Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2016, 8(8):39-44

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Effects of modified nano-particles on the mechanical properties of SiO_2/PI composite

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ABSTRACT

Nano-particle reinforced polymer composites are widely applied in many fields because of good mechanical properties. In this paper, the cell model of SiO_2/PI composite is built by the molecular dynamics simulation software Materials Studio, three processing methods are acted on the SiO_2 nano-particle, -Si-C_3H_7 treatment, directly grafted with polyimide, covalently grafted with polyimide, effects of the modification methods on the mechanical properties of nano-particle reinforced polymer composites are studied. The mechanism of nano-particle surface modification effect on the composite is discussed through analyzing the potential change between the nano-particles and polymer matrix.

Keywords: nano-composites, molecular dynamics, nano-particle, modification treatment

INTRODUCTION

Compared with the large scale reinforcement, the enhance effect of nano scale reinforcement on the mechanical properties of composites is obvious. In recent years, researchers have devoted to the simulation research of the characteristic of nano-particle reinforced polymer composites and made many valuable research results. However, the compatibility with most matrix of nano-particle is not very good because of high surface activity, easily reunite, then its excellent nano size effect is limited. based on the moderate structured with good dispersion and surface modification with efficient function are important factors to improve the performance of nano-particle reinforced composites [1-4]. Surface grafting method is an important method of nano-particle surface modification treatment, the surface grafting method including the growth of polymer grafting method, synchronize with grafting polymerization method and accidentally join copolymerization, the chemical connection of nano-particles and polymer chains can give full play to their respective advantages, to achieve optimal design of composite materials.

Studies on the nano-particles modification are many, mostly to analyze the influence of different surface modification methods of material mechanics performance by experimental methods. Zhang [5], Chan [6], Jesionowski [7], Li [8] et al. modified nano-particle with the coupling agent, found that the properties of composites were improved; Rong [9], Rong [10], Shan [11] *et al*. grafted nano-particles and polymer with different chemical methods, predicted that some kinds of orderly structure were formed; the Young's moduli, and tensile strength were improved significantly.

Because of the diversity of different researchers, their experiment results showed great differences. With the development of molecular force field, simulated molecular system and the computer hardware and software, the molecular dynamics method is widely applied in the related research of the enhanced toughening mechanism of composites. In terms of molecular dynamics simulation, researchers have also done a lot of related research.

Odegard *et al*. [12] compared the effects of different surface treatment methods, analyzed the results of nano-particle and matrix before and after grafting, the results show that the properties improved after grafting. Yang *et al*. [13] covalently grafted nanosilica polyimide composites, the mechanical properties were improved obviously. Normally, the entangle effect between grafting chain and molecular chain can obviously increase the interaction of nano-particles and matrix, and modified SiO_2 particles can improve the mechanical properties of composites. But Tinashe *et al*. [14] established the cell model of nano-particles polystyrene composite based on the atomic MD simulation, calculated the mechanical properties after the grafting treatment, put forward that with the grafting rate increased, the permeability of the free molecular chain in polystyrene reduced, the enhancement effects were not significant.

In order to study the effects of nano-particle surface modification and grafting ratio on the mechanical properties of composites further, it built the cell model of SiO_2/PI composite, treated SiO_2 particles with Si-C_3H_7 treatment, directed grafted with polyimide, covalently grafted with polyimide in this paper, studied the mechanical properties after different surface treatment, analyzed the effects of particle size, surface treatment method and grafting ratio on the mechanical properties, and the mechanism of nano-particle surface modification effect on the composite was discussed through analyzing the potential change between the nano-particles and polymer matrix.

EXPERIMENTAL SECTION

Model of SiO2/PI and Simulation Procedures

In all molecular model and simulation procedures, Materials Studio (MS) as a commercially available simulation software was used. This paper studies SiO_2 nano-particle reinforced polyimide composite, with PMDA-ODA polyimide as basic material and SiO_2 nano-particle as enhance body, the molecular structure of polyimide is shown in Figure 1.

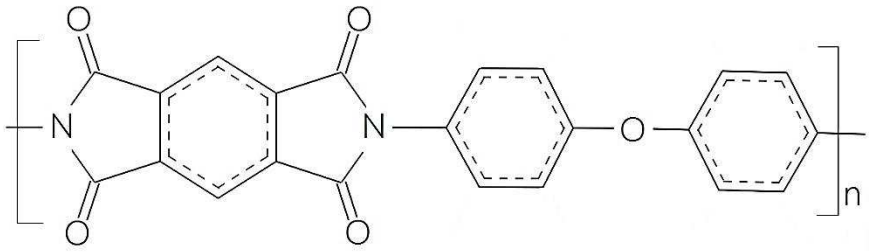

Fig. 1 The molecular structure of PMDA

The ball-and-stick model of PI repeat unit with an appropriate degree of polymerization is built by Materials Studio software, the structure with low potential is obtained by geometry optimization; the crystal cell of SiO_2 is built by its parameters, its low potential form is also obtained by geometry optimization; the periodical unit cell model of SiO_2/PI is established by Amorphous Cell module, its stable state after geometry optimization is shown in Fig. 2.

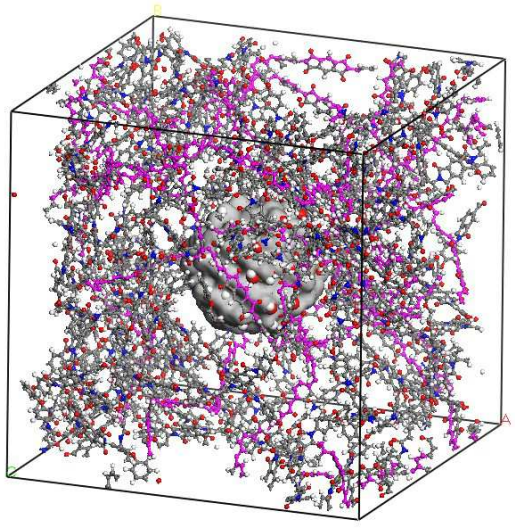

Fig. 2 the unit cell model of SiO_2/PI

Selecting Mechanical properties in the Task of Forcite module, the mechanical properties can be calculated with appropriate precision and parameters, then the stiffness matrix of the unit cell model of SiO_2/PI is obtained, further the mechanical parameters such as elastic modulus, bulk modulus, shear modulus and poisson's ratio of the unit cell under the isotropic hypothesis are obtained. In order to study the effect of the particle size and grafting ratio, the volume fraction of nano-particle is set at 5%, five models were simulated independently, the number of grafting sites of different radius and two grafting ratio are listed in Table 1.

Table 1. Nanoparticles and Number of Grafting Sites for Nanocomposites System

case	radius(Å)	NO. of surface oxygen atoms	NO. of grafting sites	
			5%	10%
1	10.00	104	5	10
2	11.41	128	6	12
3	12.56	148	7	14
4	13.53	180	9	18
5	14.50	204	10	20

Mechanical properties of untreated SiO_2/PI

As to the unit cell of SiO_2/PI in Fig.2, the mechanical properties of untreated SiO_2/PI is calculated when the volume fraction of nano-particle is 5%, the results is depicted in Table 2.

Table 2. Mechanical properties of untreated SiO_2/PI

Case	Radius(Å)	Volumn(Å3)	Density(g/cm3)	*E* (GPa)	*v*	*K* (GPa)	*G* (GPa)
1	10.00	98819.1	1.374	4.5657	0.3706	5.8804	1.6656
2	11.41	124287.6	1.382	4.4109	0.3707	5.6851	1.6090
3	12.56	166386.4	1.415	4.3837	0.3637	5.3594	1.6073
4	13.53	206089.1	1.435	4.3768	0.3625	5.3037	1.6062
5	14.50	252526.6	1.461	4.2663	0.3873	6.3101	1.5376

As can be seen from Table 2, in the condition that the volume fraction of nano-particle is constant, the Young's moduli and shear moduli of the composite decrease with the nano-particle radius increases, poisson's ratio changes little, the results are consistent with the results obtained by the homogenization method [15]. When the radius increased from 10 Å to14.5 Å, the elastic moduli decreased by 7%, it mainly due to small nano-particle with larger specific surface area. When the radius of nano-particle increases, the molecule number of the unit cell increase rapidly, limited by the computer memory, it failed to simulate SiO_2 nano-particles with larger radius.

The unit cell of -Si-C_3H_7 modified SiO_2/PI

The -Si-C_3H_7 modification is just modifying the surface of nano-particle, no bond formed between particles and polymer matrix, the silane coupling agent is usually used in the experiment. In this paper, it selects -Si-C_3H_7 to modify SiO_2 nano-particle. In the simulation process, all of the free radicals of the silicon atoms are first treated by oxygen atoms to mimic the real oxidation process, then randomly choose the surface oxygen atoms to make a direct bond with -Si-C_3H_7 ,the modified SiO_2 nano-particle is shown in Fig.3. According to the simulation introduced before, the stable configuration of -Si-C_3H_7 modified SiO_2/PI is shown in Fig.4. when the grafting ratio are 5% and 10% respectively, the simulated results are listed in Table 3 and Table 4.

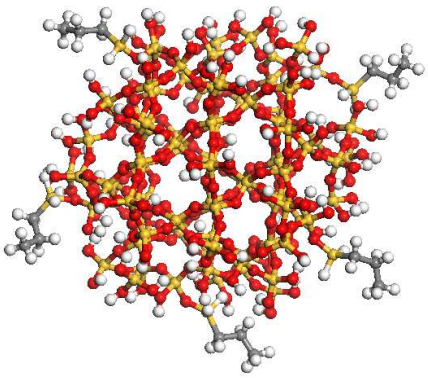

Fig.3.-Si-C_3H_7 modified SiO_2 nano-particle

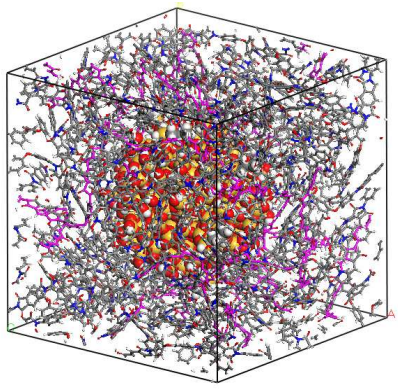

Fig.4. -Si-C3H7 modified SiO_2/PI model

Table 3. Mechanical Properties of 5% -Si-C3H7 modified SiO_2/PI

Case	Radius(Å)	Volumn(Å3)	Density(g/cm3)	*E* (GPa)	v	*K* (GPa)	*G* (GPa)
1	10.00	98881.3	1.379	4.6695	0.3725	6.1044	1.7011
2	11.41	131754.0	1.398	4.5104	0.3901	6.8410	1.6223
3	12.56	163551.7	1.400	4.4289	0.3582	5.2039	1.6305
4	13.53	208112.0	1.416	4.3543	0.3644	5.3507	1.5957
5	14.50	248240.1	1.429	4.3049	0.3833	6.1491	1.5560

Compared the results in Table2 , Table3 and Table4, with -Si-C3H7 modified, the Young moduli and shear moduli of composites increase in some extent, but the effect is not obvious. Make a comparison between Table 3 and Table 4, when the grafting ratio increase from 5% to 10%, the elastic moduli increase by 2%, the shear moduli increase by 4%, but bulk moduli decrease by 11% and poisson's ratio by 5%; the influence of radius is similar with untreated model.

Table 4. Mechanical Properties of 10% -Si- C_3H_7 modified SiO_2/PI

Case	Radius(Å)	Volumn(Å3)	Density(g/cm3)	*E* (GPa)	v	*K* (GPa)	*G* (GPa)
1	10.00	98966.3	1.384	4.7737	0.3521	5.3791	1.7653
2	11.41	131910.0	1.403	4.6718	0.3639	5.7230	1.7126
3	12.56	164931.0	1.412	4.6828	0.3698	5.9939	1.7093
4	13.53	208878.0	1.416	4.4805	0.3762	6.0299	1.6279
5	14.50	251353.7	1.438	4.4560	0.3624	5.3958	1.6354

The unit cell of directly grafted SiO2/PI

Covalent grafting is a promising way to increase the load transfer efficiently by taking advantage of the strong interaction force of the covalent bonds by inducing the interpenetration of the free and grafted chains in the vicinity of nano-particle. Direct grafting is bonding untreated SiO2 with PI and obtain the unit cell of SiO2/PI. After the stable model of SiO2/PI calculated by molecular dynamic is prepared,. The grafting process is performed. The cutoff radius has an obvious effect on the density and intermolecular interaction, according to the related simulation conclusions of previous researchers[16], the default cutoff radius was set to 4 Å and the maximum radius to complete the grafting was set to 6 Å. After finishing the grafting process, the stable configuration obtained by geometry optimization is shown in Fig.5. The mechanical properties are calculated, the results are listed in Table 5 and Table 6.

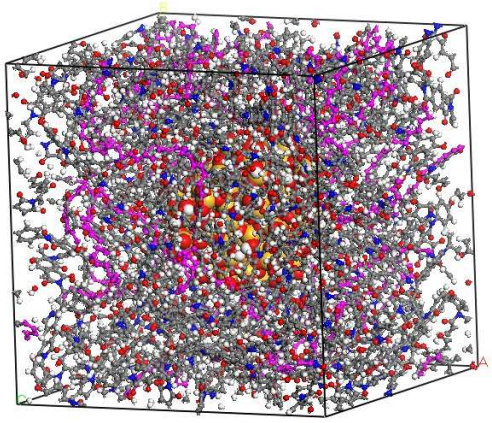

Fig. 5. directly grafted SiO2/PI model

Table 5. Mechanical Properties of 5% directly grafted SiO_2/PI

Case	Radius(Å)	Volumn(Å3)	Density(g/cm3)	*E*(GPa)	v	*K*(GPa)	*G*(GPa)
1	10.00	97181.8	1.405	4.3046	0.3866	6.3279	1.5522
2	11.41	130650.0	1.407	4.2875	0.3876	6.3584	1.5449
3	12.56	161012.3	1.450	4.2278	0.3928	6.5749	1.5177
4	13.53	204152.9	1.461	4.1635	0.4007	6.9901	1.4862
5	14.50	248125.3	1.482	4.1202	0.3962	6.6158	1.4755

Table 6. Mechanical Properties of 10% directly grafted SiO2/ PI

Case	Radius(Å)	Volumn(Å3)	Density(g/cm3)	*E*(GPa)	v	*K*(GPa)	*G*(GPa)
1	10.00	98274.0	1.389	4.5729	0.3662	5.6962	1.6736
2	11.41	130357.7	1.411	4.4277	0.3938	6.9511	1.5883
3	12.56	163296.1	1.418	4.3440	0.3795	6.0069	1.5745
4	13.53	204785.6	1.452	4.3314	0.3825	6.1447	1.5665
5	14.50	247013.3	1.474	4.2452	0.3832	6.0556	1.5346

Compared the results in Table2 , Table5 and Table6, with directly grafted, the mechanical properties of composites can hardly increase, but decrease in some extent. Make a comparison between Table 5 and Table 6, when the grafting ratio increase from 5% to 10%, the elastic moduli increase by 6%, the shear moduli increase by 8%, but bulk moduli decrease by 10% and poisson's ratio by 5%; the influence of radius is similar with untreated model.

The unit cell of -Si-C_3H_7 grafted SiO_2/PI

-Si-C3H7 grafting is treating nanoparticle with -Si-C3H7 , then bonding with PI. In the simulation process, the end carbon of the propyl unit acts as a linker atom to be covalently bonded with the aromatic hydrocarbon of the matrix molecules. The chemical bonds can be done by manual, also can be done through the script, as the grafting number is not much, manual grafting is easy to operate and can avoid puncture of the molecular chain, the unit cell after geometry optimization is shown in Fig.6, the partial enlarged figure as shown in Fig.7, the results of the mechanical properties are listed in Table7.

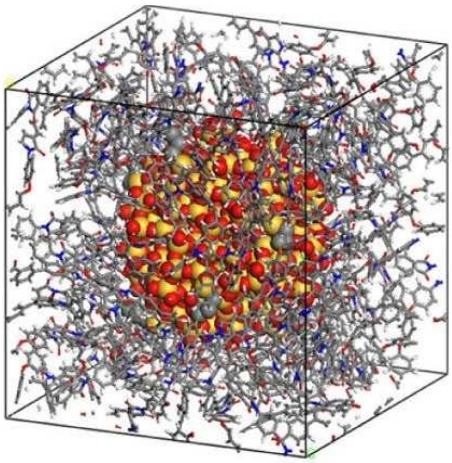

Fig. 6.-Si-C3H7 grafted SiO2/PI model

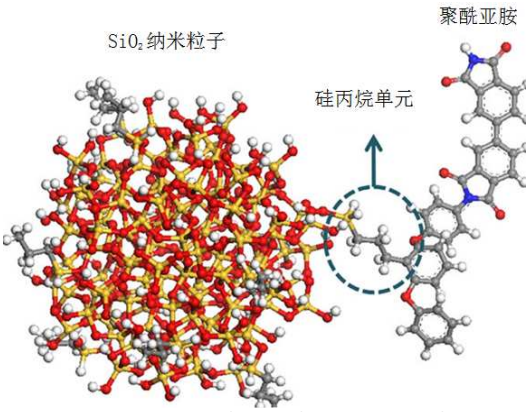

Fig. 7. the partial enlarged figure of covalently grafting

Table 7. Mechanical Properties of 5% -Si-C3H7 grafted SiO2/ PI

Case	Radius(Å)	Volumn(Å3)	Density(g/cm3)	*E* (GPa)	*v*	*K* (GPa)	*G* (GPa)
1	10.00	99199.3	1.375	5.2615	0.3718	6.8416	1.9177
2	11.41	131754.2	1.398	5.0092	0.3683	6.3372	1.8305
3	12.56	160453.9	1.417	4.9443	0.3946	7.8207	1.7726
4	13.53	207469.7	1.424	4.8451	0.3714	6.2781	1.7665
5	14.50	238916.6	1.459	4.8139	0.3666	6.0136	1.7613

Compared the results in Table 2 and Table 7, the mechanical properties of SiO_2/PI after -Si-C3H7 grafted increase obviously.

Energy Analysis

The interaction energy between nano-particle and matrix can be calculated by Material simulation software MS, in order to discuss the influence mechanism of surface modification effects on the SiO2/PI composite, the interaction energies of untreated and -Si-C3H7 grafted models are calculated when the radius is 10 Å. Interaction between particle and matrix are composed of bond energy, coupling and non-bond energy, of which non-bond energy is composed of the van der Waals force and electrostatic potentia. Select the potential calculation module in MS, each energy of two models can be obtained and the results are listed in Table8.

Table 8. interaction energy between SiO2 and PI (kcal/mol)

	E_{total}	Bond Energy	Coupling Energy	van der Waals force	electrostatic potentia
untreated	-392.84	0.00	0.00	-254.56	-138.28
Grafted ratio is 5%	-599.56	-84.20	-13.29	-465.22	-72.86

It can be seen from Table 8 that the interaction between SiO2 and PI is mostly contributed by non-bond energy when the SiO2 is not grafted, van der Waals force plays a leading role, and electrostatic potential plays a secondary role. After -Si-C3H7 grafted, the total energy increase obviously, and composed of bond energy, coupling and non-bond energy, the covalent bond between SiO2 and PI can increase bond energy and coupling energy, van der Waals force also increase, but electrostatic potential decease. van der Waals force plays a main role in the total energy, the mechanical properties increase as the interaction between SiO2 and PI increase after -Si-C3H7 grafted.

CONCLUSION

There are four models in this paper: ①untreated SiO_2/PI model ②-Si-C3H7 modified SiO2/PI model ③ directly grafted SiO2/PI model ④-Si-C3H7 grafted SiO2/PI model. As to SiO2 particle with radius of 10 Å, when the grafting ratio is 5%, the elastic moduli and shear moduli of four models and the theoretical prediction result obtained by Mori-Tanaka [17] are listed in Table 9.

In theory it is difficult to establish the analysis model which can predict the mechanical properties of modified nano-particle reinforced polymer composite, comparing the model ① and the theoretical prediction result obtained by Mori – Tanaka, the error of the elastic modulus is less than 2.5%,which shows the reliability of the simulation results. Compare four kinds of simulation results, it can be seen that -Si-C3H7 modified and directly grafted can hardly increase the mechanical properties of the composite, while the elastic moduli can increase obviously after -Si-C3H7 grafted,. When the grafting ratio is 5%, the Young's moduli increase by 15%, the shear moduli change little. Conclusions can be obtained after comprehensive analysis:

Table 9 results of four models and Mori – Tanaka

Modulus(GPa)	①	②	③	④	Mori-Tanaka[15]
E	4.57	4.67	4.30	5.26	4.68
G	1.67	1.61	1.61	1.61	1.53

(1)The mechanical properties of SiO2/PI decrease with the size of nano-particle increase;
(2)when nanoparticle is treated with -Si-C3H7, the mechanical properties of compsite increase in some extent, but is not obvious, the Young's moduli and Shear moduli increase as the grafting ratio increase, but the bulk moduli and Poisson's ratio decrease; when nano-particle is directly grafted with PI, the mechanical properties of composite decrease, but increase as the grafting ratio increases; when nano-particle is covalently grafted with PI, the mechanical properties of composite increase obviously.
(3)In the interaction between nanoparticle and matrix, van der Waals force plays a main role, and electrostatic potential plays a secondary role; the interaction can increase obviously after nanoparticle -Si-C3H7 grafted.

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