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Mechanical property prediction of starch/polymer composites by molecular dynamics simulation

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Molecular dynamics (MD) simulation was used to investigate the mechanical properties of several starch composites. The copolymer materials blended with the starch include amylose/poly(vinyl alcohol) (PVOH), amylose/poly(caprolactone) (PCL), amylose/poly (butylenesuccinate) (PBS), amylopectin/PVOH, amylopectin/PCL, and amylopectin/PBS). The starch was mixed with each of these copolymers at different weight fractions. The degree of crystallinity of each starch composite was observed by the corresponding X-ray diffraction (XRD) profile.

Introduction

In recent years, natural polymers have attracted much attention because they can be naturally biodegraded. Natural polymers have many advantages, such as biocompatibility, biodegradability and non-toxicity[1]. However, the mechanical properties of natural polymers are weaker than those of other polymer materials[2]. Hence, if we can add other polymer materials into natural polymers to enhance their mechanical properties, they can be used in more applications. Starch is one popular natural polymer material due to the fact that it can be easily produced from plants, and is therefore very inexpensive[3]. In order to improve starch's mechanical properties, some biodegradable polymer materials with better mechanical properties can be mixed with starch, such as poly(vinyl alcohol) (PVOH), poly(caprolactone) (PCL), or poly(butylene-succinate) (PBS)[4]. Many researchers have investigated composite materials in this method. In experiment, El-Hadi *et al.* investigated the relationship between mechanical property and degree of crystallinity of poly(hydroxybutyrate) (PHB)/poly(hydroxyvalerate) (PHV). They found that the mechanical property increases at a higher degree of crystallinity[5]. Jiang *et al.* discovered that the interaction between two polymer materials affects mechanical properties. When the interaction between different materials is larger than that between same material, the mechanical property of the composite material can be enhanced[6]. Yu *et al.* studied the weight fraction effect of PCL/starch composite material.When the PCL/starch composite material weight fraction is 1:9, the yield strength is superior to pristine PCL material[7]. Rosa *et al* used differential scanning calorimetry (DSC) to investigate the composite material of PCL/starch. They demonstrated that the more starch in the PCL polymer, the lower the crystallinity of the composite material. In addition, the decrease crystallinity means two materials are immiscible[8]. R. Mani et al. indicated that the degree of crystallinity for composites material at all weight fractions is better than that of pristine starch. In addition, when weight fraction of starch is 10 %, the degree of crystallinity for composite material is higher than that of pristine PCL[9]. In simulation, molecular dynamics simulation is usually utilized to investigate such composite materials. A. Adnan used molecular dynamics simulation to study the composite material of PE/bucky-ball. They found the elastic property can be enhanced because the interaction between the bucky-ball and PE is higher than PE and itself[10]. R. Zhu *et al.* discovered the mechanical property of a composite material of carbon nanotube (CNT)/Epon 862 can be enhanced. In addition, when the CNTs in the composite material become longer, its mechanical property improves[11].

The studies above have demonstrated that the degree of crystallinity has a significant effect on the mechanical property of composite material[12], and the degree of crystallinity is affected by the different weight fractions. Hence, three composite materials are here investigated at different weight fractions by molecular dynamics simulation. The base material of the three composite materials is one of two starches (amylose and amylopectin); the three polymers which are mixed with them are PCL, PVOH, and PBS. There are six weight fractions (0%, 20%, 40%, 60%, 80%, and 100%) of composite polymer/starch material. Therefore, there are a total of 24 composite mixes, as well as two 0% pure starches, and three 100% pure polymers. The degree of crystallinity and X-ray diffraction (XRD) is utilized to analyze the mechanical properties for these three composite materials at different weight fractions.

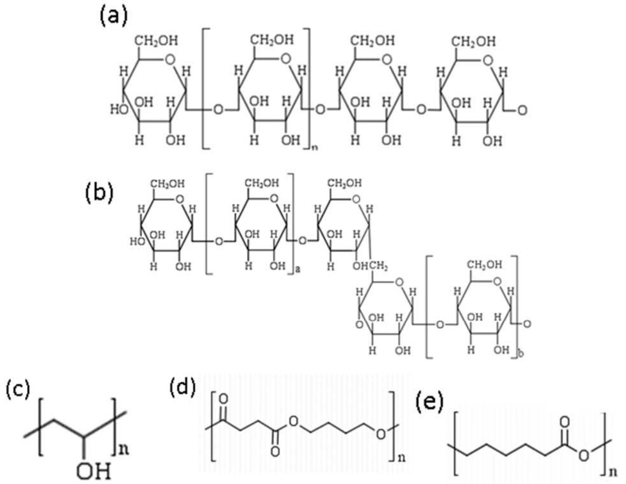

Fig.1 Chemical structures of (a) amylose, (b) amylopectin, (c) PVOH, (d) PCL and (e) PBS

Simulation model

These MD simulations were carried out by the Discover and Amorphous Cell module[13]. The COMPASS potential[14] ,velocity scale thermostat[15] and Andersen barostat[16] were used in our simulation at a time step of 1 fs for the trajectory integration. Figure 1 shows the chemical structures of amylose, amylopectin, PVOH, PCL and PBS monomers. The procedure to obtain equilibrium configurations of the pure material and mixing material systems is described as follows: (1) The material chains were randomly distributed in a large simulation box. (2) After optimization by the conjugate gradient algorithm[15], the system was quenched from 1000K to 300 K with a cooling rate of 50 K per ps at 0.1GPa by an isobaric-isothermal ensemble (NPT). (3) Finally, the MD simulation was performed at 298 K and 1 atm for 100 ps to obtain the equilibrium state. (4) Structures which reached the equilibrium state were then used to calculate the degree of crystallization. We calculated the X-ray diffraction patterns using the Reflex module[13] after equilibrium configurations of the procedure.

In the calculations, the diffract meter range 2θ was set from 1° to 45° with a step size of 0.05 degree and the copper X-ray source anodes were set to radiation wavelength of 1.540562Å. We calculated the degree of crystallization after comparing the experimental XRD patterns to the patterns of the structure generated from the MD simulations. For the degree of crystallinity calculations, the mixture diffraction pattern is composed of the crystalline phase, the amorphous phase and a background contribution. The intensity of input mixture diffraction pattern can be defined as:

$$I_m(2\theta) = I_{cr}(2\theta) + I_{am}(2\theta) + I_b(2\theta) \tag{1}$$

where I_{cr} , I_{am} and I_b, are the sums of the scattering intensities from the crystalline, amorphous phase, and background contribution, respectively.

To obtain the relative weight of the crystalline phase in the decomposition of the mixture diffraction pattern, we can calculate the degree of crystallinity (X_{cr}) from quantitative phase analysis (QPA) theory[17]. This can be defined as the scattering intensity of a powder sample of a single pure phase:

$$I_{cr} = p_{cr} I_{cr}^{norm}(2\theta) \tag{2}$$

$$I_{am} = p_{am} I_{am}^{norm}(2\theta) \tag{3}$$

$$X_{cr} = \frac{p_{cr}}{p_{cr}+p_{am}} \tag{4}$$

where p_{cr} is intensity factors, and X_{cr} describes crystalline regions (p_{cr}) and amorphous regions (p_{am}) of materials in the weight of the total value.

Table1. Number of atoms per chain and chains in the simulation system

Sample	Number of atoms	chains in the simulation system
Amylose	2102	5
Amylopectin	4181	3
PVOH	352	30
PCL	273	40
PBS	407	25

Results and discussion

In order to confirm that the COMPASS potential is suitable to represent the properties of amylose, amylopectin, PVOH, PCL and PBS, the numbers of monomer and polymer chains are listed in Table 1, and Table 2 lists the density and solubility parameters from both experiment and our simulation results. These results indicate that densities from simulation are very close to those of experiment, with an error of about 6.1%. The solubility parameter can be obtained from the cohesive energy. In addition, solubility parameters of simulation are close to those of experiment. This suggests that the COMPASS potential can indeed reflect the properties of the materials. Figure 2(a)-(e) shows the X-ray diffraction (XRD) for pristine amylose, amylopectin, PVOH, PCL and PBS from our simulation results, and clearly indicate one peak in each figure. The highest peak value of Figure 2(a) is located at 15°, with the highest peak obtained from experiment located at 18° [18]. Similar results can be found for Figure 2(b)-2(e) in comparisons of simulation and experiment[19-22]. The highest peak values in Figure 2(b)-2(e) are 17°, 20°, 20° and 20°, while those of experiment are 18°, 18°, 20° and 22°. This indicates that the structures in our simulation for pristine polymers are similar to those in experiments.

In this study, we want to enhance the mechanical properties of amylose and amylopectin, by an admixture of PVOH, PCL and PBS at different weight fractions. Figure 3(a) shows the crystallinity of starches/PVOH at weight fractions of 0%, 20%, 40%, 60%, 80% and 100%. The solid line with circle symbols and dashed line with square symbols represent amylose and amylopectin composite materials, respectively. From Figure 3(a), both pristine amylose and amylopectin have the lowest values of crystallinity. Moreover, the crystallinity of pristine PVOH is higher than that of pristine amylose and amylopectin. Hence, we may predict the mechanical property of starches/PVOH could be better than the pristine starch from Rosa's manuscript[8]. They demonstrated that composite materials have higher crystallinity, and the mechanical property of them will be better. Moreover, the pristine starch have the lowest crystallinity. Further, the crystallinities of amylose/PVOH at all weight fractions are lower than that of pristine PVOH. Only in amylopectin/PVOH weight fractions of 20, 40 and 60% are the crystallinities lower than pristine PVOH. However, when the PVOH weight fraction is 80%, the crystallinity is higher than pristine PVOH. Figure 3(b) shows the crystallinity of starches/PCL at different weight fractions. Note that the crystallinity of pristine PCL is higher than those of pristine amylose and amylopectin. The tendency in Figure 3(b) is the same as that of Figure 3(a) in terms of the relative crystallinity values of amylopectin and amylose composites. We found that the crystallinity of amylopectin/PCL is higher than those of amylose/PCL, excluding at weight fraction of 20%. This can be attributed that the fact that the amylopectin molecule has branches. Its greater number of branches causes there to be a smaller volume in the composite material. When PCL is located in the smaller volume space, the probability of forming higher crystallinity is higher because the smaller volume limits the PCL, which arranges along the boundary. Figure 3(c) shows the crystallinity of starches/PBS at different weight fractions, and shows a similar tendency as that in 3(b). Figure 3(a)-(c) demonstrates that the crystallinity of pristine PVOH is higher than those of PCL and PBS. This can be attributed to the fact that hydrogen bonding can form in the PVOH molecule. In addition, the crystallinity of PCL is higher than PBS, which can be attributed to the fact that the length of a PCL chain is shorter than that of a PBS chain. When the chain is longer, the crystallinity becomes lower. For all cases, when the weight fractions of PVOH, PCL and PBS are 20%, the crystallinity for amylose and amylopectin composites are very close because the amounts of PVOH, PCL and PBS are insufficient to influence the system. It is clear that the amylopectin composite materials have higher crystallinity because its more branches constrain the amount of the composite material, so PVOH, PCL and PBS rearrange along the boundary of amylopectin. Finally, a comparison of the crystallinity of the similarly-structured amylopectin/PCL and amylopectin/PBS shows that the crystallinity of amylopectin/PCL is higher than that of amylopectin/PBS at weight fractions higher than 40%. This is because PCL has shorter chains, and shorter chain lengths increase the probability to form higher crystallinity. In addition, form experimental results[9] which showed that the composites materials can have the highest degree of crystallinity at specific weight fraction than those of pristine starch and enhancement material. We also can find the similar phenomenon in our simulation results. Figure 4 shows the snapshots of the pristine amylopectin, and the amylopectin composites with 80% PVOH, 60% PCL, and 40% PBS, which display the highest crystallinity among the respective admixture. In Fig. 4(b), it seems the amylopectin chains tend to aggregate with the PVOH matrix, and the amylopectin chains within in the PCL and PBS look more stretched.

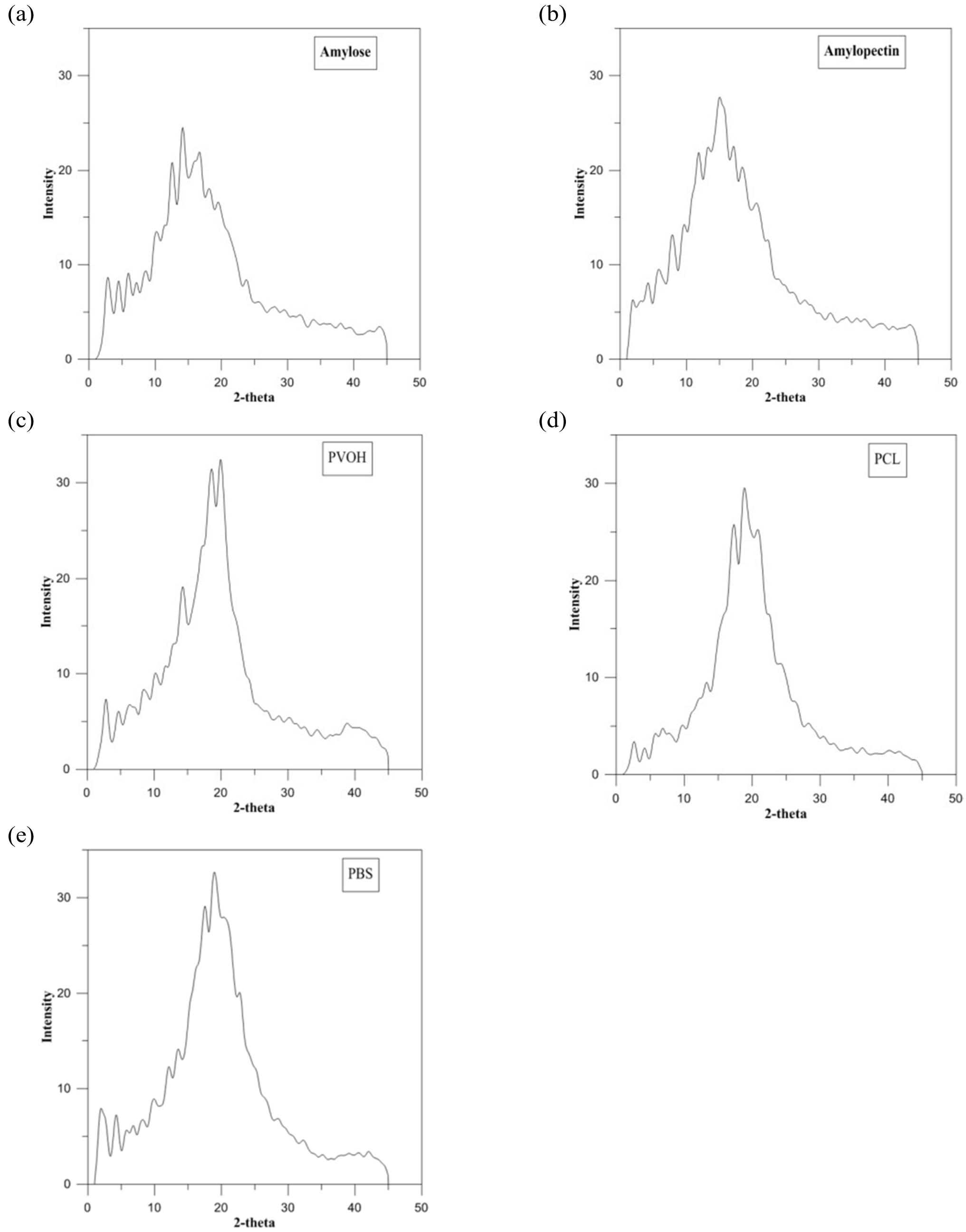

Fig.2 X-ray diffraction (XRD) for pristine (a) amylose, (b) amylopectin, (c) PVOH, (d) PCL and (e) PBS

Table2. Density and solubility parameters for amylose, amylopectin, PVOH, PCL and PBS

Sample	**Density(kg/m^3)**			**Solubility parameter,δ (cal/cm^3)$^{0.5}$**		
	Experiment	Simulation	Error	Experiment	Simulation	Error
Amylose	1.43[23]	1.41	1.3%	12.10[24]	11.97	0.3%
Amylopectin	1.43[23]	1.42	0.7%	12.10[24]	10.52	13.1%
PVOH	1.31[25]	1.23	6.1%	12.63[25]	11.03	12.6%
PCL	1.09[25]	1.05	3.7%	10.19[26]	8.82	13.4%
PBS	1.22[27]	1.16	4.9%		9.61	

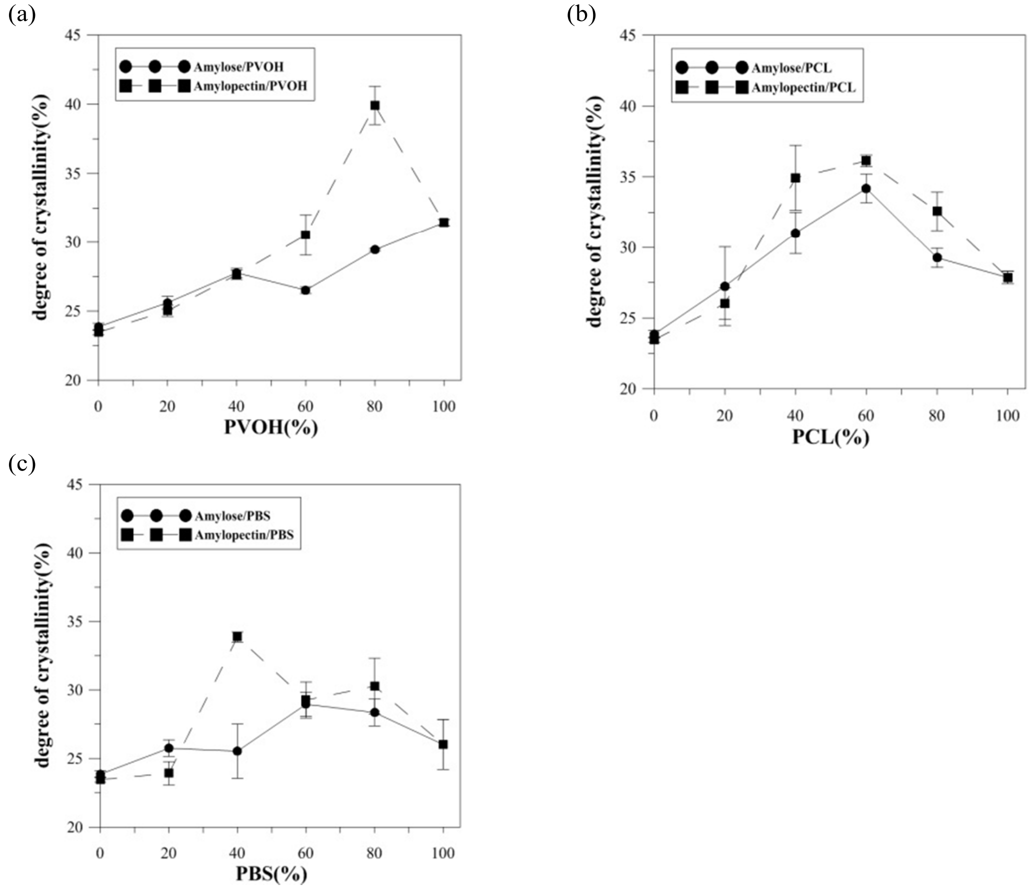

Fig.3 The crystallinity of (a) amylose/PVOH and amylopectin/PVOH, (b) amylose/PCL and amylopectin/PCL and (c) amylose/PBS and amylopectin/PBS at different weight fractions

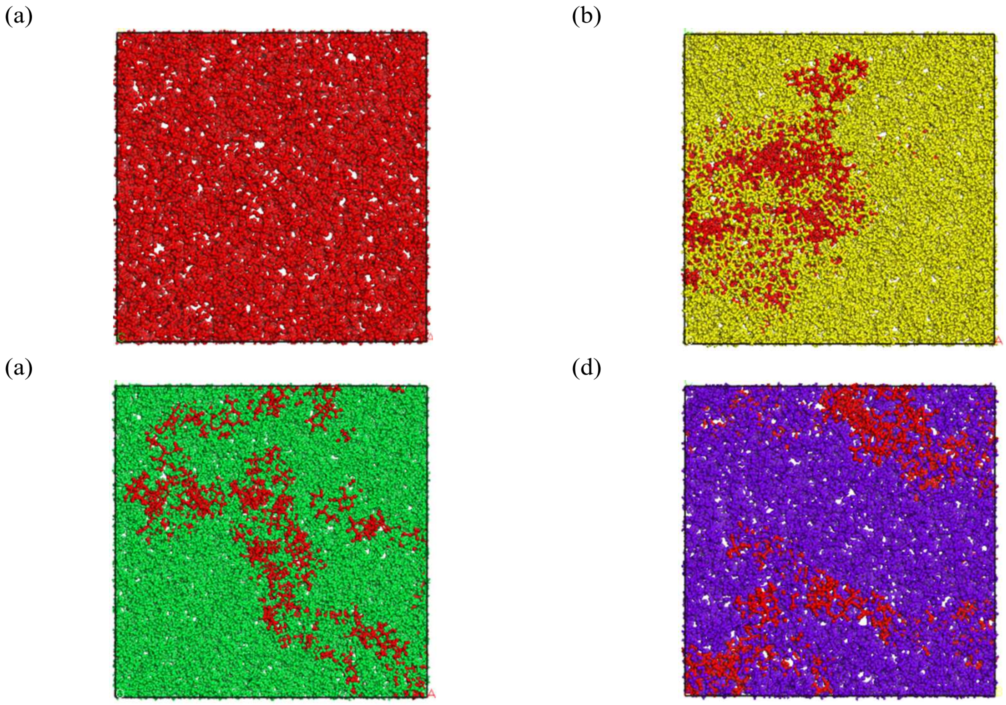

Fig.4 Simulation snapshots of (a) pristine amylopectin, and amylopectin composites at (b) 80% PVOH, (c) 60% PCL, and (d) 40% PBS. (Red: amylopectin; Yellow: PVOH; Green: PCL; Purple: PBS)

Conclusions

In this study, molecular dynamics simulation is utilized to investigate crystallinity of the composite materials amylose/PVOH, amylose/PBS, amylose/PCL, amylopectin /PVOH, amylopectin/PBS and amylopectin/PCL. At polymer weight fractions of 20%, the difference between amylose and amylopectin is insignificant. When weight fraction is higher than 40%, the crystallinity of amylopectin/polymer is higher than that of amylose/polymer. This is due the branching molecular structure of amylopectin, such that the polymers rearrange along the boundary of the volume. In addition, when the polymer chain is longer, it has lower probability to form higher crystallinity. From the mention above, the molecular dynamics simulation is a great tool to predict the crystallinity of composite, which can save the cost and time obviously in material design.

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Notes and references

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