

Effect of Nanoparticle Size on the Interface Bond Energy in $\text{KTa}_{0.5}\text{Nb}_{0.5}\text{O}_3$ / Polyimide Composites

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Abstract

The effects of particle size on the interface bond energy in $\text{KTa}_{0.5}\text{Nb}_{0.5}\text{O}_3$ / polyimide composites were investigated using the molecular dynamics method. The composites of polyimide and the $\text{KTa}_{0.5}\text{Nb}_{0.5}\text{O}_3$ nanoparticles with different size (0.4 nm, 0.5 nm, 0.6 nm, 0.8 nm, 1.2 nm, and 1.4 nm) have been established and simulated using the Forcite program package of Materials Studio software. The calculated results show that the interface bond energy is 38~150 Kcal/mol, which indicate the Van der Waals force exist between the nanoparticle and polyimide matrix. The interface bond energy of the smaller nanoparticle is greater than the larger nanoparticle due to the size effect. The introduction of the smaller nanoparticle could generate the stronger intermolecular bonding interaction between the nanoparticle and polyimide matrix.

Keywords: *Molecular dynamics method, Polyimide, Potassium tantalum niobate, Interface bond energy, size effect*

1. Introduction

Dielectric polymer films have been widely used for insulating and electrical materials as their excellent physical, chemical and charge storage properties [1-3]. Polyimide (PI) is one of the representative polymers for dielectric application, which possesses remarkable performance, such as outstanding heat resistance, good mechanical properties, electrical properties and stability. Its various products like molding compounds, composites, adhesives, membranes have been widely used in aerospace, electronic industry, light communication, bulletproof materials, and gas separation *etc* [4-6]. High-technology electronic devices require better performance of the PI with the rapid development of the electronic industry [7-9]. In recent years, many researchers has attracted to polymer composite for its multiple functions as electric devices, because the doping nanoparticles could significant improve physical and mechanical properties of the polymer, and the composite with high-performance and remarkable multi-properties could be obtained [10, 11].

Many works show that the sizes of the doping particles and the surface interaction of polymers and inorganic nanoparticles play a key role for the properties improvement of the composites [12, 13]. Zhong *et al.*, found that the size of doping calcium carbonate particles have close relationship with the toughening effect to the PVC composites [14]. The dielectric constants of the PI/CCTO ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) composites could be improved from about 100 to 10^6 , which are about 5 orders, when instead of micron CCTO particles by nanoparticles [15]. The interface layers between polyimide and silica nanocomposite will have a significant impact on mechanical properties, when the radius of silica nanocomposite filler is less than

the 100 nm [16]. Although many experimental studies have been published, the physical and chemical effect of the interface of the between inorganic particles and the polymer matrix is not exactly known, and it is difficult to find the most suitable uniform inorganic nanoparticle size by the experiment methods [17]. With the increasing complexity of the research system, molecular simulation method has become an indispensable research method, the appropriate model and ideal experiment could be developed, which provides a significant guide and support for experimental research.

Ceramic/polymer composite materials have been considered as one of the most promising materials because they could integrate the advantages of the two phases, which is the good dielectric properties of ceramic materials and the good processing properties and mechanic strength of polymer materials, and the size of the doping particles has a close relation with the dielectric properties of the composites [18, 19]. In this paper, the composites of PI and the potassium tantalum niobate nanoparticles ($\text{KTa}_{0.5}\text{Nb}_{0.5}\text{O}_3$, KTN) with different size (0.4 nm, 0.5 nm, 0.6 nm, 0.8 nm, 1.2 nm, and 1.4 nm) have been simulated using the molecular dynamics method. The effect of different particle sizes on the structure and the interface bond energy in PI/ KTN composites were investigated.

2. Modeling and Theoretical Calculation

The KTN/PI composites models with the different radius (0.4 nm, 0.5 nm, 0.6 nm, 0.8 nm, 1.2 nm, and 1.4 nm) were established through Forcite module of Materials Studio. The 3D structure of KTN/PI Composite model was shown in Figure 1 [20]. The calculations were performed through using the Forcite program package of Materials Studio, the geometry structure optimization was developed by molecular dynamics method. In order to make the system more stable, the methods of molecular dynamics were used to do further optimization, because the system may still be unstable such as high energy and local minimum. The accuracy of self-consistent field is set to 2.0×10^{-4} kcal/mol in the iterative process, the iterative number is 5.0×10^4 , the convergence error of maximum stress among ions is set to be 0.005 kcal/mol, and the convergence error of the largest sub-stress is set to be 0.05GPa and the maximum displacement error is set to be 5.0×10^{-5} Å. In each calculation, the total energy is calculated after the optimization.

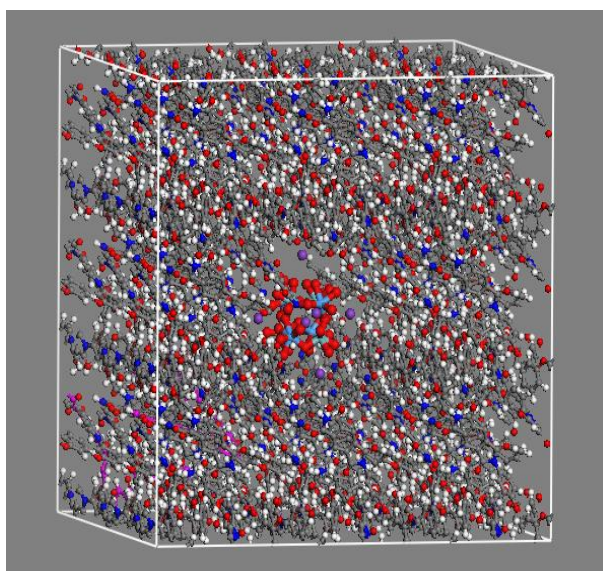


Figure 1. The 3D Structure of KTN/Polyimide Composite

3. Results and Discussion

In order to investigate the effects of particle size on the surface binding energy in composites, the energies of the KTN/PI composites, PI matrix and the nano-KTN particles with radius of 0.4 nm, 0.5 nm, 0.6 nm, 0.8 nm, 1.2 nm, and 1.4 nm were calculated respectively after molecular dynamics optimization. The expression for the surface binding energy written as:

$$U_{\text{bind energy}} = (U_{\text{nanoparticle}} + U_{\text{polymer}}) - U_{\text{total}} \quad (1)$$

Where U_{total} is the total energy of the composite, which includes the oxide particles and polymer; $U_{\text{nanoparticle}}$ is the total energy of the nanoparticles; and U_{polymer} is the total energy of the polymer.

Table 1 shows the calculated total energy and surface binding energy of PI/KTN composites. The size of the PI matrix is fixed, and the energy of the PI matrix is 52913 Kcal/mol. The results of the calculation exhibit that the surface binding energy of KTN/PI composites increases with the nanoparticle radius increasing, which is shown in Figure 2.

Table 1. Surface Binding Energy of PI/KTN Composites

Radius (nm)	PI (kcal/mol)	KTN (kcal/mol)	PI/KTN (kcal/mol)	U_{BE} (kcal/mol)
0.4	52913	38.57	42807	10144.57
0.5	52913	1604.95	42705	11812.95
0.6	52913	1503.6	42267	12149.60
0.8	52913	4155.95	42888	14180.95
1	52913	7697.32	43592	17018.32
1.2	52913	18893.77	53860	17946.77
1.4	52913	33768.74	63587	23094.74

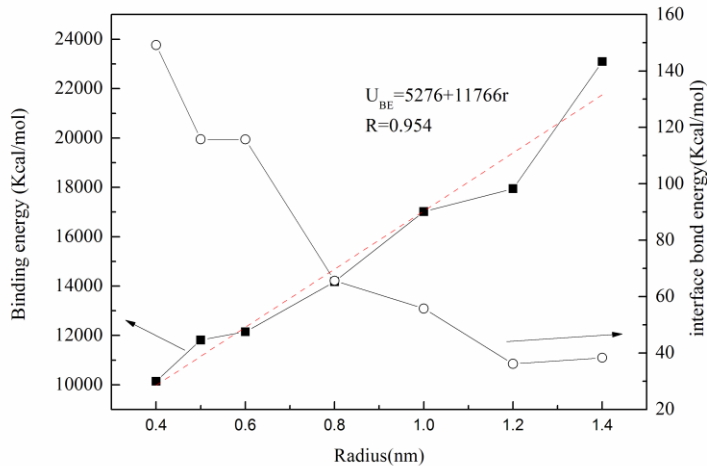


Figure 2. The Variation of the Surface Binding Energy and the Interface Bond Energy

In order to find the relationship between the surface binding energy of PI/KTN surface and the radius of KTN, the linear fitting was used, as the dot line in Figure 2. The linear fit line equation is

$$U_{BE} = B + Ar \quad (2)$$

Where U_{BE} is the total surface binding energy of PI/KTN composite and r is the radius of the particles. The parameters A and B are 11766 Kcal/mol and 5276 Kcal/mol, respectively. The linear correlation coefficient is about 0.954, which shows the good linear fitting degree.

After the calculation of the surface binding energy, it can be obviously seen what is the intermolecular bonding formed between nanoparticle and PI matrix. First, the Materials Studio software was used to calculate total atoms of different nanoparticle cluster model, the number of surface atoms can be calculated by using the formula

$$N = \frac{dn}{dr} = \frac{3n}{r} \quad (3)$$

where N is the number of surface atoms, n represents the total number of atoms and r is the radius of particles, the deriving process is shown as follows.

Assume that all the atoms are evenly and closely distributed in the nanoparticle cluster model.

$$dv = 4\pi r^2 dr \quad (4)$$

$$\rho = \frac{dn}{dv} \quad (5)$$

where v is the volume of nanoparticle and ρ is the atomic number of the unit volume.

$$d_N = \rho \times d_v = \frac{n}{\frac{4}{3}\pi r^3} \times 4\pi r^2 \times d_r = \frac{3n}{r} \times d_r \quad (6)$$

$$N = \frac{dn}{dr} = \frac{3n}{r} \quad (7)$$

Table 2. Total Atomic Number and the Surface Atomic number of KTN Clusters

Radius (nm)	Total atomic number	Surface atomic number	$U_{BE} /$ Surface atomic number
0.4	27	68	149.18
0.5	51	102	115.81
0.6	63	105	115.71
0.8	173	216	65.65
1	305	305	55.80
1.2	595	496	36.18
1.4	843	602	38.36

The total number, the surface atomic number of the nanoparticles, and the bonding energies per surface atomic ($U_{BE} /$ Surface atomic number) of the PI/KTN composites are shown in Table 2. The relationship between the $U_{BE} /$ Surface atomic number and the nanoparticles with different radius is present in Figure 2. The results show that the surface bonding energies per surface atomic decreased with the increase of the particle size, and the values are about 38~150 Kcal/mol. It is well known that the energy of Van der Waals force range from several to several dozens of KJ/mol, the Van der Waals force has additive property.

Therefore, the calculation results may indicate that the interaction forces between the polymer matrix and the nano inorganic particles are mainly molecular bonds. In other word, the combined forms of interface in the composites are mainly Van der Waals bonds. The surface atomic number of nanoparticle increases along with the nanoparticle radius increasing, which indicates the increasing total contact surface between the nanoparticle and polyimide matrix. Whereas, the average interface bond energy per atomic of the smaller nanoparticle is greater than that of the larger nanoparticle, which show an obvious size effect. The introduction of the smaller nanoparticle arise stronger interface bond energy between the nanoparticle and polyimide matrix.

4. Conclusion

The effects of the nanoparticle size on the surface binding energy and interface bond energy in KTN/PI composites were investigated using the molecular dynamics method. The $\text{KTa}_{0.5}\text{Nb}_{0.5}\text{O}_3$ / polyimide model has been established by using Forcite program package of Materials Studio software, the radius of the nanoparticle cluster model are respectively 0.4 nm, 0.5 nm, 0.6 nm, 0.8 nm, 1.2 nm, and 1.4 nm. The calculated results show that the total surface binding energy of $\text{KTa}_{0.5}\text{Nb}_{0.5}\text{O}_3$ / polyimide composites increase with the increasing nanoparticle size, the stable structure is acquired. The interface bond energy is 38~150 Kcal/mol, which indicates the Van der Waals force exist between the nanoparticle and polyimide matrix. Due to the size effect, the average interface bond energy per atomic of the smaller nanoparticles is greater than that of the larger nanoparticles, which demonstrates that the introduction of the smaller nanoparticle leads to stronger interface bond energy between the nanoparticle and polyimide matrix.

Acknowledgements

This work was supported by the Scientific Research Fund of Heilongjiang Provincial Education Department (No. 12531115), Innovative Foundation of Harbin (No.2014RFXXJ060) and Science Foundation of Heilongjiang (No. F201301).

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