ESTIMATION OF INTERFACIAL PROPERTIES OF VARIOUS CARBON FIBER EPOXY COMPOSITES USING MOLECULAR MODELLING AND SIMULATIONS

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Abstract

Molecular modelling and simulations are conducted to study interfacial interactions between various epoxies and their hardeners with T300 and CCF300 carbon fibers. Atomistic models of T300 and CCF300 carbon fibers, both in sized and unsized states are prepared on the basis of their X-ray Photoelectron Spectroscopy (XPS) data. Interaction energies between all the atomistic models of carbon fibers/epoxies and carbon fibers/hardeners are calculated separately with the help of molecular dynamics (MD) simulations using Materials Studio 4.3 software (Accelrys Software Inc.) with COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field. Subsequently, work of adhesion (WA) for every interface model is calculated on the basis of true adhesional area and finally, interfacial shear strength (τ) is estimated for all the models using WA values for respective interface models.

1   Introduction

There is a consensus that interfacial bonding term is mandatory for ascertaining properties of a composite material, in addition to the properties of its constituent materials [1-10]. Similarly, improvement in composite properties is also reliant on the quality and extent of interfacial bonding. However, exact measurement of interfacial adhesion is difficult due to the very small region involved and its submerged nature [2,7,10-14]. Various methods and techniques have been developed to date to measure the extent of interfacial bonding [3,4,15,16]. These techniques can be divided broadly into two categories: (1) Mechanical testing, and (2) Physical analysis. Mechanical testing methods include fragmentation, microbond and micro indentation tests [1,3,4,16-28] in which shear strength between single fiber and matrix is measured to estimate extent of interfacial bonding. Another very useful technique of Atomic Force Microscopy (AFM) is also being used to measure interfacial bond strength of composites [17,18,21]. Physical analysis comprises of Inverse Gas Chromatography (IGC) and wetting analysis which attempt to measure polar and dispersive components of surface energies of separate samples of matrix and fiber and then the extent of interfacial bonding is estimated indirectly by calculating the work of adhesion [2,15]. Besides the development of several mechanical and physical testing techniques

for the characterization of interfacial properties of composites, a state of uncertainty and incompleteness still exists amongst various quadrants of researchers [18]. Therefore, there is a need to develop some method to estimate interfacial adhesion of composites based on true interactions of constituents at the interface and which can bridge the gap between existing characterization techniques. Zhandarov S, and Mader E. [4] have attempted to calculate work of adhesion from interfacial shear strength values using single fiber microbond test. They evaluated various micromechanical tests particularly microbond test and showed the relationship between 'practical adhesion' (bond strength) with 'fundamental adhesion' (work of adhesion). Molecular simulation technique has been used successfully in the field of drug designing but its application to composite materials is quite rare [7,29-31]. Inaccessible and submerged interface of a composite material can be best explored with the help of molecular simulation by evaluating true interactions at the molecular scale. However, very few researchers have attempted to employ molecular simulation to study the interface of CFRP [7,14-16].

In this paper, interaction energy between T300 and CCF300 carbon fiber models and various epoxy/hardener monomer models is calculated with the help of MD simulations. Afterwards, work of adhesion values for respective models are calculated on the basis of true adhesional area. Ultimately, interfacial bond strength is calculated for each model with the help of work of adhesion data. In this manner effect of surface oxidation of carbon fibers and effect of true adhesional area of an interacting monomer on work of adhesion and interfacial shear strength is investigated. Physical and mechanical phenomenon in CFRP composites is correlated quantitatively and compared with respective experimental literature data.

2 Experimental
2.1 Materials
Sized and unsized, T300 (Toray Japan) and CCF300 (Weihai Guangwei China) carbon fibers were selected as reinforcement fibers. DGEBA (di-glyceridyl ether of bisphenol-A) and TGDDM (Tetra Glycidyl Diamino Diphenyl Methane) were the epoxies and DDS33 (3,3-diaminodiphenyl sulfone), DDS44 (4,4-diaminodiphenyl sulfone) and IPD (isophorone diamine/1-amino-3-aminomethyl-3,5,5-trimethylcyclohexane) were chosen as hardeners. In addition, long chain JEFFAMINE[®] diamines i.e. D400, D2000, D4000, and JEFFAMINE[®] triamines i.e.T403, T300, T5000, were also used as hardeners.
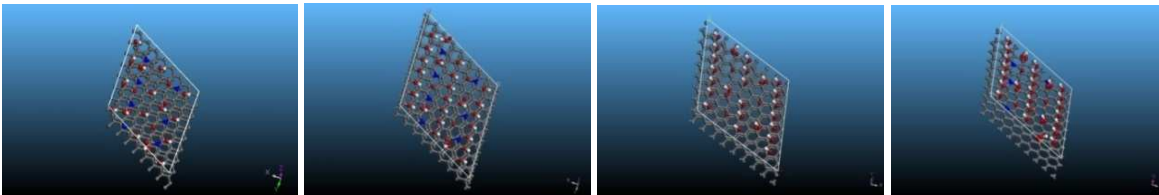

Figure 1. Atomistic models of T300 and CCF300 carbon fibers

2.2 Models development
Carbon fiber models were developed on the basis of XPS data and respective atomistic models were constructed by using 'Build' menu of Material Studio 4.3 (Accelrys Software Inc.), that are shown in Figure 1. It may be noted that T300 (unsized) has highest O/C ratio and number of oxidative functional groups on its surface. T300 (sized) can be graded at second tier. CCF300

either sized or unsized has very less difference as far as O/C ratio is concerned. Detail of carbon fiber models development can be found elsewhere [9]. All 11x types of monomer models for epoxies and hardeners were developed by using 'Build' menu of Material Studio 4.3 (Accelrys Software Inc.). Each crystal form of monomer model was structurally optimized by using MD simulations for 50 ps at 598°K with time step of 1fs and using NVT ensemble. Structures were again energy minimized using 'smart minimizer' so that energy converges to less than 0.1 Kcal/mole. COMPASS force field was used for all the simulations. Final monomer structures are shown in Figure 2.

2.3   MD Simulations

Separate interface models for each of carbon fiber and every monomer model were constructed using 'Layer builder' module of Materials Studio 4.3 software. Vacuum slab of 100A° was inserted in each model to avoid any interactions with subsequent layers due to periodic boundary conditions. Figure 3 reflects, as an example, the models of T300 carbon fibers, creating interfaces with monomers. 'Discover' module was used to perform MD simulations using COMPASS force field. All interface models were energy minimized using 'smart minimzer' tool of 'Discover' module so that the energy converges to less than 0.1 Kcal/mole. MD simulations were conducted using NVT ensemble for 80 ps with time step of 1fs at 598°K for equilibration. Post MD minimization was also carried out with energy convergence below 0.1 Kcal/mole for structure optimization. Separate MD simulations were carried out for all 11 kinds of monomer models with four types of carbon fiber models. All simulations were conducted with five different orientations and starting configurations. Average values of potential energy are used in subsequent calculations. For the comparison purposes, simulations with pure graphitic structure (carbon fiber without any surface moieties) are also conducted. All energy values are the total potential energies of the structures concerned.
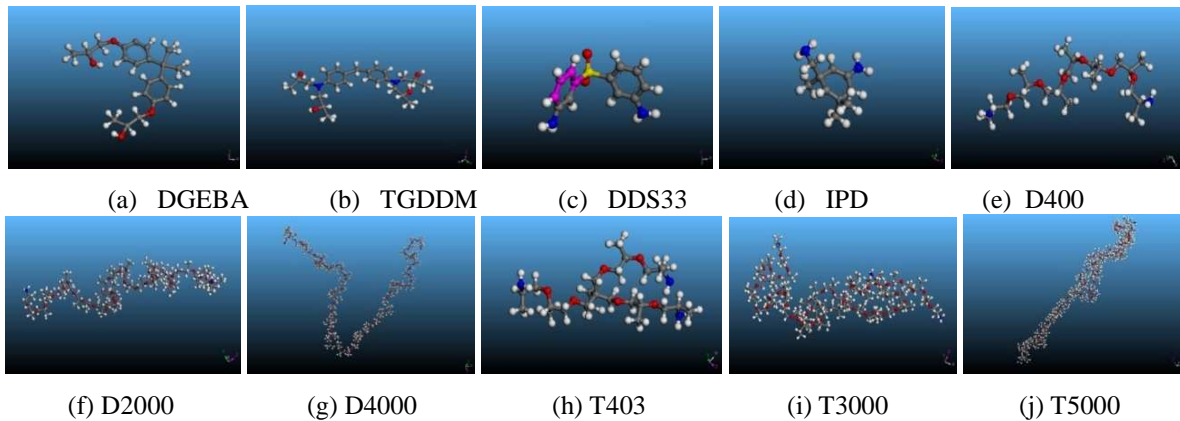

| (a) DGEBA | (b) TGDDM | (c) DDS33 | (d) IPD | (e) D400 |
| (f) D2000 | (g) D4000 | (h) T403 | (i) T3000 | (j) T5000 |

Figure 2. Atomistic models of monomers of epoxies and hardeners

3   Results and Discussions

MD data obtained by molecular simulations can be used to calculate interaction energy, work of adhesion and interfacial shear strength values for every model by using following relationships [20,22,31-33]:

$$E_{(interaction)} = E_{(carbon\,fiber+monomer)} - \left(E_{carbon\,fiber} + E_{monomer}\right) \qquad (1)$$

where,

$E_{(interaction)}$ = interaction energy,

$E_{(carbon\,fiber+monomer)}$ = total potential energy of the interface model, and

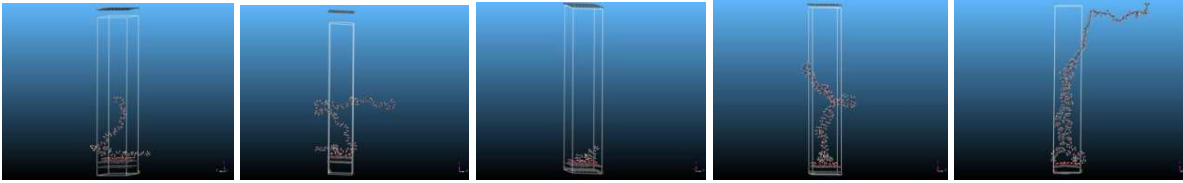$(E_{carbon\,fiber} + E_{monomer})$ = sum of potential energies of fiber and monomer in separate states.

Figure 3. Atomistic model of carbon fiber making interface with various monomers

$$W_A = \frac{-\Delta G_{ads}}{a_{mol} \times N} \qquad (2)$$

where,

W_A = work of adhesion,

$-\Delta G_{ads}$ = negative of interaction energy,

a_{mol} = molar adhesional area of respective monomer on carbon fiber surface, and

N = Avogadro's number (6.0221415×10^{23})

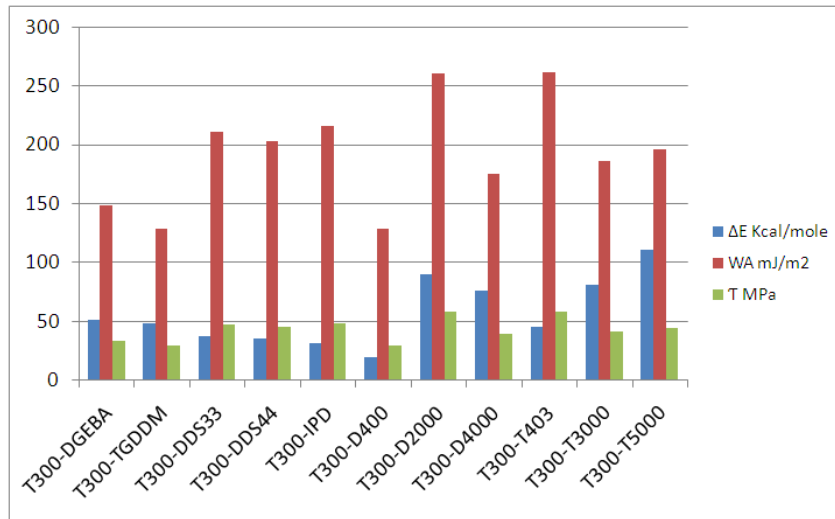$$T = kW_A = \frac{1}{\lambda}\left[\frac{E_m}{E_f}\right]^{1/2}W_A \qquad (3)$$

**Figure 4.** Interactions between T300 carbon fibers and various monomers

where,

T = interfacial shear strength,

k = proportionality constant for specific interaction,

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λ = distance up to which molecular forces are supposed to act (5 ^{o}A used during simulations)

E_m = matrix modulus (for simplicity used as 2.82 GPa)

E_f = fiber modulus (for simplicity used as 230 GPa)

Results calculated by using equations-1, 2 and 3 are presented in Figure 4, as an illustration, for interactions of all 11x monomers with T300 (sized). It may be noted that high value of ΔE for a specific model does not always mean to have a high value of W_A or T due to the effect of actual adhesional area. However, W_A and T are directly proportional to each other and this fact is evident from equation-3 and Figures 5-b and 5-c. In general, highest values of ΔE, W_A, and T are demonstrated by T300 (unsized) carbon fiber model due to higher level of oxidizing functional groups present on its surface. At the same time, it may also be noted that Jeffamine® Diamines and Triamines have shown the highest degree of ΔE during interaction with all kinds of fiber models as compared with both of the epoxies and other conventional hardeners (Figure 5-a). In the case of W_A, and T, still most of the high magnitudes belong to Jeffamine® Diamines and Triamines (Figures 5-b and 5-c).
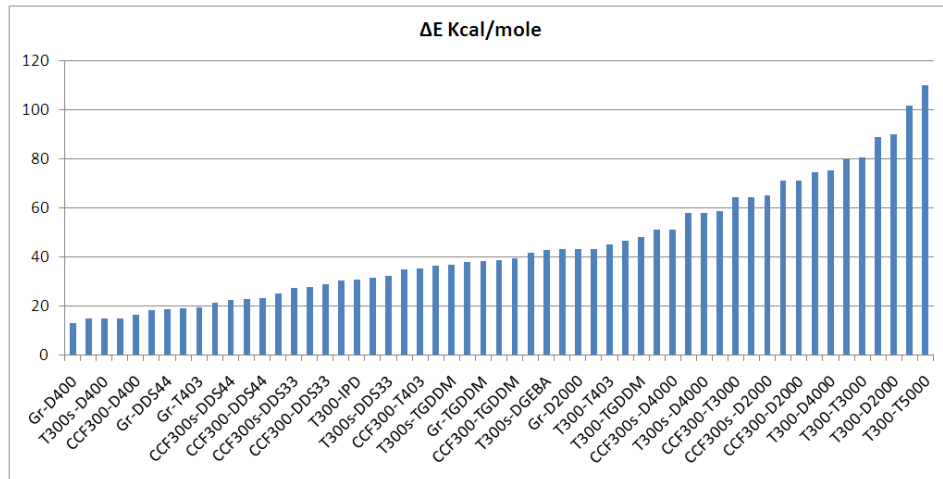
(a) Interaction energy
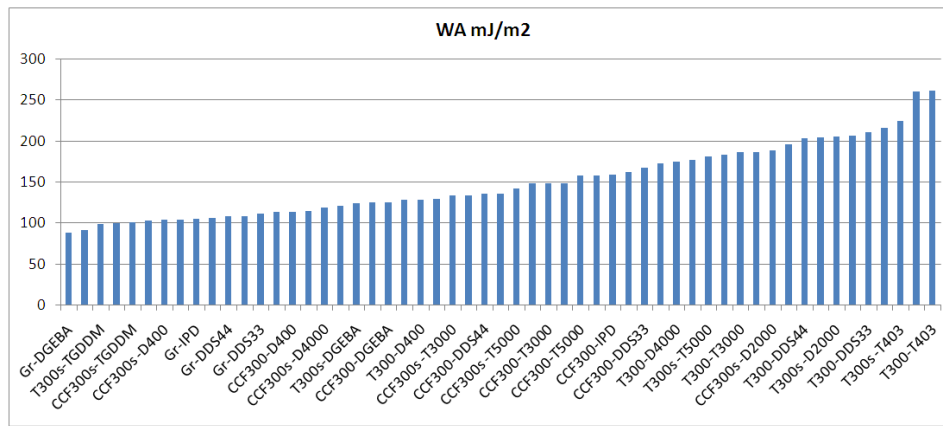
(b) Work of adhesion
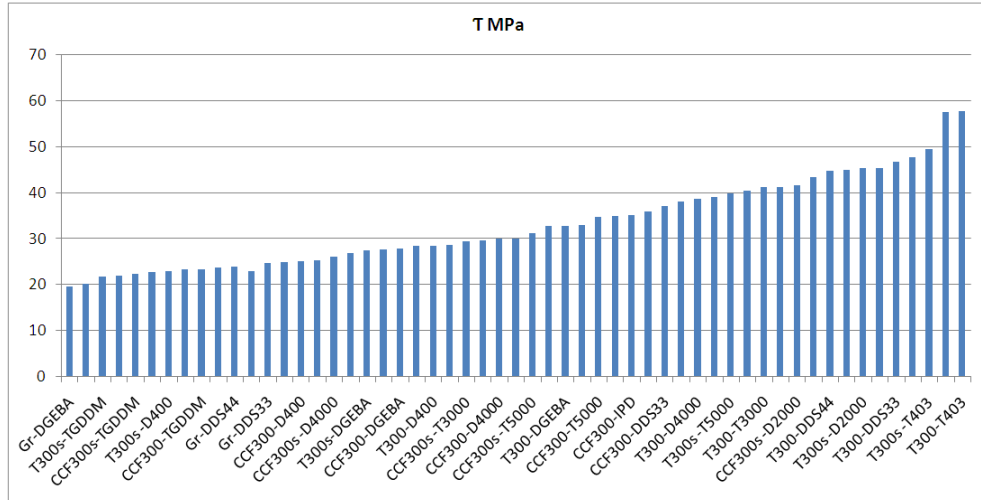
(c) Interfacial shear strength

Figure 5.   Interaction energy, Work of adhesion, and Interfacial shear strength values of various monomers against graphite and carbon fiber models

According to the results, the lowest value of τ is estimated for Graphite-DGEBA interaction i.e. 19.53 MPa and the highest value is predicted for T300 (unsized)-T403 combination i.e. 57.7 MPa (Figure 5-c). Results for interfacial strength obtained in this study are corroborated well by numerous data cited in literature. Choi et al [23] has introduced quasi disk specimen microbond test for the measurement of interfacial shear strength and reported a value of 20 MPa for a carbon/epoxy specimen. Allen Yu & Vijay Gupta [24] has calculated the stress at the interface of carbon fiber/epoxy composite with the help of FEM modeling to be 214 MPa. But they admitted that maximum possible value of interfacial shear strength cannot exceed 55 MPa, therefore, they concluded that composite must have failed beyond the threshold of 55 MPa. J. P. Ryan [25] has found that interfacial shear strength of high modulus (HM) carbon fiber with epoxy matrix is increased from 20 MPa to 58 MPa after plasma surface treatment. A.N. Netravali [26] has discovered that interfacial shear strength of carbon fiber with stiff, moderate and weak epoxy matrices are 38, 66 and 42 MPa respectively. Pratt B.A. and Bradley W.L [27] have estimated the interfacial strength of carbon fiber/epoxy composites to be 43 MPa at most at 0% moisture content. N. Melanitis et al [28] has calculated IFSS value of carbon fiber epoxy composite as 42 MPa. As a result, literature values mentioned above clearly support the results obtained in this work and proved that the modeling and methodology to estimate interfacial shear strength of carbon fiber/epoxy composites to be adequate. Specially, effect of true adhesional area and extent of surface oxidative functional groups in various types and states of carbon fiber models are quite obvious.

4   Conclusions

Interfacial shear strength of carbon fiber/epoxy composites is estimated with the help of molecular dynamics (MD) simulation technique. Work of adhesion is calculated using interaction energy values of interfacial models of various carbon fibers, epoxies and hardeners on the basis of real adhesional area. Derived values of interfacial shear strength are corroborated well by the numerous data cited in literature. Results have shown very clearly that interfacial adhesion increases with the increase in oxidative functional groups on carbon fiber surface. It is

also established that true value of interfacial shear strength can be achieved only after normalizing the attraction force with real adhesional area.

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