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Research on the Glass Transition Temperature and Mechanical Properties of Poly(vinyl chloride)/Dioctyl Phthalate (PVC/DOP) Blends by Molecular Dynamics Simulations

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Abstract To effectively improve the performance and expand the applications of polymers, molecular dynamics (MD) simulations with the COMPASS force field have been applied to predict the miscibility, glass transition temperature (T_g), and mechanical properties of poly(vinyl chloride)/dioctyl phthalate (PVC/DOP) blends. The solubility parameter values obtained are in good agreement with the reference data and the little difference ($|\Delta\delta| < 2.0$ MPa$^{0.5}$) between two components indicates that PVC/DOP is a miscible system. T_g is predicted by the slope of the free volume and density versus temperature simulation data based on density and free volume theory which is agree well with the experimental data. In addition, the analyses of mechanical properties results indicate that the values of Young's modulus (E), bulk modulus (K), and shear modulus (G) decrease with the addition of DOP, demonstrating that the rigidity of material is weakened and the ductility is improved. The mechanical properties can also be effectively improved by increasing the temperature, which may provide a more flexible mixture, with lower E, K, G but an increased ductility.

Keywords Poly(vinyl chloride) (PVC); Dioctyl phthalate (DOP); MD simulations; Glass transition temperature; Mechanical properties

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INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the earliest thermoplastic plastics that achieves industrialization production and it exhibits excellent flame retardancy, chemical resistance, abrasion resistance, and electrical insulation.[1] Owing to these remarkable properties, PVC is widely used in medical devices, food packages, chemical industry, coal, computer and radio communications, and many other areas.[2,3] However, neat PVC has high glass transition temperature (T_g) and poor mechanical properties, which has greatly restricted its development and widespread application.[4] To improve the thermal and mechanical properties of PVC, a common method is to add various auxiliaries, such as plasticizer.[5] Dioctyl phthalate (DOP), a versatile PVC plasticizer,[6] can significantly reduce the intermolecular interaction of PVC, thereby lowering T_g and ameliorating the mechanical properties.[7]

In order to ensure the excellent performance of the polymer, the ideal plasticizer must have good compatibility with it. During the design of polymer modification, numerous experiments are needed to find out the most suitable plasticizers that can match polymers, which will cost a great quantity of manpower, materials, and financial resources. Compared with the experimental research, computer simulation that allows systematic variation of structural or physical parameters of the materials is a more direct research method. The miscibility between two components,[8,9] glass transition temperature (T_g),[10−12] and mechanical properties[13−15] of blends can be well predicted by the molecular dynamics simulation technology. These approaches are helpful to predict and understand the properties of materials before experiments. Besides, computer simulations can shorten the development cycle of new materials and greatly reduce the cost and risk of experiments.

In this work, the miscibility between PVC and DOP has been verified by comparing the difference of solubility parameters ($\Delta\delta$). T_g and mechanical properties of the system after adding plasticizer have also been analyzed to study the influence of DOP on PVC performances. An attempt has been made to establish MD simulations versus miscibility, T_g, and mechanical properties of polymers, which can effectively expand the applications of polymers.

SIMULATION METHODS

Modeling

PVC and DOP molecular models were built by visualizer module of Materials Studio (MS) 6.0. Then according to

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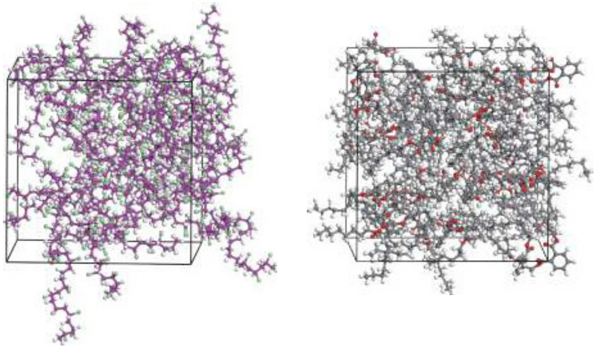
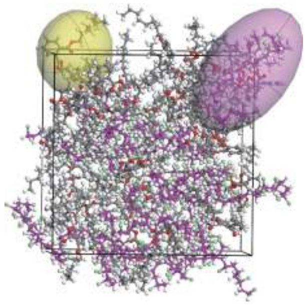
the corresponding density of materials under 298 K and 1.01×10^5 Pa, amorphous cell (AC) models of neat PVC, DOP, and PVC/DOP binary system with DOP mass fractions of 0.092, 0.281, and 0.498 were built by Amorphous cell tool of MS, respectively. In this simulation, the length of each cubic AC model was greater than 3.5 nm, and the total number of atoms in each model was more than 2000. The AC models of PVC, DOP, and PVC/DOP are depicted in Fig. 1.



PVC AC model DOP AC model



PVC/DOP AC model

Fig. 1 Amorphous cells of PVC, DOP, and PVC/DOP blends

Simulation Details

The PVC and DOP molecular models were firstly optimized by molecular mechanics (MM) adequately. Generally, MM is carried out at 0 K, under which the optimal geometry can be obtained for small molecular structure such as DOP but not for macromolecules like PVC. To acquire the equilibrium conformation of PVC, we should conduct the MD simulation under relatively high temperature. Thus, we performed 400 ps MD simulation under NVT (constant number of particles, volume, and temperature) ensemble and COMPASS[16−20] force field at 298 K to explore the optimal conformation of PVC. After the optimal structures of DOP and PVC were obtained, amorphous cell (AC) models of neat PVC, DOP, and PVC/DOP binary system with DOP mass fractions of 0.092, 0.281, and 0.498 were built by Amorphous cell tool of MS, respectively. An annealing process at high temperature was conducted in the following, in which the temperature was lowered from 458 K to 148 K at an interval of 20 K under atmospheric pressure. To acquire the equilibrium conformation fast, the amorphous cell structures of neat PVC and DOP were subjected to a MD simulation of 400 ps under NPT (constant number of particles, pressure, and temperature) ensemble, and then another MD simulation of 400 ps was performed under NVT (constant number of particles, volume, and temperature) ensemble to analyze the properties.

In all the simulations, the periodic boundary condition was applied. Andersen thermostat[21] and Berendsen barostat[22] were selected to control the temperature and pressure, respectively. The Verlet velocity time integration method[23] with a time step of 1 fs was used to integrate the Newtonian equation of motion. The van der Waals interactions were calculated by the atom-based method and the electrostatic interactions were approximated by the Ewald method[24] with an accuracy of 0.4186 $\mathrm{J \cdot mol^{-1}}$. Kitson and Hagler[25] showed that the non-bond energy accounted for changes from 63% to 97% of the asymptotic value as the cutoff distance (d_c) was increased from 0.8 nm to 1.5 nm. Moreover, with the consistent increase of d_c, the accuracy increased very slow while the simulation time sharply increased. Therefore, d_c of 1.55 nm was selected in this study.

RESULTS AND DISCUSSION

The Size of PVC

As the size of PVC molecule used in the model is important for calculating accurate properties, it is necessary to verify the minimum molecular size that is sufficient to represent the real polymer. Only when the system reaches the equilibrium state can the property analysis with production trajectory be meaningful. The equilibrium of temperature and energy should be achieved simultaneously, that is, the fluctuations of temperature and energy are in the range of 5%−10%.[26] As an example, the equilibrium curves of the temperature and energy of 24 repeating units for PVC are displayed in Fig. 2. Based on the former study,[27] the minimum molecular size can be set as when the solubility parameter did not change with the increasing molecular weight. Thus, the solubility parameter of PVC at different molecular weights was studied, and the calculated results are depicted in Fig. 3.

As shown in Fig. 2, the fluctuation of energy is less than 5% and the temperature fluctuates within the range of about 10 K, which means that the system has reached the equilibrium state of the temperature and energy.

Fig. 3 shows that the solubility parameter of PVC decreases sharply at first as the number of repeating units increases but levels off when the number of repeating units is greater than 24 ($M_n = 25534$). Therefore, using 24 repeating units for PVC was sufficient for the simulation.

Simulation of Miscibility of PVC/DOP Blends

Hildebrand *et al.*[28] noticed that the interaction between substances depended on their cohesive energy density (CED). Furthermore, the concept of solubility parameter (δ) defined as the square root of CED was introduced, which is widely used for predicting compatibility between two materials. It refers to the energy required to vaporize a mole of liquid per unit volume and is mathematically defined as below:[29]

$$\delta = (\mathrm{CED})^{\frac{1}{2}} = \left(\frac{\Delta E_{\mathrm{v}}}{V_{\mathrm{m}}}\right)^{\frac{1}{2}} = \left(\frac{\Delta H_{\mathrm{v}} - RT}{V_{\mathrm{m}}}\right)^{\frac{1}{2}} \tag{1}$$

where ΔE_{v} represents the internal energy change of

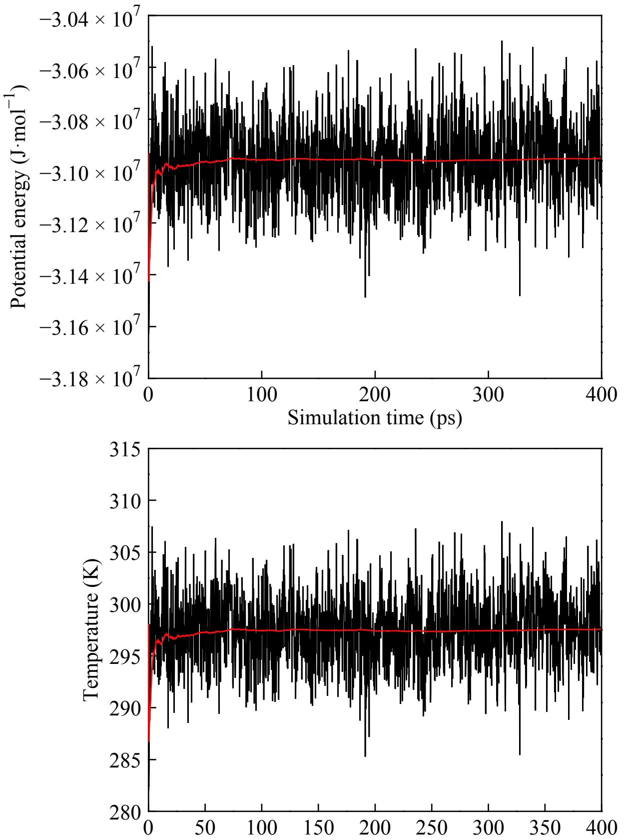


Fig. 2 (a) Energy fluctuation curve and (b) temperature fluctuation curve of 24 repeating units for PVC

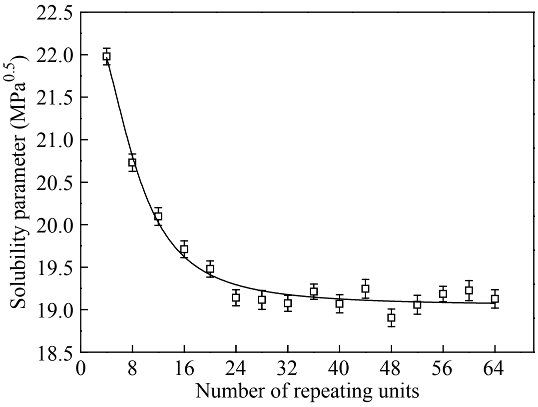


Fig. 3 Computed solubility parameter of PVC versus number of repeating units

vaporization, ΔH_v is the enthalpy of vaporization, and V_m stands for the molar volume of the liquid at the temperature of vaporization. R and T are gas constant and absolute temperature, respectively.

Compounds with similar values of δ are likely to be miscible. This is because the energy of mixing released by interactions within the components is balanced by the energy released by interactions between the components.

When two substances are mixed, the thermodynamic conditions for forming a compatible system are as follows:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} < 0 \tag{2}$$

where ΔH_{mix} and ΔS_{mix} are the enthalpy and entropy of mixing, respectively, and T is the absolute temperature. In general, ΔS_{mix} is usually positive, so ΔH_{mix} is the determining factor. ΔH_{mix} can be expressed in terms of the Hildebrand-Scratchard equation:[30]

$$\Delta H_{mix} = (\delta_1 - \delta_2)^2 V \Phi_1 \Phi_2 \tag{3}$$

where V is the volume of mixture, and Φ is the volume fraction of the components. The smaller difference between δ_1 and δ_2 results in the smaller ΔH_{mix} and ΔG_{mix}, which indicates the better solubility of a system. That is, the difference of the solubility parameters ($\Delta\delta$) can be used as a theoretical prediction index for compatibility between components.

Forster *et al.*[31] have proven that for a polymer system, two components are compatible when the difference of solubility parameter satisfies $|\Delta\delta| < 2.0$ MPa$^{0.5}$ in the absence of strong polar groups or hydrogen bonds between molecules. To ensure the reliability of simulated results, we first calculated the solubility parameters (δ^{cal}) of PVC and DOP and then compared simulated results with the corresponding experimental results (δ^{exp}) taken from literature,[32] as displayed in Table 1.

Table 1 Prediction of miscibility for PVC with DOP by MD simulations

Material	δ^{exp} (MPa$^{0.5}$)	δ^{cal} (MPa$^{0.5}$)	$\lvert\Delta\delta^{cal}\rvert$ (MPa$^{0.5}$)
PVC	19.200–22.100	19.140	0.778
DOP	18.200	18.362	

Table 1 shows obviously that the calculated solubility parameters for PVC and DOP agree well with the experimental values, indicating the reliability of the simulation method applied. Accordingly, PVC and DOP are miscible due to a small $|\Delta\delta^{cal}|$ of 0.778 (< 2.0 MPa$^{0.5}$) between the two components. Therefore, MD simulations can be used to calculate the solubility parameters of other polymers, especially for the polymers whose δ value is difficult to be measured by experiment. However, the repeating units of polymer models constructed by MS are much fewer than those in the real molecules, which will result in some deviation for the simulation results.

Simulation of Glass Transition Temperature (T_g) of PVC/DOP Blends

The glass transition temperature (T_g), which determines the processing and working temperature range, is a key index to evaluate the properties of polymers. Many parameters have been used to predict T_g by MD simulations such as free volume, specific volume, density, radial distribution function, and mean squared displacement modulus,[33] among which free volume (V_F) and density are selected in this work. Both the two methods are based on Fox-Flory's free volume theory. When the temperature is below T_g, V_F and density of a polymer increase slowly with the increasing temperature. Conversely, these two values change dramatically with the variation of temperature.

The comparisons of T_g between experimental and calculated results are summarized in Table 2, where the calculated T_g values agree well with the experimental results. The fitting calculation results are displayed in Figs. 4 and 5.

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According to the change in density or free volume as a function of temperature, it is clear for all PVC/DOP systems (Figs. 4 and 5) that density decreases with increasing temperature and the variation tendency of free volume is just the opposite. We can observe the change in the slope, which is due to different linear relationships between free volume and temperature below and above the glass transition temperature.

Table 2 The comparison of T_g between experimental and calculated results

Sample	Experiment (K)	Density method (K)	Volume method (K)
PVC	354.15	365.42	363.68
90.8PVC/9.2DOP	328.15	334.61	335.86
71.9PVC/28.1DOP	295.15	305.91	304.02
50.2PVC/49.8DOP	228.15	234.06	235.47

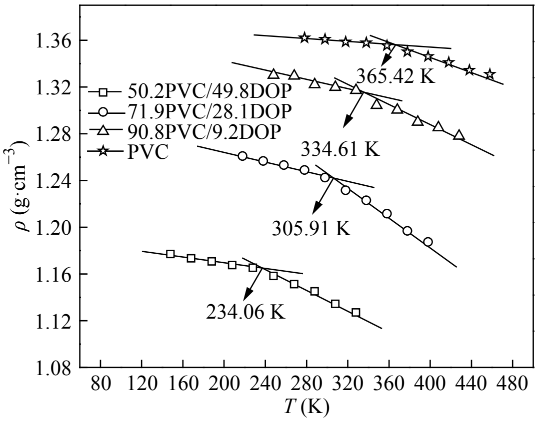

Fig. 4 Variation curves of calculated ρ versus T of PVC/DOP systems with different DOP mass fractions

An obvious turning point exists in the slope of each curve, which determines T_g of the PVC/DOP sample. When the temperature is below T_g, the initial interactions between PVC are strong, which constrains the motion of atoms and results in the small V_F. The interactions between PVC molecules decrease gradually with the increase of temperature so that the motivations of atoms are enhanced and V_F will increase. When the temperature is higher than T_g, PVC molecules can move along the molecular chain to some extent, which results in the significant increase of V_F. Besides, we also find that T_g decreases with an increase of the DOP mass fraction in both density and volume methods, because the interactions between PVC are weakened by DOP.

Although the T_g values obtained by MD simulation method agree well with the experimental values, T_g of polymers determined by the experimental method is usually on the time scale of seconds or minutes, while that of the MD method is on the time scale of picoseconds or femtoseconds. The difference between these two methods is more than 10^{12}, which is one of the reasons for the controversy of using MD simulation to study T_g.[34] Since the cooling rate in molecular dynamics simulation is much faster than that in normal experiments, the T_g value obtained by simulation is slightly

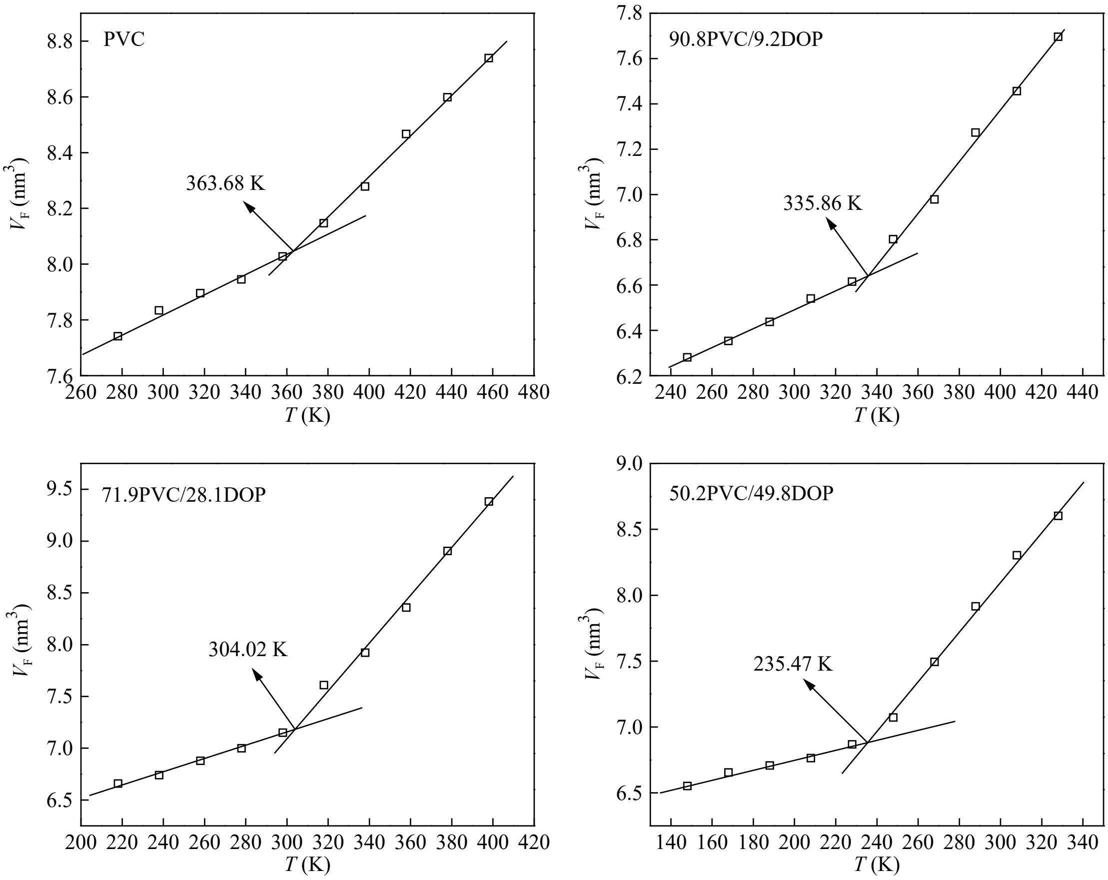

Fig. 5 Variation curves of calculated V_F versus T of PVC/DOP systems with different DOP mass fractions

higher than the experimental value.[35]

Simulation of Mechanical Properties of PVC/DOP Blends

Mechanical properties are related to the preparation, processing, production, and application of polymers. The most general relation between the stress σ and strain tensors ε of a material obeys the generalized Hooke's law as the following equation:[36]

$$\sigma_i = C_{ij}\varepsilon_j \tag{4}$$

where C_{ij} is a symmetric (6 × 6) matrix of elastic coefficients. The symmetry of the matrix reduces the number of coefficients to 21 to describe the relationship between stress and strain for anisotropic materials.

Based on Reuss mean method,[37] the effective bulk modulus and shear modulus are given by the following equations:

$$K_{\mathrm{R}} = [S_{11}+S_{22}+S_{33}+2(S_{12}+S_{23}+S_{31})]^{-1} \tag{5}$$

$$G_{\mathrm{R}} = 5[4(S_{11}+S_{22}+S_{33})-4(S_{12}+S_{23}+S_{31})+(S_{44}+S_{55}+S_{66})] \tag{6}$$

where the subscript R denotes the Reuss average. The compliance matrix S is equal to the inverse matrix of elastic coefficient matrix C, *i.e.*, $S = C^{-1}$, which can be calculated by MD simulation.

The equilibrium PVC/DOP AC models with DOP mass fractions of 0.092, 0.281, and 0.498 are subjected to further series of dynamics in NPT ensembles for 400 ps, followed by the MD simulation in NVT ensembles for 400 ps to calculate K and G of the PVC/DOP system. Afterwards, the tensile modulus (E) and Poisson's ratio (v) can be calculated by the following equation:

$$E = 2G(1+v) = 3K(1-2v) \tag{7}$$

Plastic properties, such as hardness, tensile strength, fracture strength, and elongation in tension, can be related to the elastic moduli.[38] Hardness and tensile strength representing the resistance to plastic deformation are proportional to the shear modulus G. Fracture strength is proportional to the bulk modulus K. The quotient K/G indicates the extent of the plastic range (elongation in tension), so that a high value of K/G is associated with ductility and a low value with brittleness.

It is well known that temperature and plasticizer content are two main factors affecting the mechanical properties of polymers. To research the effect of temperature on mechanical properties of PVC, mechanical moduli were calculated at different temperatures (298, 318, 338, and 358 K), with the results shown in Table 3 and Fig. 6.

Table 3 Elastic coefficients and effective isotropic mechanical properties of PVC at different temperatures

	298 K	318 K	338 K	358 K
C_{11}	4.4557	3.6880	3.5541	4.1272
C_{22}	3.8095	4.4420	2.8771	3.6831
C_{33}	5.0691	4.4124	3.5244	4.5177
C_{44}	1.3983	0.9125	0.8722	0.8996
C_{55}	1.4193	1.0138	0.9337	0.7132
C_{66}	1.0151	1.3610	0.5342	0.5367
C_{12}	2.5908	1.9710	1.6018	1.9736
C_{13}	2.5411	2.2380	1.8282	1.4259
C_{23}	2.0022	2.4770	1.6889	2.1595
$C_{12} - C_{44}$	1.1925	1.0585	0.7296	1.0740
E (GPa)	2.8651	2.3266	1.7165	1.3262
K (GPa)	2.9470	2.6544	2.1309	1.8160
G (GPa)	1.0707	0.8592	0.6284	0.4811
v	0.3380	0.3539	0.3657	0.3783
K (GPa)	2.7524	3.0894	3.3910	3.7747

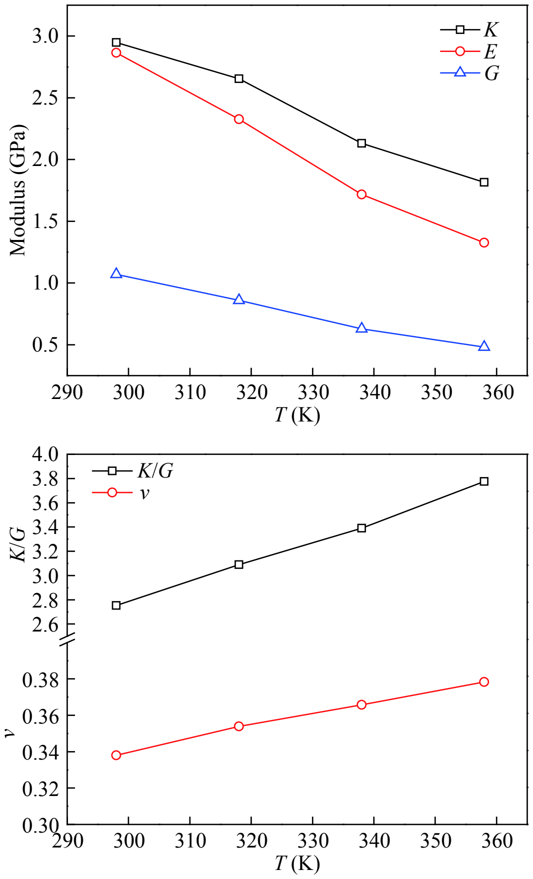

Fig. 6 Mechanical properties of PVC at different temperatures

From the relations between elastic moduli and plastic properties as well as the data of E, K, and G in Table 3, it can be clearly found that the hardness, tensile strength, and fracture strength of PVC decrease significantly with the increasing temperature. Due to the intensification of thermal motion of molecular segments, relaxation process accelerates, resulting in the decrease of modulus and rigidity of materials, and materials gradually change from glass state to high elastic state.

As for K/G and Poisson's ratio (v), Fig. 6 reveals the changing regularity, which agrees with the intuition. The ratio of K/G reflects the extent of plastic range. Higher value of K/G suggests better ductility. On the other hand, v reflects the flexibility. Materials exhibit excellent flexibility when the value of v is between 0.2 and 0.4. The simulation results show that the value of K/G increases with the rise of temperature and the values of v are about 0.3, indicating that the isotropy and flexibility of PVC increase with the increasing temperature.

Among these elastic coefficients, C_{12} is only related to tensile stress and C_{44} is related to shear stress. When C_{12} is greater than C_{44}, materials are prone to shear deformation,

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namely their ductility is better. The tensile deformation readily occurs when C_{12} is smaller than C_{44}, resulting in the brittleness of materials. Accordingly, the ductility and brittleness of materials can be evaluated by Cauchy pressure ($C_{12} - C_{44}$). The positive values of ($C_{12} - C_{44}$) indicate good ductility of PVC.

In addition, we have studied the influence of DOP content on mechanical properties of PVC. The engineering moduli of PVC/DOP binary system were calculated at 298 K with different DOP mass fractions (0.092, 0.281, and 0.498), with the results listed in Table 4 and Fig. 7.

From the data in Table 4, we can see that the engineering moduli of all those of PVC/DOP blends become dramatically low compared with those of neat PVC, and as the concentration of DOP increases, the moduli of PVC/DOP decrease. This is because the chain of plasticizer DOP, owing to the internal rotation of their bonds, is more flexible than PVC molecule. So, when the DOP concentration increases, PVC/DOP blends contain more flexible molecular chains and become more easily deformed once they are acted by external force, and thus the moduli decrease. We can deduce that the fracture strength, hardness, and tensile strength of the PVC/DOP blends also diminish greatly compared with those of neat PVC.

Table 4 Elastic coefficients and effective isotropic mechanical properties of PVC/DOP systems

	PVC	90.8PVC/ 9.2DOP	71.9PVC/ 28.1DOP	50.2PVC/ 49.8DOP
C_{11}	4.4557	5.0392	4.6554	2.7080
C_{22}	3.8095	3.8733	4.0044	3.9271
C_{33}	5.0691	4.4109	3.8805	3.7188
C_{44}	1.3983	1.1010	0.6529	0.5969
C_{55}	1.4193	0.9559	0.9467	0.9486
C_{66}	1.0151	1.0292	0.7692	0.4488
C_{12}	2.5908	1.9507	1.9678	1.8470
C_{13}	2.5411	2.6142	2.0144	1.6751
C_{23}	2.0022	3.2295	2.0310	1.9899
$C_{12} - C_{44}$	1.1925	0.8497	1.3149	1.2501
E (GPa)	2.8651	2.6482	2.2835	1.4070
K (GPa)	2.9470	2.8743	2.6853	2.0803
G (GPa)	1.0707	0.9834	0.8406	0.5071
v	0.3380	0.3464	0.3583	0.3873
K/G	2.7524	2.9228	3.1945	4.1023

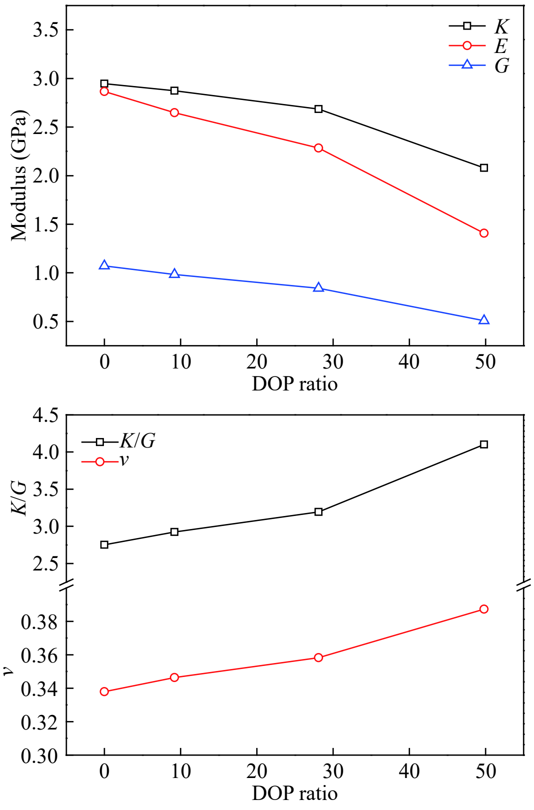

Fig. 7 Mechanical properties of PVC/DOP systems

Furthermore, the simulation results show that the value of K/G increases with an increase of DOP mass ratio. So, the addition of DOP can improve the ductility of PVC. Poisson's ratios of the PVC/DOP systems are between 0.2 and 0.4, demonstrating that PVC/DOP systems have properties of plastomer. Moreover, the positive values of ($C_{12} - C_{44}$) indicate that the PVC/DOP blends are ductile materials at 298 K.

CONCLUSIONS

According to the molecular dynamics (MD) simulations of neat PVC, DOP, and PVC/DOP blends, the miscibility, glass transition temperature, and mechanical properties of the PVC/DOP binary system are calculated and predicted. $|\Delta\delta^{\mathrm{cal}}|$ between PVC and DOP is 0.778 (< 2.0 $\mathrm{MPa}^{0.5}$), indicating that the two components are miscible. Besides, T_g values calculated by two methods decrease with the increase of DOP mass fraction, which shows a good agreement with the literature values. So, molecular dynamics can be used as a powerful tool for predicting T_g of polymer materials and their blends. Finally, mechanical properties of PVC can be effectively improved by blending suitable plasticizers or increasing temperature according to the analysis of elastic constant. All in all, MD simulations on the PVC/DOP binary system provide us with much information about their miscibility, glass transition temperature, and mechanical properties. To choose an optimal polymer binder, it is necessary to consider various aspects comprehensively according to the practical requirements. These are useful for promoting the applications of polymers.

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