the FFV increases. An increase in the amount of free volume voids enables the diffusant molecules to move more easily, and thus D increases.

The calculated FFV depends strongly on R_p, as shown in Figure 8. The larger the probe, the smaller the calculated FFV. It is noticeable that the plot of FFV against temperature increases almost linearly over the whole temperature range, while the calculated diffusion coefficient increases nonlinearly. The possible reason is that small free volume voids are insignificant in enhancing the diffusion performance[24] and the size of cyclohexane molecule is relatively large. Table I presents the values of FFV at different temperatures, based on free volumes detected by a probe with a radius of 3.03 Å (the collision radius of cyclohexane molecule)[28] and a probe with a radius approaching zero. At lower temperatures, there are few big free volume voids. And the connectivity of these big voids is poor. When enough big free volume voids arise as the temperature increases, a so-called "passage" for cyclohexane molecules to move more easily might occur. Thus, there appears a big increase in D at around 400 K.

Experimental Determination of Diffusion Parameters at Different Temperatures. Diffusion experiments were conducted, and the diffusion parameters obtained are shown in Figure 9. Obviously, the experimental results show a similar trend as the simulation results in Figure 6. After the NR samples were kept in the mixture of naphthenic oil and pine tar for 1 h under the constant pressure of 1 MPa at different temperatures, the diffusion parameters were measured by two methods. Both P_w (the
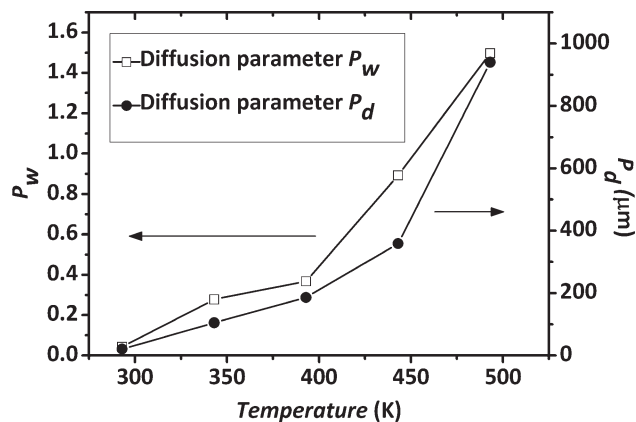
increase in weight per unit weight after diffusion) and P_d (the increase in thickness after diffusion) increase significantly as the temperature goes up. It should be noticed that in equilibrium conditions, P_d would be 1.0 mm, half of the sample thickness. In the diffusion experiments, the highest P_d is only 940 μm, which means the permeation of the oil mixture into the NR samples did not reached the equilibrium. In the other words, the calculated diffusion parameters are about the process of diffusion, which are the same as the simulation.

Besides, the increases are much more remarkable above 400 K, showing good agreement with the simulated diffusion coefficients. The calculated diffusion parameters by both simulation and experiment are listed in Table II.

Effect of Pressure on Diffusion
MD Simulation of Diffusion Coefficients and FFV Under Different Pressures. The diffusion coefficients of cyclohexane molecules in polyisoprene under different pressures from 1 to 5 MPa at the constant temperature of 293 K were calculated through the Einstein relation after the simulation. As shown in Figure 10, unlike the variation in D with temperature, D just fluctuates in the narrow range 0.003–0.015 cm^2·s^{-1} under different pressures. For further confirmation of the relationship between D and pressure, the diffusion coefficients under higher pressures were also calculated. Similar to the slight fluctuations under 5 MPa, the calculated diffusion coefficients under higher pressures also fluctuate slightly.

The inset in Figure 10 compares the effects of temperature and pressure on the calculated D of the studied system. Obviously, the effect of pressure is almost negligible compared with that of temperature.

The FFV of the polyisoprene-cyclohexane system can be determined by MD simulation. Figure 11 shows the calculated FFV

Table I. Values of Fractional Free Volume Calculated by MD Simulation at Different Temperatures of the Polyisoprene-Cyclohexane System

Temp (K)	293	313	333	353	373	393	413	433	453	473	493	513	533
FFV (%) ($R_p = 0.00$Å)	37.75	38.70	39.94	39.94	41.02	42.32	41.91	43.05	45.01	44.09	44.64	45.40	44.25
FFV (%) ($R_p = 3.03$Å)	0.23	0.09	0.32	0.16	0.82	0.59	0.73	0.72	0.61	1.73	1.01	1.15	1.04

Table II. Comparison of Diffusion Parameters Between Simulation (Ds) and Experiment (P_w & P_d)

	$\Delta(T_{393\ K} - T_{293\ K})^a$	$\Delta(T_{493\ K} - T_{393\ K})^b$	$\Delta(T_{493\ K} - T_{393\ K})/\Delta(T_{393\ K} - T_{293\ K})$
D (cm^2 s^{-1}) Sim.	0.00809	0.05051	6.2
P_w Exp.	0.325	1.130	3.5
P_d (μm) Exp.	164.99	754.21	4.6

[a] Increments of calculated diffusion coefficient and parameters from 293 to 393 K.
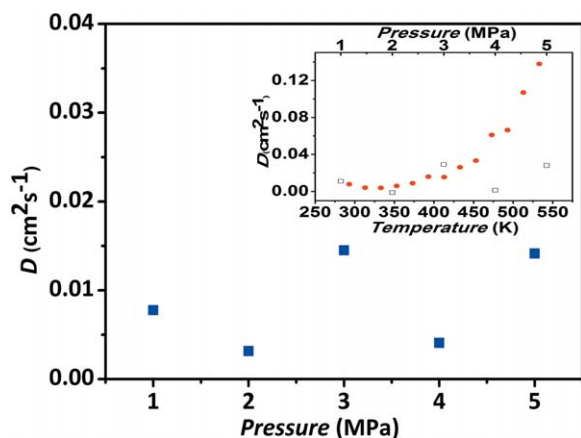[b] Increments of calculated diffusion coefficient and parameters from 393 to 493 K.

Figure 10. Calculated diffusion coefficients of cyclohexane in polyisoprene as a function of pressure at 293 K. The inset compares the temperature dependence and the pressure dependence of the calculated diffusion coefficient. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the system based on free volume measured by a probe of radius close to zero. Similar to the variation in the calculated diffusion coefficients with pressure, the FFV hardly changes as the pressure increases. The inset in Figure 11 compares the
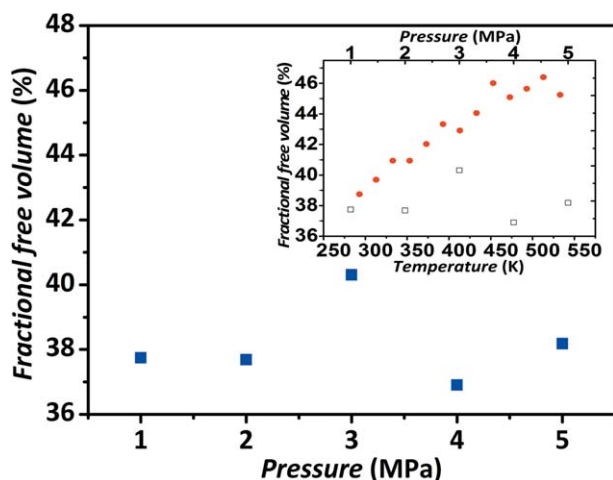

Figure 11. FFV of cyclohexane in polyisoprene calculated by MD simulation as a function of pressure at 293 K. The inset compares the temperature dependence and the pressure dependence of FFV. A hard spherical probe with a radius approaching zero was used to measure the free volume. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

effects of temperature and pressure on FFV of the system. Apparently, the effect of pressure is weaker than that of temperature. The FFV results, in addition to the diffusion coefficient results, indicate that it is of little significance to promote the diffusion by changing the operation pressure.

Experimental Determination of Diffusion Parameters Under Different Pressures. MD simulation shows that the diffusion coefficients hardly change with changing pressure. Subsequent experiments showed good agreement with MD simulation. Figure 12 shows the pressure dependence of the diffusion parameters P_w (the increase in weight per unit weight after diffusion) and P_d (the increase in thickness after diffusion) measured after the NR samples were kept immersed in the mixture of naphthenic oil and pine tar for 1 h at the constant temperature of 293 K under different pressures.

Similar to the simulation results, the experimental results show that the pressure dependence of the diffusion parameters is weak. The slight fluctuations of P_w and P_d with pressure at higher temperatures (not shown) are similar to those shown in Figure 12.

The above results showed that increasing the temperature could accelerate the diffusion process significantly while the effect of pressure on diffusion was small. So it is recommended from both experimental and theoretical points of view to reclaim waste rubber at relatively high temperatures. It is important to note, however, at very high temperature (about 540 K), degradation of the NR main chains occurs, leading to poor quality of the reclaimed product. So the waste rubber should not be over heated.
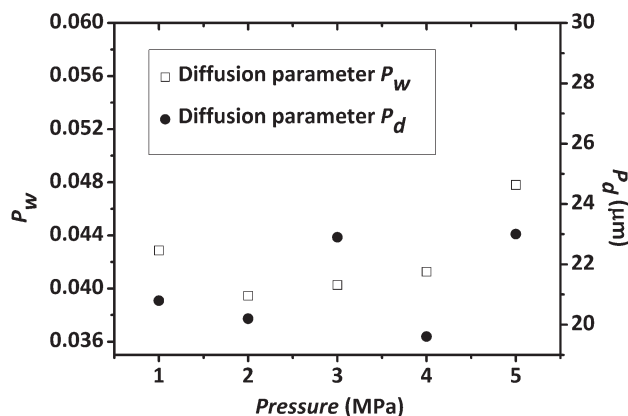

Figure 12. Experimental values of diffusion parameters at different pressures. The temperature was 293 K, and the test time was 1 h.

CONCLUSIONS

MD simulation was conducted to calculate the diffusion coefficients (Ds) and FFVs of the polyisoprene-cyclohexane system over a wide range of temperatures. The simulation results showed that both D and FFV increased as the temperature increased. The increase in D was much more obvious above 400 K. The effect of pressure was also estimated, exhibiting no obvious relationship between D, FFV, and pressure within the range of pressure studied.

The simulation results were in good agreement with experimental results. In the experiments, two diffusion parameters, P_w (the increase in weight per unit weight after diffusion) and P_d (the increase in thickness after diffusion) were measured after the NR samples were kept immersed in a mixture of pine tar and naphthenic oils, whose representative structure is cyclohexane, under different conditions. The combination of simulation and experimental results suggested that relatively high temperatures (below the degradation temperature of the main hydrocarbon chains of the rubber) would be favorable during the reclamation. MD simulation was helpful in understanding the influence of processing parameters in rubber reclamation. The simulated results would provide theoretical guidance for the selection of processing parameters.

ACKNOWLEDGMENTS

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