

NOTE

On the Correlation of Some Theoretical and Experimental Parameters in Polycondensation Crosslinked Networks. III. Network-Constrained Repeating Units

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Received 19 June 1997; accepted 15 July 1997

Key words: polymer networks; constrained monomers; molecular mechanics; networks properties

INTRODUCTION

Recently, an equation and simpler regressions, also, correlating the relative deflections 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.¹⁻² Namely, $f = -km/(\alpha E)$ (or $f = km/(\alpha E)$, according to the convention used for E), where k is a constant depending on 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 synthetic polymer-substrate and of the internal cohesive energy of the synthetic polymer (the internal energy of the substrate is not considered because the deflections measured are 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 provision that the coefficient α is not Flory's coefficient of branching anymore but a coefficient calculated in a similar manner,³ and also for non-crosslinked entanglement networks.^{1,3}

The equation presented above, however, is based on the correlation between the values of parameters obtained by thermomechanical analysis (TMA) with the molecular mechanics values of E obtained by calculating the energy of interaction with a substrate of a poly-

merizable monomer, hence, not of the repeating unit of the polymer itself. Thus, while the equation is useful to forecast the values of m in a network (and vice versa of E) from a polymerizable monomer, it must be realized that the limitation of the number of degrees of freedom to account for the constraints introduced by the formation of the network itself had to be introduced at the level of m and α .

While interesting conclusions on polymer networking^{1,3} and good network forecasting have been obtained already with such an approach, the validity of the same equation can be checked for molecular mechanics calculations in which the repeating unit of the polymer, rather than the monomer, is considered. Thus, the validity of the equation can be checked by decreasing the number of degrees of freedom m directly in the molecular mechanics calculations. This can be done by introducing constraints in the repeating unit of the polymer, namely, with the reactive groups of the monomer already reacted and fixed in the position of minimum energy found for the monomer alone, hence, with the crosslinking nodes fixed. This can then be used to reproduce directly in the molecular mechanics calculation the situation a repeating unit finds itself in a covalently crosslinked network: the position of the nodes is fixed; and the number of degrees of freedom m of the segments between nodes is actually limited in the actual calculation, with some equally interesting results.

EXPERIMENTAL

Molecular Mechanics Computational Methods

Three photopolymerizable primer monomers, namely, the linear hexandiol diacrylate (HDDA), the branched

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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. A model of the two top chains of an elementary cellulose I crystallite, with the two parallel chains considered composed of four glucose residues each, the refined conformation of which has already been reported,² was used as the substrate. The conformation of minimum energy of the three monomers in the presence of the substrate already calculated and reported² was used as the starting point for further calculation. All the terminal C=C groups of the three monomers were fixed in the conformation of minimum energy already calculated and were fixed and were not allowed to move. All the other previously defined² internal degrees of freedom of the molecules were allowed to move instead.

The number of degrees of freedom for such calculations is considerable; and the following technique, already used in previous work,^{2,4,5} was used to facilitate the computation. The 360° rotations were performed simultaneously for all the degrees of internal rotational freedom (bonds of the molecule rotated) at first by steps of 120°, then secondly in steps of 60°, and finally in steps of 30°. Further refinements were not possible as a consequence of the already very considerable volume of calculations. The calculations yielded the energy of the system composed of the primer and the cellulose surface E_1 (with the cellulose internal energy taken as 0, as the cellulose and its groups were not allowed to move, due to the energy and configuration stability of the crystallite). However, this is not representative of the energy of interaction at the interface as the gain and/or losses of energy due to movement of the primer from its configurations of minimum internal energies have not been taken into consideration. As a consequence, the internal energies of the primer molecules both in their configuration of minimum internal energy when standing alone (E_2) and in their configuration of minimum internal energy on the surface of the cellulose (E_3) were also calculated. The energies of interaction (E) of the primers with the surface of cellulose are then obtained from $E = E_1 + (E_3 - E_2)$.

The main computational program used for the calculations of the secondary force interactions between primers and substrate and between varnish and the primer-cellulose assembly was a constrained force field model,^{6,7} which has already been checked many times against automatic unconstrained force field models for its accuracy on proteins,⁸ cellulose,^{6,7} cellulose derivatives,⁹ and cellulose interfaces with other polymers or simpler molecules,³⁻⁵ the results of which have also been checked by other authors to obtain good interfacial forecasts of experimental phenomena.¹⁰⁻¹² The potential functions used were of the Buckingham type, and the set of coefficients used for the functions was the Liquori set.¹³ 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 a more rapid computation.

Thermomechanical Analysis

Two of the primers were tested dynamically by thermomechanical analysis (TMA), namely, TMPTA and TPGDA. The third (HDDA) could not be tested as due to very low viscosity it impregnated the substrate and could not be maintained between the two substrate plies. Samples of beech wood alone and of beech wood treated with photopolymerized layers of TMPTA and TPGDA of 350 μm were tested isothermally at 25°C with a Mettler 40 TMA apparatus in three points bending, exercising a force cycle of 0.1N/0.5N on the specimens with each force cycle of 12 s (6 s/6 s). The classical mechanics relation between force and deflection $E_Y = [L^3/(4bh^3)][\Delta F/(\Delta f_{\text{wood}} - \Delta f_{\text{finish}})]$ allows the calculation of the Young's modulus E_Y for each of the cases tested. As the deflections Δf obtained were proven to be constant and reproducible,² 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 $E_{Y1}/E_{Y2} = \Delta f_2/\Delta f_1$.

DISCUSSION

In Table I, the molecular mechanics results obtained with the monomer ends fixed are shown. First of all, if α did not count ($\alpha = 1$) and $f \sim km/E$, in this case, the values of m/E for TMPTA and TPGDA leads to a k , which is not the same (25.5 and 36.3); thus, this cannot be correct. If α is reintroduced in the expression $f = km/\alpha E$ and one considers again $\alpha = 0.33$ and 0.2 as with the monomer calculation,² then m/E presents values of 7.48 ($k = 8.4$) and 6.06 ($k = 8.1$) if the number of degrees of freedom is not reduced from the monomer; thus, a very acceptable difference of 81% between the calculated values against a difference of 78% for the experimental values, and k is again a constant $\sim \pm 8.2$. On this basis then, the original equation $f = km/\alpha E$ also appears to be valid for calculations based on constrained structures, at least in the example at hand.

It could be argued that if the number of degrees of freedom is reduced to 13 and 9.5, then m/E yields 7.03 and 5.23 and $k = 9.4$ and 9, respectively. However, this approach is invalid as the decrease in degrees of freedom can only be arbitrary. This is so because, looking at the structural formulas of the two molecules,² since the groups that have now reacted were not rotatable groups, even when only the unconstrained monomer was considered, there is no justification now in decreasing the number of degrees of freedom.

One problem that remains is that the numerical value of k obtained by applying the formula to energies

Table I Molecular Mechanics Calculated Energies of Interaction, $m/\alpha E$ Values at Primer–Cellulose Interface, and TMA Experimental Values of f

	Energies (kcal/mol)				Primer Monomer Degrees of Freedom (m)	f (experimental; μm)	$m/\alpha E$	k
	E_1	E_2	E_3	E_{total}				
HDDA–cellulose	–11.77	–10.60	–1.06	–2.23	7	—	—	—
TPGDA–cellulose	–12.96	–8.37	–1.08	–5.67	14	63	7.48	8.4
TMPTA–cellulose	–13.29	–4.46	–0.26	–9.08	11	49	6.06	8.1

calculated on constrained structures is just about exactly one-half of the value of k obtained from comparing experimental and calculated results for the unconstrained monomer cases² (± 8.2 versus 16). The reason for this discrepancy can only reside in the value of m taken in consideration because both f and E are obtained experimentally: the first by TMA, and the second by molecular mechanics. It is clear then that when the repeating unit is fixed in the final network, while all the bonds that can rotate can still rotate, they are also not free to rotate freely and throughout the whole 360° field. This would lead to a lower value of m , and if m is considered to be one-half of that of the unconstrained monomer, which is about right for a network situation, then the value of $m/\alpha E$ halves and k is again ~ 16 . While this consideration is conceptually correct, it introduces several considerable disadvantages in the use of constrained monomers in the calculations, as follows.

1. The exact value of m in the network cannot be estimated directly from the monomer formula. While in the cases at hand, the constrained cases m is one-half of the unconstrained cases m , this may only be a chance just applicable to the type of repeating units used. For other polymers, the two values can differ of a factor other than one-half and which might also vary considerably between one system and another one. This means that although the equation $f = km/\alpha E$ is still clearly valid for constrained structures calculations, m is not easily, if at all, obtainable; thus, such an approach cannot be used. Thus, because a clear relationship ($f = km/\alpha E$) exists between f , E , and m , for both the unconstrained monomer and the constrained one, and because m can be derived easily by just observing the structural formula of the unconstrained monomers one wants to test, while it cannot for the constrained cases, the unconstrained monomer approach already presented^{1,2} is preferable as it can be used to good effect. However, if the difference between the two values of m can be proven to always be of one-half also for other systems, then this disadvantage in using constrained structures calculations would not apply.

2. The molecular mechanics calculations have to be performed anyhow first on the unconstrained monomer to identify the spacial positions of the groups to fix in the constrained monomer calculations. It is then necessary in the case of the constrained structures to do the calculations twice, which is much less acceptable.

In conclusion, because the equation $f = km/\alpha E$ is clearly valid for both the unconstrained monomer and the constrained one, and because m can be derived easily by just observing the structural formula of the unconstrained monomers while it cannot for the constrained cases, and, furthermore, because the calculations need to be repeated twice in the case of the constrained structures approach, the unconstrained monomer approach already presented^{1,2} is preferable as it can be used with ease and to good effect.

REFERENCES

1. A. Pizzi, *J. Appl. Polym. Sci.*, **63**, 603 (1997).
2. A. Pizzi, F. Probst, and X. Deglise, *J. Adhes. Sci. Technol.*, **11**, 573 (1997).
3. R. Garcia and A. Pizzi, *J. Appl. Polym. Sci.*, submitted.
4. A. Pizzi and N. J. Eaton, *J. Adhes. Sci. Technol.*, **1**, 191 (1987).
5. A. Pizzi and G. de Sousa, *Chem. Phys.*, **164**, 203 (1992).
6. A. Pizzi and N. J. Eaton, *J. Macromol. Sci., Chem. Ed.*, **A21**, 1443 (1984).
7. A. Pizzi and N. J. Eaton, *J. Macromol. Sci., Chem. Ed.*, **A22**, 105 (1985).
8. A. Damiani, P. De Santis, and A. Pizzi, *Nature*, **226**, 542 (1970).
9. R. M. Wolf, E. Francotte, L. Glasser, I. Simon, and H. A. Scheraga, *Macromolecules*, **25**, 709 (1992).
10. E. Alvira, L. Vega, and C. Girardet, *Chem. Phys.*, **118**, 233 (1987).
11. E. Alvira, V. Delgado, J. Plata, and C. Girardet, *Chem. Phys.*, **143**, 395 (1990).
12. E. Alvira, J. Breton, J. Plata, and C. Girardet, *Chem. Phys.*, **155**, 7 (1991).
13. P. De Santis, E. Giglio, A. M. Liquori, and A. Ripamonti, *Nature*, **206**, 406 (1967).