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Molecular modelling of interactions at the composite interface between surface-treated carbon fibre and polymer matrices: the influence of surface functional groups

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To simulate the results of surface treatments, commonly encountered functional groups were introduced onto the surface of the carbon fibre model. The carbon fibre model used in this study is based on the single layer diagonal graphitic plane, comprising 52 six-membered rings, in a 4 × 13 configuration, and of 150 carbon atoms. Surface treatment was represented by the introduction of functional groups (—R): each time, a C—C bond was broken along the edge of the plane, and a pair of —R groups was added to the graphitic plane. The total number of functional groups (n) was six. The effect of these functional groups on the non-covalent bonding interactions at the composite interface between carbon fibre and epoxy resin was investigated using a previously established BLENDS method. The compatibility of the resin and fibre in this model, indicated by the interaction parameter $\chi(T)$, was dependent upon two factors: steric bulk and electrostatic interactions. The halogen substituents show a decrease in $\chi(T)$, as one descends the group. Maximum interaction tends to be a function of steric bulk and polarizability in this group. The alkyl (C_nH_{2n+1}) and phenyl substituents also show a decreasing trend in $\chi(T)$ with increasing size, although the interaction parameter with methyl is anomalously low in all cases.

Reinforcement in composites such as those containing epoxy resin matrices (*e.g.* the diglycidyl ether of bisphenol A, DGEBA) incorporating carbon fibres, is achieved by sufficient stress transfer between fibres and matrix. The stress transfers can be realised by mechanical interlocking, physical adhesion and chemical bonding.[1] The technology to improve stress transfer within composites, as indicated by the improved interlaminar shear strength (ILSS), consists of surface treatment methods such as (*a*) treating fibres in oxidative acids,[2] (*b*) catalytic oxidation in air,[3] (*c*) anodic treatment in aqueous solutions,[4] (*d*) plasma surface treatments,[5] and (*e*) metal oxide coating.[6] Despite its importance, the nature of the interfaces/interphase region in fibre reinforced polymers remains largely unresolved. Wright suggested[7] that carbon fibre surface treatments lead to increased fibre surface area, removal of a weak surface layer, and modification of the surface chemistry. All three phenomena serve to improve resin wetting and bonding, and of these the available evidence suggests that the change in surface area is not a significant parameter, although polar surface free energy was found to increase on treatment.

Increasingly, there is a need to understand the properties and features of polymeric materials at the molecular level. Recent advances in molecular modelling have led to new methods able to predict the properties of structural, electromagnetic and optical materials.[8–14] Simulation based on simplified models has been carried out using *ab initio*, semi-empirical and force-field methods in the area of composite interfacial properties.[12,13] Our previous work[14] demonstrates that the molecular modelling method, BLENDS, can be used to simulate the non-covalent bonding interaction between electrolytically surface treated carbon fibre and various amine cured epoxy polymer models. The carbon fibre was modelled as graphitic layer(s) with —OH and —COOH functional groups attached to one edge. The polymers were modelled as an homopolymer and as both alternating and random copolymers to represent different degrees of cure of the epoxy resin. The change in the free energy of mixing ($\Delta_{mix}G$) was used to indicate the magnitude of the interaction and, hence, the interfacial adhesion. The results show a trend, in relation to the level of surface treatment, in agreement with literature data of composite interfacial strength.

The effect of other functional groups, apart from the most common ones such as —OH, —COOH and —NH_2 on the interfacial properties is of great interest to both chemists and materials scientists alike. Current surface treatment techniques limit the number and type of functional groups that can be introduced onto the carbon fibre surfaces, hence preclude investigation by experimental methods.[15] Molecular simulation provides a useful tool to tackle these problems by introducing ‘artificial’ surface functional groups. As a result, our understanding of the complex nature of the fibre-reinforced composite at interfaces can be increased. In this paper, we report our investigation into the effect of various surface functional groups on the interactions between carbon fibres and polymer matrices, using the BLENDS method.

Calculation

A Silicon Graphics Indy workstation (MIPS R4000) running the computer program CERIUS2 v.1.6 (Molecular Simulations Inc.) was used to generate models and to calculate the nonbonding interaction. The Dreiding 2.21 force field[16] was used in this work. The charge calculation method, charge equilibration (Q_{eq}),[17] was used to assign, edit and calculate point charges.

Models

The monomer models (Fig. 1) include the diglycidyl ether of bisphenol A (DGEBA), bis(4-aminophenyl) sulfone (DDS), bis(4-aminophenyl)methane (DDM) and ethylene. The polymer models include the linear DGEBA homopolymer chain, and the amine-cured epoxy resins, both alternating (alt-co) and random (ran-co) copolymers of DGEBA–DDM and DGEBA–DDS. The homopolymer, random copolymers (amine : epoxy monomers in the ratio 2 : 8), and alternating copolymers represent different degrees of chain extension of the epoxy resin. The carbon fibre models are a series of graphitic planes. The basic considerations for model construction and details of the polymer models have been described elsewhere.[14]

Single-layered graphitic models for carbon fibres. The carbon fibre model used in this study is based on the single layer

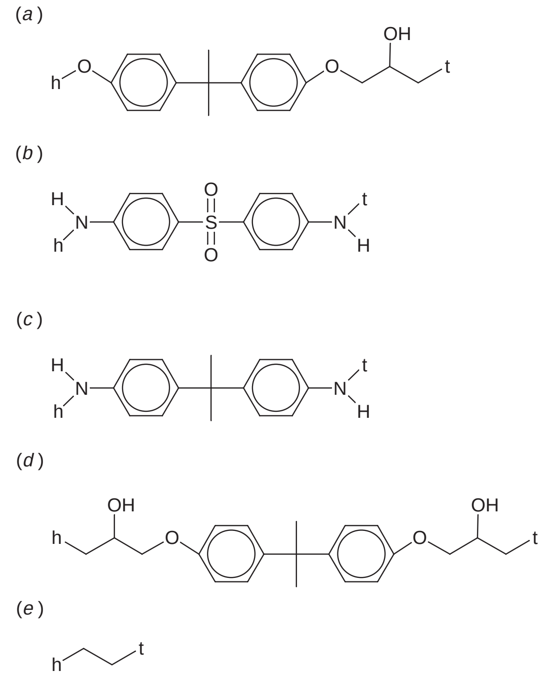

Fig. 1 Structural repeat units for (*a*) the diglycidyl ether of bisphenol A (DGEBA) in homopolymer and random copolymers, (*b*) bis(4-aminophenyl) sulfone (DDS), (*c*) bis(4-aminophenyl)methane (DDM), (*d*) DGEBA in alternating copolymers and (*e*) polyethylene (PE). h = head linkage, t = tail linkage for the polymer builder.

graphitic sheet. A diagonal graphitic plane, comprising 52 six-membered rings, in a 4 × 13 configuration, and of 150 carbon atoms, was built as the principal, non-surface treated carbon fibre model. In this structure the carbon atoms have sp^2 hybridisation, and form partial double bonds (the perfect graphitic structure is a flat plane). Those carbons at the outermost edge form CH (in closed ring) or CH_2 (open end). A further 18 variants of the model were built based on this structure. Surface treatment was represented by the introduction of functional groups (—R): each time, a C—C bond was broken along the edge of the plane, and a pair of —R groups was added to the graphitic plane (Fig. 2). The total number of functional groups (n) was six. The functional groups were arranged in such a way as to be evenly distributed along the edge of the plane. These structures were then relaxed by molecular mechanics energy minimisation, using conjugate gradients and charges derived from the Q_{eq} method, until energy convergence (at 0.01 kcal mol^{-1}; 1 cal = 4.184 J) was achieved.

For $R = CH_3$, Bu^t, CF_3, models with $n = 12$ were constructed using the same procedure described above.

Molecular simulation method

The property prediction method, BLENDS,[18] was used to investigate the interactions between two macromolecules. The module combines a modified Flory–Huggins model[19] and molecular simulation techniques to calculate the compatibility of binary mixtures. The theoretical and computational considerations were developed by Blanco and co-workers.[20] In implementing the Flory–Huggins lattice model for polymers, BLENDS requires that the lattice sites be occupied by polymer segments. BLENDS is also an off-lattice calculation, meaning that molecules are not arranged in a regular lattice as in the original Flory–Huggins theory. In practice, each of the graphitic models and the polymer models occupy one lattice site. The degrees of polymerisation X_1 and X_2 were both set to 1, and the total molecular weight of the polymers was ignored.

BLENDS also provides options that place restrictions on both molecule alignment and atom contact during packing, and thus allows one to obtain more representative interaction energies of ij pairs, E_{ij} values. Graphitic structures in carbon fibres are highly oriented, therefore models are aligned along the principal axes (the allowed range of orientation was 10°). On the other hand, the epoxy and polyethylene polymer models have an isotropic (random) packing with no restrictions at all.

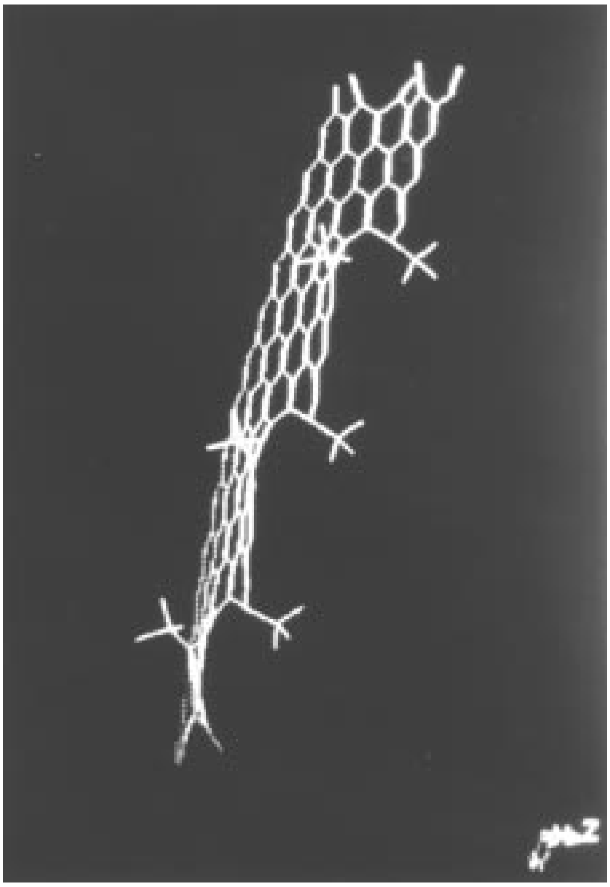

Fig. 2 Structure of the single-layered graphitic plane as an example of the surface-treated carbon fibre model, in which $R = Bu^t$ and $n = 6$

The interaction parameter $\chi(T)$ is defined as eqn. (1),

$$\chi(T) = \frac{E_{\mathrm{mix}}(T)}{RT} = \frac{(Z_{12}E_{12} + Z_{21}E_{21} - Z_{11}E_{11} - Z_{22}E_{22})}{2RT} \tag{1}$$

where E_{ij} is the interaction energy for a pair of ij. BLENDS uses Monte Carlo atomistic simulations both to generate thousands of different molecular orientations and to calculate their pair-interaction energies (this method results in four Boltzmann averaged E_{ij} values); Z_{ij}, the coordination number, is the number of molecules of type j that can be packed around a single molecule of type i. A single coordination number has a definite physical significance only when two components of the binary mixture have a similar volume or surface area. Z is explicitly calculated for each of the possible molecular pairs using a molecular simulation method called nearest-neighbours packing. It involves generating clusters in which nearest neighbours are packed around the central molecule until no more will fit. The van der Waals surface is used to represent the shape of the molecules. We matched the single layer graphitic model (150 atoms) with polymer models comprising ten repeat units (about 200 atoms).

BLENDS analysis options can be used both to calculate thermodynamic functions (entropy, enthalpy and free energy of mixing) for a binary system, and to create plots of these functions *versus* composition at a specific temperature. The plots generated reflect the current choice of the interaction parameter model $\chi(T)$ and the degree of polymerisation of the two components in eqn. (2),

$$\frac{\Delta_{\mathrm{mix}}G}{RT} = \frac{\phi_1}{X_1}\ln\phi_1 + \frac{\phi_2}{X_2}\ln\phi_2 + \chi\phi_1\phi_2 \qquad (2)$$

where $\Delta_{\mathrm{mix}}G$ is the free energy of mixing, ϕ is the volume fraction of each component, X_1 and X_2 are the degrees of polymerisation (or chain length) of each component. The plots of thermodynamic isotherms showed that $\Delta_{\mathrm{mix}}G$ is sensitive to the change of volume fraction, but not to temperature in the range 300–400 K. When other parameters such as $\phi_1 = \phi_2 = 0.5$, *and* $T = 300$ K are equal, $\Delta_{\mathrm{mix}}G$ is proportional to $\chi(T)$. Therefore $\chi(T)$ is used to characterise the interaction between the carbon fibre and polymer models in this work.

Results and Discussion

This work is part of an ongoing program involving both experimental and simulation studies of fibre–resin interactions covering XPS, SIMS analysis,[4] surface radioisotope and stable isotope labelling, surface chemical reaction,[21] and inverse gas chromatography (IGC).[8g] The object of this paper was to look at the specific interactions between functionalised carbon fibre surfaces and matrix resins. The model only deals with the improvement in the compatibility between the fibre and the resin owing to the functionalisation. It does not deal with mechanical keying, pores or clefts, *etc*. It is currently impossible to model at the atomistic level a whole fibre and this may not be productive. Such a model would contain too many variables to allow for the systematic control of each. The models used simulate, to the best of our current knowledge, a representative section of the fibre surface, in effect a close up of a section of the surface. These models could be extended in three dimensions to produce the entire surface of a fibre but would contain no extra information than that used.

The dependence on size of the models used has been dealt with in our previous paper, where it was demonstrated that both the multi-layer graphitic models and the single layer models gave quantitatively similar results.[14] The size of the polymer needs to be commensurate with that of the graphitic model. Obviously, as with any simulation technique, the results obtained depend on the force field used. We have employed the Dreiding 2.21 force field for these simulations. This force field has been validated by calculating the physical and mechanical properties of structural polymers in a number of previous papers.[8] Naturally, in a study of this kind the electrostatic model is important and the magnitude of the point charges can vary depending on the calculation used to derive them. The ideal method would be to use *ab initio* calculations to derive these but this method is limited to structures containing about 40 atoms or less, and is not feasible with the current models. The force field chosen is balanced (*i.e.* the charges are scaled up or down) so that the point charges do not dominate the covalent interactions and any alternative calculation would also need to have the charges scaled. A further proof of the validity of the models and force field employed can be found in a study which showed that simulation of the electrostatic effects compared very well with IGC experimental results.[8g]

The geometry of the graphitic plane

All structures of the carbon fibre model with functional groups attached deviated from the perfectly flat graphitic plane after energy minimisation. In the oxidised portion of the models (where functional groups were added), the graphitic planes curved when energy minimisation was performed (Fig. 2). The bulkier groups resulted in more severe distortion. Similar distortion was also observed when the concentration of the groups increased. The curvature induced in the surface is a direct result of substitution with the functional groups, *i.e.* it represents a change in the hybridisation state of the carbon atom (from sp^2 to sp^3) and the requirement for bond angles of 109.5° rather the 120° to which the group is attached. The electrostatic repulsion between functional groups on each layer also contributed to the deformation in these carbon fibre models. The models in all cases are relaxed to the same energy convergence criterion (0.001 kcal mol^{-1}) in order to be directly comparable. This, of necessity, also requires the use of the same force field (in this case Dreiding 2.21).

The nature of the surface functional groups

It is important to remember that the nature of the interfacial region between bulk resin and fibres is the subject of this study and the results will be discussed with regard to the interaction between these two components. The compatibility of the resin and fibre in this model depends upon two factors: steric bulk and electrostatic interactions. The halogen substituents (the second group in Table 1) show a decrease in the interaction parameter $\chi(T)$, as one descends the group. Fluorine has the greatest interaction parameter and iodine the least. Therefore, the interaction with iodine would be the most favourable. Maximum interaction tends to be a function of steric bulk and polarizability from this group. The group of substituents which comprises the alkyl homologues and the phenyl ring (the third group in Table 1) also shows a general trend with increasing size, although the interaction parameter with methyl is anomalously low in all cases. Interestingly, in most cases the substitution of fluorine atoms for the hydrogen atoms (*i.e.* in changing the substituent from $-\mathrm{CH_3}$ to $-\mathrm{CF_3}$) causes a decrease in the interaction parameter and hence an increase in the compatibility. This does not follow for the case when polyethylene is the polymer matrix.

Considering the functional groups which actually exist on the carbon fibre surface as a result of the electrolytic oxidation (*e.g.* $-$OH, $-$COOH and $-$CHO, the seventh group in Table 1), there is a general decreasing trend from $-$OH to $-$COOH to $-$CHO for the epoxy and polyethylene homopolymers and the alternating epoxy–amine copolymers. With the random epoxy-amine copolymers there is no obvious trend. The small steric bulk of the $-$OH group appears to predominate over its hydrogen bonding potential. Conversely, in the case of the $-$COOH group its large steric bulk reduces its ability to form hydrogen-bonds. Therefore, the $-$CHO group, being of intermediate size with hydrogen-bonding potential gives the strongest interaction with all of the polymer matrices. These results, in line with experimental data,[7] do suggest that mild oxidative conditions might facilitate optimal interfacial adhesion. Further complication might arise from the potential of the $-$COOH group to form covalent bonds, leading to increased stress at the interface between the matrix resin and the carbon fibre surface. Having said that there is also evidence to show that the ILSS does not necessarily decrease with a decrease in the oxygen–carbon ratio when the functional groups introduced by oxidative treatment are eliminated.[22] The result highlights the importance of physical or mechanical effects in determining fibre–matrix adhesion.

Interactions between single-layered graphitic models and polymers

A linear free energy treatment[23] was attempted for the entire Table 1 by plotting $\sigma_{\mathrm{I}} + \sigma_{\mathrm{R}}$ *versus* the interaction parameter $\chi(T)$. However, as expected this problem cannot be treated simply in terms of inductive effects, and a poor correlation was obtained. Furthermore, a multiple linear regression analysis of $\chi(T)$ against C$-$X distances (which were obtained from the centre of the carbon to the centre of the outermost atom for each functional group after optimising the structure on CERIUS2), $\sigma_{\mathrm{I}} + \sigma_{\mathrm{R}}$ (the Hammett substituent constants[23]) and $\Delta H^{\ominus}$ (the sum of bond enthalpy[24]) gave an r^2 value of 29% with a constant of 211 indicating that most of the variation

Table 1 Interaction parameter $\chi(T)$ at 300 K between polymer models and single-layered carbon fibre models with different surface functional groups

functional group $n=6$	DGEBA homopolymer	DGEBA copolymers DDS alt-co	DDM alt-co	DDS ran-co	DDM ran-co	polyethylene
H	306.2	279.9	355.2	312.3	307.1	226.4
F	159.7	137.7	214.3	165.5	164.5	95.4
Cl	129.5	61.1	111.1	96.6	109.7	68.7
Br	113.6	67.6	102.9	78.2	96.5	41.1
I	57.3	77.3	63.1	22.0	56.5	2.8
OMe	138.8	87.7	144.8	107.2	109.7	91.2
SMe	145.3	145.7	155.5	118.9	150.2	99.5
CF_3	105.5	67.8	82.4	138.9	71.6	81.6
Me	157.6	154.2	185.2	149.3	124.8	74.4
Et	179.4	181.0	163.4	163.7	196.0	144.6
Pr^i	153.6	164.7	145.3	135.7	171.4	88.3
Bu^t	149.8	163.9	152.8	174.8	164.4	72.3
Ph	108.8	95.2	96.6	93.9	118.2	22.9
CN	142.2	118.8	148.9	137.0	154.8	89.5
NO_2	98.2	74.0	74.5	75.7	72.0	67.9
NH_2	148.9	124.7	175.4	150.5	139.5	58.4
OH	169.9	136.5	216.8	188.3	149.3	145.5
COOH	142.0	125.9	131.3	137.9	162.6	107.3
CHO	118.5	92.0	115.6	143.0	121.3	72.0

was not in the parameters chosen. Perhaps the situation is just too complex for these simple treatments.

In order to find a simple parameter to correlate, the steric substituent constant (E_s),[23] which is a function of the steric bulk for spherical substituents, was plotted against the interaction parameter $\chi(T)$. The plot for the halogens is shown in Fig. 3 where an approximately linear decrease with E_s is found as one descends the group. This provides some support for the idea that steric bulk favours interaction between the polymer matrix and the carbon fibre surface where the groups are essentially spherical and inherently polarizable. Similarly, for the alkyl and phenyl residues a plot of $\chi(T)$ against E_s is given in Fig. 4. This shows a non-linear increasing trend with increasing E_s with the most favourable interaction being formed with the phenyl substituent. The hydrogen substituent is the least favourable and this supports the idea that both steric bulk and polarizability are the important parameters to consider. E_s contains information pertaining to steric bulk and it is interesting to note that this parameter gives a better correlation than that relating to polarizability.

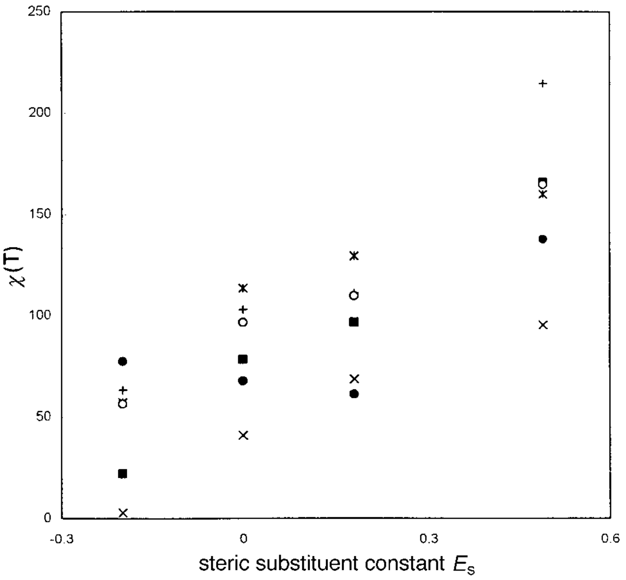

Fig. 3 Plots of $\chi(T)$ *vs.* steric substituent constant (E_s) representing interaction of halogen substituted carbon fibre models with (+) DDM–DGEBA alternating copolymer, (*) DGEBA homopolymer, (○) DDM-DGEBA random copolymer, (●) DDS–DGEBA alternating copolymer, (■) DDS–DGEBA random copolymer and (×) polyethylene

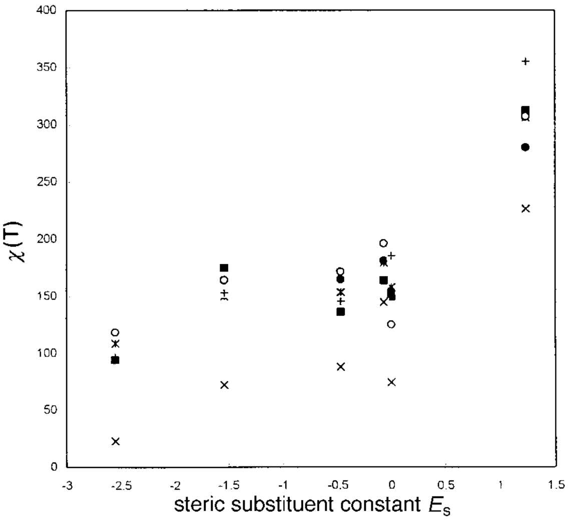

Fig. 4 Plots of $\chi(T)$ *vs.* steric substituent constant (E_s) representing interaction of alkyl and phenyl substituted carbon fibre models with (+) DDM–DGEBA alternating copolymer, (*) DGEBA homopolymer, (○) DDM-DGEBA random copolymer, (●) DDS–DGEBA alternating copolymer, (■) DDS–DGEBA random copolymer and (×) polyethylene

Effect of changing surface group concentration

Table 2 lists the interactions between a DGEBA homopolymer and multi-layered carbon fibre models at different values of n (number of functional groups on the carbon fibre model's surface). An increase of methyl group concentration on the carbon fibre model does not result in much change (+10%) in $\chi(T)$. An increase of *tert*-butyl group concentration on the

Table 2 Interaction parameter $\chi(T)$ at 300 K between DGEBA homopolymer and carbon fibre models at different number of surface functional groups (n)

functionality	$n=6$	$n=12$
Me	157.6	172.8
Bu^t	149.8	104.7
CF$_3$	105.5	200.0

carbon fibre model results in a decrease (-30%) in the value of $\chi(T)$. An increase in the concentration of $-CF_3$ groups on the carbon fibre model results in an increase ($+90\%$) in the value of $\chi(T)$. The substitution of hydrogen for methyl and then fluorine in low surface concentrations improves the interaction, but at higher concentrations the more bulky *tert*-butyl group is preferred.

Effect of changing the polymer matrix

Similar trends in interfacial adhesion were observed for polyethylene. However, the absence of polar groups in the polymer chain tends to decrease the interaction parameter $\chi(T)$. This is probably because being a graphitic structure the bulk of the carbon fibre surface is non-polar in nature and the surface groups are present at low concentration ($<10\%$ surface coverage),[14] therefore making the carbon fibres more compatible with the non-polar polyethylene chains. The thermodynamic work of adhesion can be expressed by eqn. (3),[25]

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (3)$$

where W_a is the thermodynamic work of adhesion, γ_{SV} is the surface energy of the solid–vapour interface, γ_{LV} is the surface energy of the liquid–vapour interface, γ_{SL} is the surface energy of the solid–liquid interface. The surface energy of the fibre (γ_{SV}) should be greater than that of the matrix (γ_{LV}) for proper wetting to occur. Better wetting can enhance the adhesive bond strength by increasing the thermodynamic work of adhesion W_a which is directly proportional to the fracture energy of the adhesion bond.[26] Thus, carbon fibres (typically with surface energy of 40–50 mJ m^{-2}) can be wetted readily by polymer matrices such as epoxy (with surface energy of 43 mJ m^{-2}) and polyethylene (with surface energy of 31 mJ m^{-2}).[26] These analyses are consistent with our simulation results above.

Conclusions

The interfacial interaction between carbon fibres and polymer matrices can be modelled in terms of steric bulk and hydrogen-bonding potential of the substituent. There is a trade-off between these two parameters and, in practice, mild oxidation is the preferred route to enhance interfacial adhesion. More polar groups (such as $-CF_3$, $-I$ and $-NO_2$) give more favourable interactions, but we accept that these are not easily accessible nor in some cases desirable with current technologies for surface treatment. Whilst similar trends in interfacial adhesion were observed for epoxy polymers and polyethylene, the presence of polar groups in the polymer backbone tends to reduce the interaction. This is probably because being a graphitic structure the bulk of the carbon fibre surface is non-polar in nature and is more compatible with the non-polar polyethylene chains.

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