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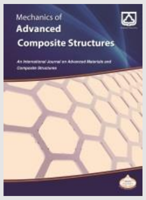

Investigation of Capsulated Epoxy and DCPD in Epoxy Based Self-healing Composites - DFT Calculation and Experimental Analysis

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ABSTRACT

Epoxy and dicyclopentadien (DCPD) are two common healing agents, which are introduced into epoxy matrix through encapsulation in order to prepare self-healing composites. In a comparative study, the compatibility of healing agents and epoxy matrix is investigated through experimental tests and DFT calculations. The interaction energy is considered to be the determinative parameter in DFT calculation. The values of total interaction energy are -0.14eV for DCPD and +0.169eV for epoxy absorbing on epoxy matrix. According to the obtained results from DFT, an attraction between DCPD and epoxy matrix is observed. DOS and charge analysis of these systems are fulfilled and demonstrated the charge transfer of 0.07 e from epoxy to DCPD. The obtained data reveal the most charge transfer is occurred in DCPD-epoxy, which affects the mechanical properties of healed composites. To examine the mechanical properties, tensile strength parameters are measured experimentally and demonstrated the improved ultimate strength of 783.49 MPa in DCPD/epoxy system rather than the ultimate strength of 571.87 MPa in epoxy/epoxy system. Also elongation at break in DCPD-epoxy system is improved to 3.44% compared to 1.84% in epoxy/ epoxy blend. These findings highlight the role of interaction energy in mechanical properties of polymeric interface, and prompt further experiments and simulations to confirm this effect.

1. Introduction

Damage treating is one of the costly and time consuming processes in many industries, which may interrupt the operation of part or device. A new efficient method to overcome these problems is the use of self-healing materials. Although this method cannot be used for large-scale damages, but as soon as a crack is created, a healing agent would repair it and prevent the growth of the crack and the consequent further damages [1]. Self-healing materials can be made by different processes; among which, encapsulation of healing agents can be mentioned as one of the useful methods. In this method, when a crack is generated, the shell of the capsule would be broken and the healing agent, which is a pre-polymeric agent, will be diffused in the crack. Then, a new polymer would be produced in the presence of polymerizatoin catalysts, so the crack would be repaired [2-4]. Two common agents that are used in encapsulation process are dicyclopentadiene and epoxy monomer [5-6].

Actually, a blend of polymeric matrix and new polymerized healing agent is formed in the region around the cured crack. Interfacial interaction energy is a determinative parameter in strength of polymeric blends, which has a significant effect on the properties of heterogeneous polymer systems, including blends, filled polymers and advanced composites and its importance is clearly shown by the widespread research activities in this field [7, 8]. Interfacial interaction energy can be determined through both experimental tests and calculation procedure; however, according to the difficulty and

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complexity of estimating interaction energy by experiments, calculation procedures are preferred.

Computer programs can calculate the configuration of the electrons accurately based on density functional theory (DFT). DFT is a computational quantum mechanical modelling method used in physics and chemistry for studying different properties such as electronic structure, dynamic and mechanical properties of various materials. In fact, DFT is a universal tool for calculating the electronic structure due to its ability in treating with relatively large-sized models (several hundred atoms) compared to other first principles methods as well as the its accuracy degree, so it can be applied in various systems. The results of DFT calculations are comparable with highly correlated ab-initio methods, and even, in some cases, DFT is superior according to its reduced computational cost [9, 10].

In this paper, two important healing agents were assessed: epoxy and DCPD; and both computational and experimental methods were applied for investigating the interfacial interaction energy. In the computational study, epoxy and DCPD healing agents were examined individually by DFT calculation to estimate the interaction energy between epoxy matrix and healing agent, which is activated and polymerized in crack curing. Also density of states and Mullikan charge analysis were performed to calculate the states and charge transfer. Interaction energy could emphasize the contrast between ultimate mechanical properties. Tensile properties are mostly used for the characterization of polymers and polymer composites, so in this paper, tensile strength of polymerized epoxy-epoxy and epoxy-DCPD polymer were measured experimentally.

2. Computational method

The systems were optimized by the use of the self-consistent charge density functional tight-binding (SCC-DFTB) calculations [11], as implemented in the DFTB+ program package [12] and the geometrical optimizations were performed using the conjugate gradient algorithm; also, calculating the total energy of the systems were done with DFT calculation framework implemented in the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) code [13–16]. For all calculations, a double-z plus polarization (DZP) basis set with an energy shift of 50 meV was used and the mesh cut-off was chosen to be 120 Ry. The exchange and correlation potentials were applied using a generalized gradient approximation (GGA) with the PerdewBurke–Ernzerhof (PBE) function [17]. Both epoxy and DCPD monomer were simulated by the gaussview software and optimized by DFT, as implemented in the SIESTA code.

According to DFT, the interaction energy between a stable molecule A formed by the bonding of K atoms with a total number of NA electrons and a stable molecule B formed by the binding of L atoms with a total number of NB electrons [18] is given by Eq. (1):

$$E_i = E_{AB} - E_A - E_B \tag{1}$$

And the interaction energy for the adsorption of the healing polymerized agent onto the polymer matrix surface can be obtained from the above expression, in which, E_{AB} is the total energy of the epoxy matrix interacting with the healing agent.

3. Experimental Test

3.1 Materials

For preparing a polymeric nanocomposite, D. E. R. 332 epoxy resin from Sigma Aldrich with an epoxy equivalent weight of 175 equiv.g^{-1} was used as a matrix. Triethylenetetramine, which is a liquid aliphatic amine with a molecular weight of 146.24 g.mol^{-1} and density of 0.977 g.ml^{-1} at 20˚C used as the hardener and was purchased from Merck. Distilled DCPD, toluene, methanol, hydrochloric acid and WCl_6 were also prepared from Merck and used without further purification.

3.2 Sample preparation

Stoichiometric ratio of the diamine was added to 40 g of epoxy and stirred mechanically for about 5 min. The samples were moulded, and placed in vacuum for 15 minutes in ambient temperature, afterward it was cured in two steps: first about 30 min in 60˚C and then 1 hour in 100˚C. The samples were then laser cut and filled with epoxy and DCPD polymers individually. A 3D drawing of the testing samples from different views in Solidworks software is shown in Fig.1. For DCPD polymerization, 1 equivalent of WCl_6 catalyst and 300 equivalents of distilled DCPD were placed into a 20 mL vial containing a stirring bar and the vial was sealed with a rubber septum. Approximately 0.05 mL of toluene was added to the mixture and it was stirred slowly to dissolve the solids. The stirring was continued until the stirring was stopped due to increased viscosity. The reaction was quenched with acidic methanol (methanol /conc. HCl = 50/1) and the solid was filtered and dried under vacuum at 60˚C for 12 h. Finally, a blend of epoxy and DCPD polymer was used to fill in the cut of the mould.

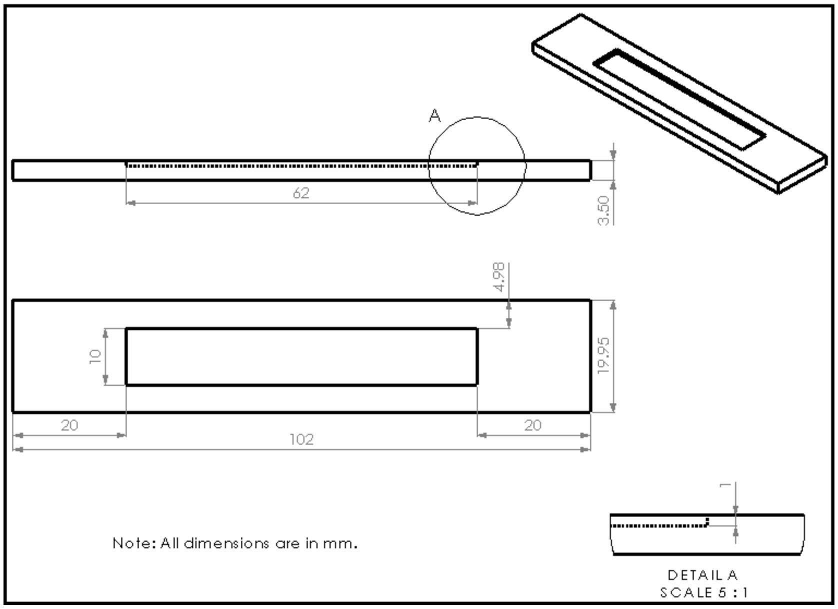

Figure 1. Drawing of the testing samples in different views in Solidworks software.

3.3 Tensile test

Samples were tested by a Santam testing unit. The gauge length was 50 millimetres. Tensile tests were conducted at the cross head speed of 0.5 mm.min^{-1}; the elongation of the gauge was measured by a non-contact extensometer. For each experiment, three specimens of composites were used at least.

4. Results and discussions

4.1 Interaction energy between two epoxy monomer

Figs. 2 and 3 show two most possible situations for monomers of epoxy as the healing agent can be placed in the surface of epoxy polymer matrix. Interaction energy of these two situations where analysed by DFT calculations. The best energy was 0.169 eV, which indicates no interaction between two epoxy monomers.

4.2 Interaction energy between epoxy monomer and DCPD

For modelling the DCPD monomer, we should first consider DCPD polymerization. In Fig. 4 the polymerization of DCPD in the presence of catalyst proposed by T. A. Davidson et. all [19] study is illustrated.

In this research, a monomer of a polymeric phase (Fig. 5) was considered to estimate the interaction energy. Fig.6 shows the different sites of DCPD monomer on the surface of epoxy monomer. The best calculated interaction energy was about -0.140 eV for the configuration depicted in Fig.6. Table 1 lists the interaction energy and the equilibrium distance of the closest atoms on the surface of epoxy monomer in different situations of DCPD monomer. The data in table 1 shows a similar equilibrium distance of about 3.6 across all sites. By observing the interaction energy value, it can be concluded that physical attraction is established between DCPD and epoxy.

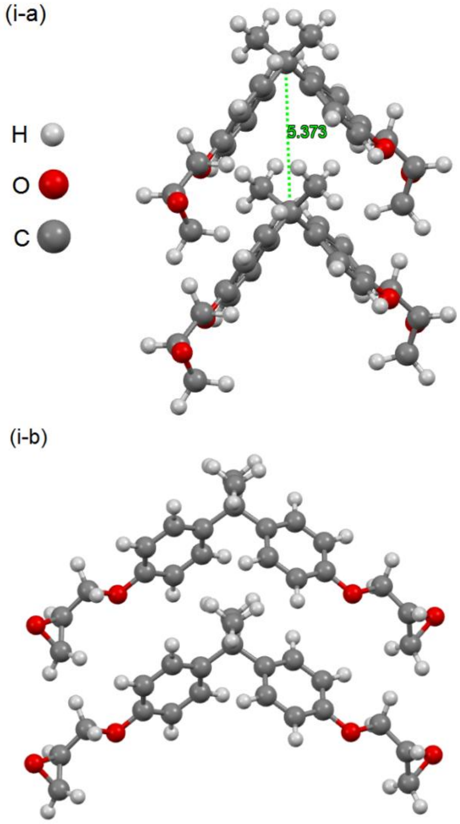

Figure 2. Optimized configurations of an epoxy monomer on the epoxy monomer in site i in different orientations.

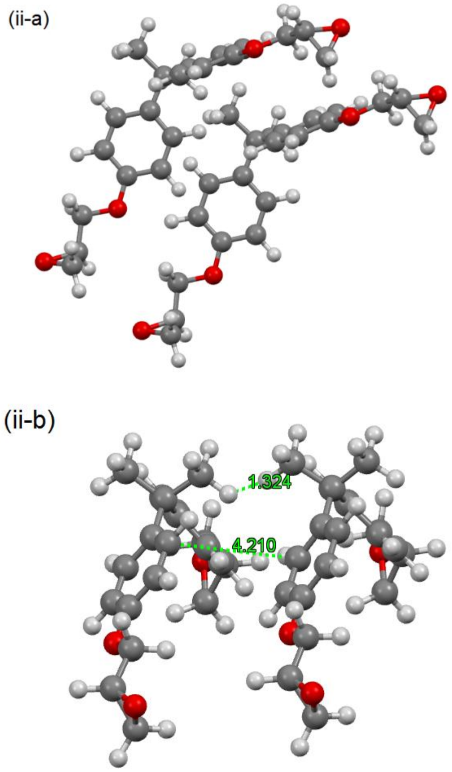

Figure 3. Optimized configurations of an epoxy monomer on the epoxy monomer in site ii in different orientations.

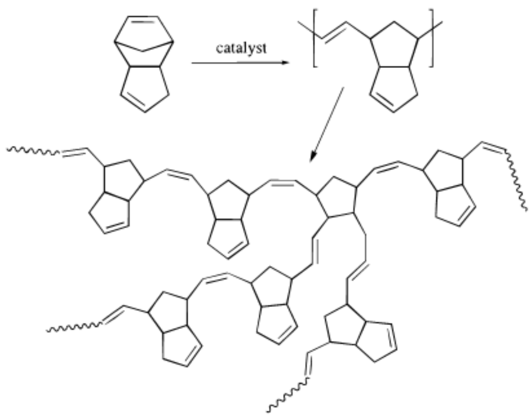

Figure 4. Currently accepted mechanism for the polymerization of dicyclopentadiene (DCPD)[19].

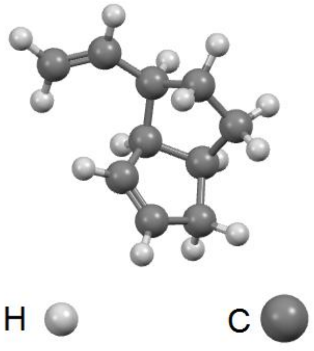

Figure 5. DCPD monomer designed by the guassview software for the calculation.

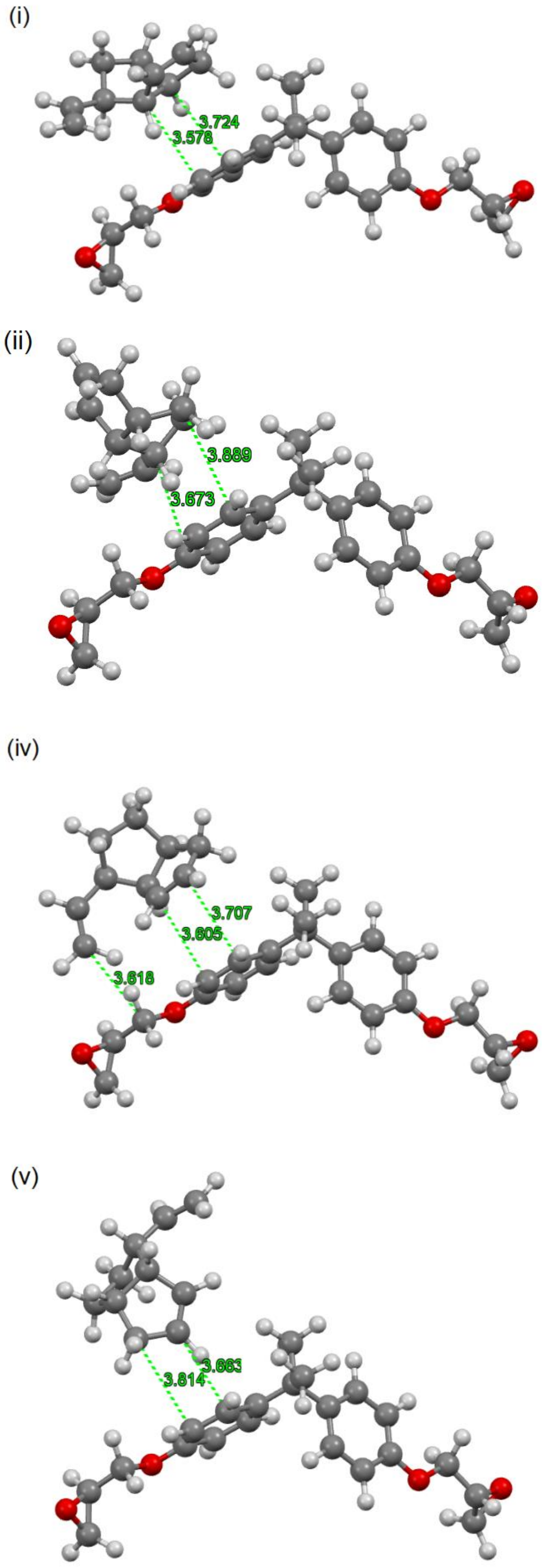

Figure 6. different sites of DCPD monomer on the surface of epoxy monomer

Table 1. Calculated interaction energy of DCPD monomer on the surface of epoxy monomer

Index	Total energy (eV)	$d_{epoxy-DCPD}$ (Å)
Site i	-0.069	3.57
Site ii	-0.139	3.63
Site iii	-0.117	3.95
Site iv	-0.016	3.61
Site v	-0.068	3.66

4.3 Density of state and Mulliken charge analysis

Density of state (DOS) along with molecular orbital (MO), gives the overall electronic structure and reactivity of a system. Fig. 7 presents the total electronic DOS between –5 and 8 eV, where the Fermi level (E_f) is set at 0 eV for systems, consequently, the vacuum level alignment rule does not hold.

The overall energy levels of the occupied orbital of all systems are almost the same. The most significant difference between them, which can be obviously seen in Fig. 7, is the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). According to charge densities, the HOMO– LUMO gap for epoxy-epoxy and epoxy-DCPD complex are 4.69 and 3.39 eV, respectively. In fact, adsorption of DCPD on epoxy leads to a decrease in the HOMO- LUMO gap. The values of HOMO– LUMO gap for the calculated systems are summarized in Table 2.

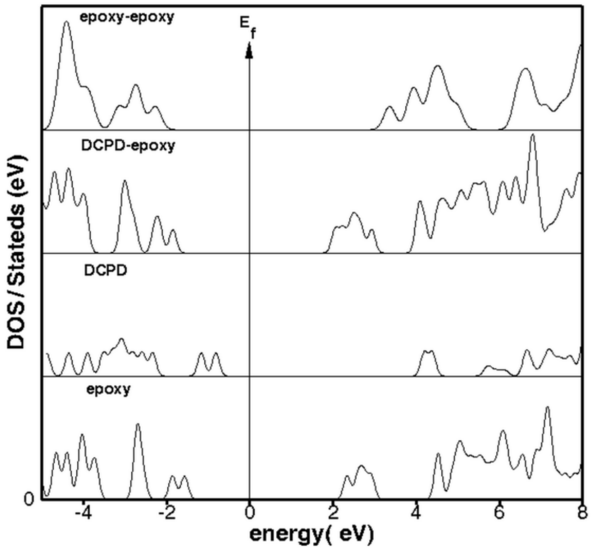

Figure 7. Total electronic density of states

Table 2. HOMO– LUMO gap of epoxy, DCPD, DCPD-epoxy and epoxy-epoxy calculated by DOS analysis system

Content	Neat epoxy	DCPD	Epoxy-Epoxy	DCPD-Epoxy
Band gap	3.2	4.4	4.69	3.39

Electron transfer contributes the change in DOS and increased LUMO density of DCPD-epoxy rather than epoxy-epoxy complex. This shows more electron transfer in the DCPD-epoxy system. To investigate the change in the electronic structures of absorbed DCPD on epoxy, the net charge transfer from the DCPD to the monomer was calculated using the Mullikan charge analysis. The calculations indicate that a charge of 0.07e was transferred from epoxy to DCPD that, which satisfies the increased LUMO density. According to calculations, no remarkable electron transfer was observed in epoxy-epoxy system.

4.4 Experimental Validation

In order to validate the obtained theoretical results, experimental investigation was performed. The stress – strain graphs are displayed in Fig.8 for three systems, including: A: neat epoxy as the polymeric matrix before cure, B: epoxy polymer cut moulded filled with epoxy polymer and C: poxy polymer cut moulded filled with DCPD/epoxy polymeric blend. The results of the tensile strength are provided in Table 3.

Comparing the results of the samples reveals an increase in tensile strength and elongation at break in DCPD-epoxy sample (Fig. 8). Higher interaction would cause higher tensile strength and elongation at break and subsequently, improved mechanical properties can be achieved [20].

The results show that DCPD curing would have a positive effect due to the better interaction with epoxy system. It can be interpreted that after a crack is created in the epoxy polymer and the polymer is then restored with new polymerized epoxy, there are no crosslink (which is formed in the thermosetting polymer network during polymerization) between old and new polymer. So the interaction between new and old polymer matrix plays an important role. From both experimental and computational results, it can be inferred that encapsulated DCPD is a better healing agent in epoxy matrix compared to encapsulated epoxy due to the better interaction.

Table 3. Mechanical properties of block specimens: neat epoxy, DCPD/epoxy and epoxy/epoxy composites

Content	Neat epoxy	Epoxy-Epoxy	DCPD-Epoxy
Bending strength, MPa	886.28	571.87	783.49
Bending modulus, GPa	1.71	1.60	1.21
Elongation ε, %	2.55	1.84	3.44
Stress, MPa	36.63	23.64	32.38

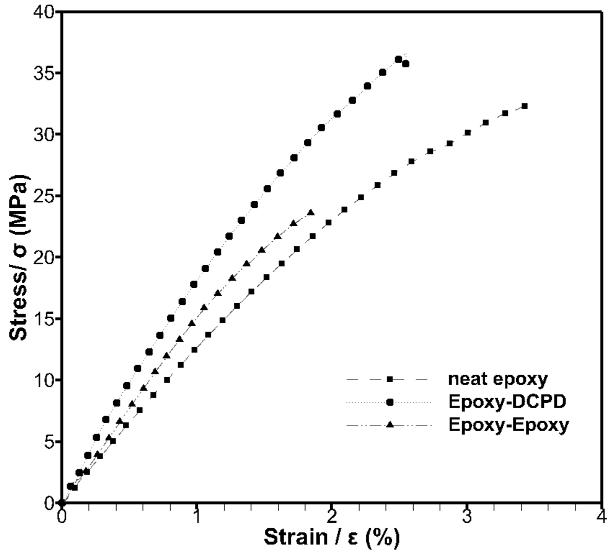

Figure 8. Stress-strain graphs of neat epoxy and DCPD/ epoxy - epoxy, conducted at 0.5 mm/min of cross head speed.

5. Conclusion

In this study, it was tried to compare two different types of encapsulated self- healing agents through calculation method and experimental test, which was a missing part in resent researches. This goal was achieved by calculating the interaction energy between encapsulated agent and the epoxy matrix. The results of DFT calculation showed the interaction energy of -0.13 eV for DCPD-epoxy system, which means physical absorption of DCPD monomer on the epoxy surface; however, no significant interaction energy was observed between two epoxy monomers. Physical properties, i.e. tensile strength, modulus and elongation at break, were measured in neat, epoxy-epoxy and epoxy-DCPD systems. According to the obtained results, the physical properties were improved for higher interaction energy between the components in DCPD-epoxy system. Therefore, it can be suggested that encapsulated DCPD would be better for crack curing in self-healing composites and nanocomposites in contrast with encapsulated epoxy.

Acknowledgements

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