On the Correlation of Some Theoretical and Experimental Parameters in Polycondensation Crosslinked Networks. II. Interfacial Energy and Adhesion on Cellulose Substrates

A. PIZZI

ENSTIB, University of Nancy 1, Epinal, France

INTRODUCTION

Molecular mechanics in the broader sense of the term is a computational technique that is, among its other applications, particularly suited for determining at the molecular level the interactions at the interface of molecularly well-defined polymers. It has already been used in the wood field, for instance, to calculate the relative energies of interaction between synthetic polycondensation oligomers used as adhesives and their cellulosic substrate with excellent correspondence between calculated and applied results and some interesting applied consequences,[1–6] as well as to address other interfacial energy problems.[7]

Recently, an equation, as well as its simpler regressions, correlating the relative deflection obtained by thermomechanical analysis with the sum of the interfacial energy of interaction of a synthetic polymer with wood plus the internal cohesive strength of the hardened synthetic polymer has been obtained,[8–10] namely

$$E = -km/(\alpha f)$$

where k is a constant dependent upon the testing conditions used, m is the average number of degrees of freedom between crosslinking nodes of a hardened network, E is the sum of the energy of interaction at the interface of the synthetic polymer and the substrate and of the internal cohesive energy of the synthetic polymer (the internal energy of the substrate is not considered because the deflection measured is relative to the substrate alone), and α is Flory's coefficient of branching for polycondensates. The above equation has been shown to work also for radical hardening polymers, with the proviso that the coefficient α is no longer Flory's coefficient of branching but a coefficient calculated in the same manner by substituting the number of reactive carbon atoms to the functionality [i.e., for each $C=C$ present this gives two reactive carbons, and thus $\alpha = 1/(f - 1)$, where f is 2 rather than 1 as it would be in polycondensates[8]].

Although interesting conclusions about the covalent networking of polymers, both polycondensates and others,[9] have already been obtained, some equally interesting considerations on the interfacial adhesion between an adhesive and a lignocellulosic substrate, and by inference on the interfacial adhesion between any two materials, can also be derived. This article, then, addresses this aspect of the above formula's application.

EXPERIMENTAL

Materials

Three photopolymerizable primer monomers, namely the linear hexanediol diacrylate (HDDA), the branched trimethylol propane triacrylate (TMPTA) and the linear tripropyleneglycol diacrylate (TPGDA), supplied by CIBA-GEIGY, Basel, Switzerland, and a model of a linear unsaturated polyester–alkyd varnish repeating unit, were used for the study. The following polycondensation resins were used: (1) An industrial pure resorcinol–formaldehyde (RF) cold set resin having a solids content of 53%, a pH of 8.3, and a manufacturing molar ratio R : F of 1 : 1.5, to which was added one further molar proportion of paraformaldehyde as hardener to yield a final molar ratio R : F of 1 : 2.5, supplied by Bakelite AG (Duisburg-Meiderich), Germany, and specifically prepared for these series of experiments. (2) An industrial melamine–formaldehyde (MF) thermosetting resin having a molar ratio M : F of 1 : 1.5, a whitening point of 130%, a pH of 10.2, and a solids content of 63%, prepared by Chimica Pomponesco, Italy, to which was added 1.5% NH_4Cl as hardener. (3)

A phenol–formaldehyde (PF) thermosetting resol resin having a molar ratio P : F of 1 : 2.0, a solids content of 51%, and a pH of 12.6, supplied by Bakelite AG (Duisburg-Meiderich), Germany. (4) A tannin novolak resin based purely on a commercial profisetinidin–prorobinetinidin tannin (quebracho tannin, water-extracted from *Schinopsis balansae*) having a pH of 7.3 and a solids content of 45%, to which was added 10% paraformaldehyde as hardener, prepared jointly by Silva S.p.a., Italy, and Indunor, Argentina.

Thermomechanical Analysis

The resins were tested dynamically by thermomechanical analysis (TMA). Samples of beech wood alone, and of two-beech-wood treated plys bonded with a polycondensate resins layer of 350 μm, for a total samples dimensions of $21 \times 6 \times 1.1$ mm were tested isothermally at 25°C with a Mettler 40 TMA apparatus in three points bending on a span of 18 mm exercising a force cycle of 0.1 N/0.5 N on the specimens with each force cycle of 12 s (6 s/6 s). The classical mechanics relation between force and deflection $E = [L^3/(4bh^3)][\Delta F/(\Delta f_{wood} - \Delta f_{adhesive})]$ allows the calculation of the Young's modulus E for each of the cases tested. Since the deflections Δf obtained were proven to be constant and reproducible,[8] and they are proportional to the flexibility of the assembly, the relative flexibility as expressed by the Young's modulus of the two primers can be calculated for the two finishes through the relationship $E_1/E_2 = \Delta f_2/\Delta f_1$.

The values of m, E, and α for the resins presented in Table 1 were known from previously reported work, and the relationship used between them was the phenomenological equation $f = -km/\alpha E$, which has already been reported.

The dynamic bending TMA experiments were repeated for the same size samples, but starting from the liquid resins, and the bending variation of the assembly under dynamic stress was monitored with the variation of the temperature for a heating rate of 10°C/min. The results obtained are shown in Table I.

Molecular Mechanics Results

The values of the energies of interaction E, which were used for the radical hardening polymers and for melamine–formaldehyde, resorcinol–formaldehyde, phenol–formaldehyde dimers and real number average degree of polymerization profisetinidin-formaldehyde (quebracho tannin), have already been calculated and published and have hence been taken from the literature.[1–6,8,9] The main computational program used for the calculations of the secondary forces interactions between primers and substrate and between varnish and the primer–cellulose assembly was a constrained force-field model called BONDS,[11–13] which has already been

checked many times against automatic unconstrained force-field models for its accuracy on proteins,[14] on cellulose,[11–13] on cellulose derivatives,[15] and on cellulose interfaces with other polymers or simpler molecules,[1–6] and the results of which have also been checked by other authors to obtain good interfacial forecasts of experimental phenomena.[16–18] For the photopolymerizable primers, since the contribution of H-bonds in the systems studied was found to be very small or nonexistent, the calculations of energy minimization were based for these three materials and for the unsaturated polyester only on all the van der Waals and electrostatic interactions and torsional bonds potentials. For the polycondensates the contribution of the H-bond was also considered. The potential functions used were of the Buckingham type, and the set of coefficients used for the functions was the Liquori set.[19] In this program all the covalent bond lengths and bond angles between covalently bonded atoms are fixed to specific values without allowance for their adjustment or modification during computation. Such a constrained force-field approach was taken to render computation more rapid. The results obtained have already been presented in considerable detail in the literature,[1–6,8–10] and the energy results are summarized in Table I.

DISCUSSION

Table I presents the computational results of the energies of interaction between different synthetic polymers and crystalline cellulose I derived from previous work.[1–6,8–10] It must clearly be pointed out that the molecular mechanics–derived energies of interaction at the molecular level are considered to determine the interfacial energy of the system and not the strength of the joint, which mainly depends on viscoelastic energy dissipation. Molecular mechanics is then used here only to ascertain if useful deductions can be derived from an approach simpler and different from the well-established viscoelasticity of polymeric adhesives.

The first conclusion that can be drawn is that all the energies of interaction of all the systems studied are attractive (the sums of all interactions indicate attraction of the molecules of the system for each other as denoted, by convention, with a minus sign). This means that it is energetically favorable at least for the different synthetic polymer–substrate systems studied to adhere together, a fact which is obvious from previous experimental results,[8–10] but it is nonetheless useful to see these results confirmed at a theoretical level to check the correctness of both the approach and of the algorithm used.

The following single formula is used to define the flexibility of the system:

$$E = -km/(\alpha f) \quad \text{and conversely} \quad f = -km/(\alpha E) \quad (1)$$

where m is the number of degrees of freedom, E (kcal/mol) is the interaction energy of the molecule of monomer with the substrate, and f (μm) is the relative de-

Table I Experimental Results and Derivation of the Value of k for the Different Resin Systems

	m	α	E[b] (kcal/mol)	f[a] (μm)	k
HDDA	7	0.33	−5.87	58	16.1
TMPTA	11	0.20	−13.58	63	15.6
TPGDA	14	0.33	−13.83	49	16.0
Polyester	8	0.33	−13.83	28	16.0
MF adhesive	1.9	0.2	−10.3	15.0	16.3
RF adhesive	6.1	0.5	−14.5	13.5	16.0
PF adhesive	9.1	0.5	−14.5	20.1	16.0
QF adhesive	2.7	0.148	−12.1	24.1	16.0

[a] Experimental TMA deflection.
[b] By molecular mechanics.

flection obtained for the system by TMA. It was also necessary to introduce a multiplicative constant k to be able to compare numerically the values of relative flexibility expressed in the experimental form of relative TMA deflection with the actual values of the energy of interaction in kilocalories per mole. The formula can be used as above with a minus sign if the interfacial energy is expressed with a minus sign as it is conventionally in molecular mechanics for attractive energies. The formula can also be used without a minus sign if the purely numerical value of the energy is used. From the TMA and calculated results, the numerical value of k is always approximately 16 (Table I), when E is expressed in kilocalories per mole, and depends exclusively on the dimensions of the samples used and conditions under which the tests were performed (different conditions could give a different value of k).

It is important to point out that the flexibility expressed in eq. (1) for the results presented in the table is not only the interfacial flexibility but the sum of the interfacial and internal cohesive flexibilities of the synthetic polymer adhering to the substrate; hence, if one names the interfacial energy of adhesion calculated by molecular mechanics in eq. (1) for what it really is, namely the work of adhesion[20] W, then the total energy $\mathbf{E}$ of the system can be expressed as

$$\mathbf{E} = W + E_{\text{coh}} \tag{2}$$

where E_{coh} is the average internal energy of interaction between segment and segment of the same synthetic polymer and between crosslinking nodes in a tridimensional hardened network.

It is interesting to apply the foregoing discussion to existing models relating adhesion strength and adhesion energy. In the rheological model,[20] the peel adhesion strength is simply equal to the product of the adhesion energy W by a loss function Φ, which corresponds to the energy irreversibly dissipated in viscoelastic or plastic deformations in the bulk materials (and particularly by the contribution of the crack tip propagation) and which depends on both peel rate ν and temperature T. Thus,

$$G = W \Phi(\nu, T) \tag{3}$$

The value of Φ is usually far higher than that of W, and the energy dissipated can then be considered as the major contribution to the adhesive strength G. It is more convenient in eq. (3) to use the intrinsic fracture energy G_0 of the interface in place of W and thus to have $G = G_0 \Phi(\nu, T)$. When viscoelastic losses are negligible, as in the case of the results of peel adhesion strength when a test has been chosen in which their influence has been minimized, Φ tends to 1 and G must tend towards W. However the resulting threshold value G_0 is generally a few orders of magnitude higher than W. Carrè and Schultz[21] have concluded that the value of G_0 can be related to W for crosslinked elastomer–substrate assemblies through the expression

$$G_0 = Wg(M_c) \tag{4}$$

where g is a function of molecular weight M_c between crosslinked nodes and corresponds to a molecular dissipation.

This conclusion leads to a few interesting considerations as regards the results derived from applying molecular mechanics to the primer–cellulose interfaces. From the equation [eq. (1)] obtained to relate the flexibility at the interface to the interaction energy, it is also evident that

$$\mathbf{E} \sim E = (W + E_{\text{coh}}) \sim m/(\alpha f) \sim m/\alpha \tag{5}$$

and, since the concept of M_c is intrinsic in the $(m/n)/\alpha$ ratio relating the number of degrees of freedom m per number of atoms n of the segments between crosslinking nodes as determined by α, $g(M_c)$ can be represented by $m/(\alpha f)$ and, hence, $M_c \sim m/\alpha$; thus,

$$G_0 = Wg(M_c) \sim Wg(m/\alpha) \tag{6}$$

and as a consequence

$$G_0 \sim Wg(\mathbf{E}) = Wg(W + E_{coh}) \qquad (7)$$

and

$$G_0 \sim W^2 + WE_{coh} \qquad (8)$$

In tests where viscoelastic energy dissipation is eliminated ($E_{coh} = 0$) or at least strongly minimized (E_{coh} tends to 0), as in the case at hand in which

$$G_0 \sim W^2 \qquad (9)$$

which is indeed true, since E is by definition as calculated by molecular mechanics equal to W. This is an important finding and would at least partly explain in a manner somewhat different from the more accepted ones why G_0 is generally 100 to 1000 times higher than the thermodynamic work of adhesion W.[20] It indicates, then, that $G \sim W\Phi(\nu, T)m/(\alpha f)$, or differently expressed, $G \sim W^2\Phi(\nu, T)$. Apart from this, the interesting consideration still holds that the flexibility at the interface is inversely proportional to both the intrinsic fracture energy and to the peel adhesion strength (at least where the preponderant effect of Φ is minimized).

Because, from crosslinked and not-crosslinked rubbers, the rubber plateau modulus using the theory of rubber elasticity[22,23] is

$$G_0 = (\rho/M_c)RT \qquad (10)$$

(where ρ is the density, M_c is molecular weight, and R and T are respectively the gas constant and the absolute temperature) in cases where viscoelastic energy dispersion has not been eliminated or minimized

$$G_0 \sim W^2 + WE_{coh} \sim (\rho/M_c)RT$$
$$\sim [\rho/(m/\alpha)]RT \sim [(\rho\alpha)/m]RT \qquad (11)$$

and, as from previous work,[9] $M_c = M_0(m/2)$, where M_0 is nothing else than the molecular weight of the repeating unit of the polymer, or equally

$$G_0 = [(2\rho)/(mM_0)]RT \qquad (12)$$

This indicates that some of the values derived from the material characteristics also belong in G_0 and not only in the viscoelastic energy dispersion function $\Phi(\nu, T)$. What this means is that supporters of $G_0 \sim W^2$ (Ref. 24) and of $G_0 \sim W$ (Ref. 25) in adhesion theory are both correct and incorrect, but to different extents, because if the component of G_0 in viscoelastic properties of the material is maintained in G_0, then really $G_0 \sim \geq W^2$, but if its viscoelastic component is removed, and passed as it should be unto the viscoelastic energy function $\Phi(\nu, T)$ as total viscoelastic energy function $\Phi(\nu, E_{coh}, T)$, then $G_0 = W^2$. Conversely, in the theoretical case in which viscoelastic energy dissipation has been mini-

mized or eliminated, $G_0 \sim W^2 \sim [(\rho\alpha)/m]RT$ and, consequently, the viscoelastic component characteristic of the material (not of crack tip propagation within the material) is still present, $W \leq G_0 \ll W^2$, and thus most likely $G \sim W$, considering the importance of any viscoelastic energy component.

This reasoning also leads to the interesting conclusion that, owing to the calculation of E by molecular mechanics,

$$G_0 \sim k(\Sigma_{ij}[a_{ij}\exp(-b_{ij}r_{ij}) - c_{ij}r_{ij}^{-6}])^2$$
$$\text{or equally } G_0 \sim k(\Sigma_{ij}[(d_{ij}/r_{ij}^{12}) - (c_{ij}/r_{ij}^{6})])^2 \quad (13)$$

thus E depends upon the Lennard–Jones or Buckingham expressions used for the calculation of the van der Waals nonbonded atoms interactions (a type of relationship already in principle advanced by other authors),[26–28] and thus E depends indirectly on the mass of the molecule, since the greater the mass, the greater is the number of interactions. However, the greater the mass does not mean that the attractive energy of interaction is greater. G_0 then depends on the coefficients a, b, c, and d, which notwithstanding the care with which they have been developed to keep the results of Lennard–Jones or Buckingham expressions as close as possible to the experimental reality,[19,29] are empirically derived coefficients, hence molecular mechanics equations are only a model, although a very well experimented one. As a consequence, a Lennard–Jones equation or a Buckingham equation or a mixture of the two types[30] can give equally acceptable results, with the Buckingham expressions accepted as presenting better flexibility than the Lennard–Jones one. The mass of the molecule features then as influencing G_0 because it is the more accessible parameter, but in reality the number and type of atoms constituting the other parameters on which their interactions depend are what really counts. This is also the reason why the results in Table I have rather been expressed by number of atoms rather than by molecular mass.

One must not only take into account the van der Waals interactions, but from eq. (1) the other energies must be considered. Although in the cases of the radical crosslinking polymers the $E_{H\text{-bond}}$ was inconsequential owing to the particular molecular species used, in the polycondensates case, it has already been shown to be a very important contribution[1–6,9] and is included in the values of E reported in the table. Thus,

$$G_0 \sim kW_{Tot}^2 = k[E_{vdW} + E_{H\text{-bond}} + E_{ele} + E_{tors}]^2 \quad (14)$$

where the molecular mass is represented by the molecular degrees of freedom, the type of atoms involved, the coefficient of molecular branching and crosslinking, the atoms polarizability, the angle and direction of the interactions, the electrostatic charges, the number of effective electrons participating, and the dipolar mo-

menta. The mass is then used, incorrectly, only as a simplified blanket parameter covering all this. Furthermore, to be conceptually correct, even symmetrical and asymmetrical bond and angle stretching movements as well as molecular translational movements (even if their contribution is quite small) should be considered.

The influence of chemical bonds on intrinsic adhesion fracture energy G_0 has already been analyzed in several studies, applied to well-defined substrates, and has yielded different proportionalities for different substrates and systems, such as linear and square relationships between the number of bonds per unit interfacial area and peel energy.[24,25] Thus, it must be clearly pointed out that all the relationships discussed are only valid on a cellulose substrate, which is not the easiest substrate to work with at any time but the substrate that had to be used to understand adhesion of glues, varnishes, and primers on wood. The results obtained might well imply the possibility of transferring the relationships found to substrates other than lignocellulosics. However, this does not mean that the results obtained are applicable to any other substrates, since molecular mechanics calculations require well-defined substrate configurations. The same approach, however, is still applicable to other substrates–polymers interfaces.

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