NOTE

Thermomechanical Analysis of Entanglement Networks: Correlation of Some Calculated and Experimental Parameters

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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,[1-3] namely

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

where k is a constant depending from 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 deflection 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 proviso that the coefficient α is no longer Flory's coefficient of branching; but a similar coefficient calculated in the same manner.[1,4] Indications were obtained that the above equation, and the more practical regression equations derived from it,[1,2] may be valid not only for covalently crosslinked networks but also for noncovalently linked entanglement networks.[2,3]

While interesting conclusions on the covalent networking of polymers, both polycondensates[2] and radical crosslinking,[1] have already been obtained with some equally interesting considerations on the interfacial adhesion between two materials,[1,5] the applicability of the above equation still needs to be addressed as regards pure entanglement networks. This article then addresses this aspect of the application of the above formula, again on lignocellulosic substrates.

EXPERIMENTAL

Work on the formation of polymer networks by photopolymerizable and polyester surface finishes on wood and of polycondensation resins used as wood adhesives has yielded a mathematical relationship[1,2] between the energy of interaction (E) at the synthetic polymer/wood interface calculated by molecular mechanics (work of adhesion), the number of degrees of freedom (m) of the segment of the synthetic polymer between two nodes, the coefficient of branching α, hence the functionality of the starting monomer, and the relative deflection (f) obtained by thermomechanical analysis (TMA) of wood specimens coated or bonded with the adhesive through the expression $f = km/\alpha E$, where k is a constant.[1,2] Regression equations[2] correlating directly m with E and m with f have been also derived. These relationships have been used to calculate m for (1) beech wood joints composed of two plies of beech wood of dimensions $21 \times 6 \times 0.6$ mm, each joined by a 70% solution in water of polyethylene glycol (PEG) of different weight average molecular mass (M_w) and (2) the same assembly in which the PEG had been impregnated by vacuum pressure into the wood. The PEGs used in (1) above had weight average molecular mass (M_w) values (as delivered by the manufacturer) of 10000, 8000, 4600, 3500, 2000, 1500, 1000, 900, 600, 300, and 200, while in experiment (2) the same PEGs were used with the

exclusion of the first three, which had viscosity too high in a 70% solution to be impregnated into the timber. Triplicate specimens for each case were tested by a heating rate of 10°C/min and the variation of the modulus increase curve of the joint as a function of the temperature obtained.

To this purpose the specimens above were tested dynamically by TMA on a Mettler apparatus. Samples of beech wood alone, and of two beech wood plies bonded with each system in a layer of 350 μm, for total sample dimensions of 21 × 6 × 1.1 mm, were tested in nonisothermic mode between 40°C and 220°C at a heating rate of 10°C/min with a Mettler 40 TMA apparatus in three points bending on a span of 18 mm, exercising a force cycle of 0.1/0.5 N on the specimens with each force cycle of 12 s (6s/6s). 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 case tested. As the deflections Δf obtained were proven to be constant and reproductible,[1,2] the values of m for the resins were calculated.

DISCUSSION

The appearance of a joint modulus step due to entanglement networks is not determined by the polymer having to reach a fixed value of the average length of the polymer. Such a critical length varies: the higher is at any moment the concentration of the polymer (the greater is the amount of water lost), the lower is the critical length of the polymer needed to form entanglement networks. As a consequence, a linear polymer such as PEG will show within a limited range of water contents, at parity of all other conditions, a variation in the extent of formation of entanglement networks as a function of its average length. Thus, it will show an increase in the value of the modulus of the joint it is bonding or impregnating and a variation in the number of degrees of freedom, m, hence of the length of the polymer segments between entanglement nodes, with increasing PEG degree of polymerization. A "tighter," or less tight entanglement network is the consequence of the combination of these effects: in short, there will be an optimum condition in which all the effects will combine to give the tightest network possible, hence a network of minimum m and maximum value of the joint modulus.

In Tables I and II are shown the results obtained experimentally from the TMA of wood joints bonded with PEGs of different M_w, and the results calculated through the regression equation $m = 0.919\ \alpha f - 0.579$ derived[2] from the general equation $f = km/(\alpha E)$. The calculated results in Table I are based on the concentration in mol/L of the PEGs present at the beginning of the tests, the PEGs having been dissolved in water at a concentration of 70% by mass. In Table II instead are

shown the results calculated on the final concentration of 100% at the end of the tests, this concentration being due to the complete loss of water during the test. Table I indicates that initially, at 70% concentration, the critical length of the polymer needed for entanglement networks to occur is $m_c = 47.7$, corresponding to an average DP_w of 15.9 (Table I). By the time the entanglement-induced increase of modulus occurs (Figs. 1 and 2) at temperatures at which most if not all of the water has been lost, the critical length of the polymer needed for entanglement networks to occur is $m_c = 68$, corresponding to an average DP_w of 22.7 (Table II). In both cases comparison of the experimental and calculated data indicate that for PEGs of M_w in the range 200–900 the value of m and of DP_w are lower than the critical values needed for entanglement to occur. This means that only the small fraction of the polymer with values of m and of DP_w higher than the critical values needed for entanglement may contribute to entanglement. Thus, the entanglement-induced modulus increase in the thermograms will be noticeably smaller than in cases in which extensive entanglement occurs, a condition which can be observed as indeed occurring in both Figures 1 and 2. As the value of the PEGs M_w increases, a progressively greater fraction of the material has a length greater than the critical one, and hence the value of the entanglement-induced modulus will increase rapidly when passing from PEG 200 to PEG 300, to PEG 600, and to PEG 900. A graph of the increase of modulus as a function of the PEG M_w (Fig. 3) shows that indeed this is the case.

The PEGs with M_w in the range 2000–10,000 present instead a different behavior. As from the results in Tables I and II their values of m and of DP_w are higher than the critical values needed for entanglement; most of their polymer mass contributes to the formation of entanglement networks and to the increase in the joint modulus this entails. The maximum value of the modulus still increases when passing from the PEG 2000 to the PEG 10,000, but the increase is much smaller than for what has been observed for the PEGs of smaller M_w, and the slope of the increase of modulus as a function of M_w is much lower (Fig. 3). The average values of m_{min} (and DP_{wmin}) between entanglement nodes also decrease with increasing PEGs M_w, hence the greater the average length of the chain of a polymer the greater the degree of entanglement and the shorter the segments between entanglement nodes, a fact which is already known in entanglement networks.[6,7] Here again there is good correspondence between experimental and calculated results.

The effects outlined above would be expected, as entanglement networks are formed by the interaction of polymer chains when the product of polymer concentration (C) and its molecular weight (M) becomes greater than some critical molecular weight M_c.[6,7] Within each of the experiments at hand C of the polymer increases (as the solvent is lost), and M remains the same (the

Table I Calculated Critical Values for Entanglement for DP_W and m at the Initial Concentration of 70%, and TMA Value for $m_{\min}$ for PEGs of Different M_W

M_W	DP_W	Initial Conc. (mol/L)	$DP_{WCritical}$[a]	m_c $(3 \times DP_{WC})$	$m_{\min}$ Experimental (by TMA)	m at M_W	E (kcal/mol)
10,000	227.3	0.0700	15.91	47.7	37.6	682	14.496
8000	181.8	0.088	15.91	47.7	39.8	546	14.498
4600	104.5	0.152	15.91	47.7	40.6	315	14.500
3400	77.3	0.206	15.91	47.7	43.8	231	14.509
2000	45.5	0.350	15.91	47.7	50.3	135	14.527
1500	34.1	0.467	15.91	47.7	54.7	102	14.538
1000	22.7	0.700	15.91	47.7	57.8	69	14.564
900	20.5	0.778	15.91	47.7	60.2	60	14.563
600	13.6	1.167	15.91	47.7	83.0	42	14.610
300	6.82	2.333	15.91	47.7	101.5	21	14.618
200	4.54	3.500	15.91	47.7	114.3	13.5	14.630

[a] $DP_{WCritical}$ calculated as (concentration) $\times$ (DP_W).

given M_w of the PEGs used). By using PEGs of different M_w, then M will also be different between the different cases. As a consequence, $C \times M > M_c$ quite rapidly. For each of these noncrosslinkable polymers of fixed average molecular weight the same applies with the reaching of the $C \times M > M_c$ condition just relying on the increase of concentration due to the loss of solvent as the temperature increases. This type of polymer than exhibits "pseudo-gel" behavior[6–9] at applied higher frequencies (hence at temperatures higher and time scales shorter) than the "lifetime" of entanglements, as the lifetime (relaxation) of entanglements has been shown[8,9] to be directly proportional to M.[3] Thus, the

longer the PEG the higher the joint modulus increase due to entanglement will be. In Tables I and II are also reported the values of E in kcal/mol backcalculated from the experimental values of $m_{\min}$. These are very similar for all the different PEGs, as would be expected according to previous findings[10] for other polymers in which the value of E for each repeating unit of a polymer chain of sufficient length is practically constant.

The range of M_w at which a noticeable change between the two conditions should occur is between the PEG 900 and the PEG 2000. The results in Table I indicate that at 70% concentration the weight average m value of the polymer is greater of the critical m_c value

Table II Calculated Critical Values for Entanglement for DP_W and m at the Final Concentration of 100%, and TMA Value for $m_{\min}$ for PEGs of Different M_W

M_W	DP_W	Initial Conc. (mol/L)	$DP_{WCritical}$[a]	m_c $(3 \times DP_{WC})$	$m_{\min}$ Experimental (by TMA)	m at M_W	E (kcal/mol)
10,000	227.3	0.100	22.7	68.1	37.6	682	14.496
8000	181.8	0.125	22.7	68.1	39.8	546	14.498
4600	104.5	0.217	22.7	68.1	40.6	315	14.500
3400	77.3	0.294	22.7	68.1	43.8	231	14.509
2000	45.5	0.500	22.7	68.1	50.3	135	14.527
1500	34.1	0.667	22.7	68.1	54.7	102	14.538
1000	22.7	1.000	22.7	68.1	57.8	69	14.564
900	20.5	1.111	22.7	68.1	60.2	60	14.563
600	13.6	1.667	22.7	68.1	83.0	42	14.610
300	6.82	3.333	22.7	68.1	101.5	21	14.618
200	4.54	5.000	22.7	68.1	114.3	13.5	14.630

[a] $DP_{WCritical}$ calculated as (concentration) $\times$ (DP_W).
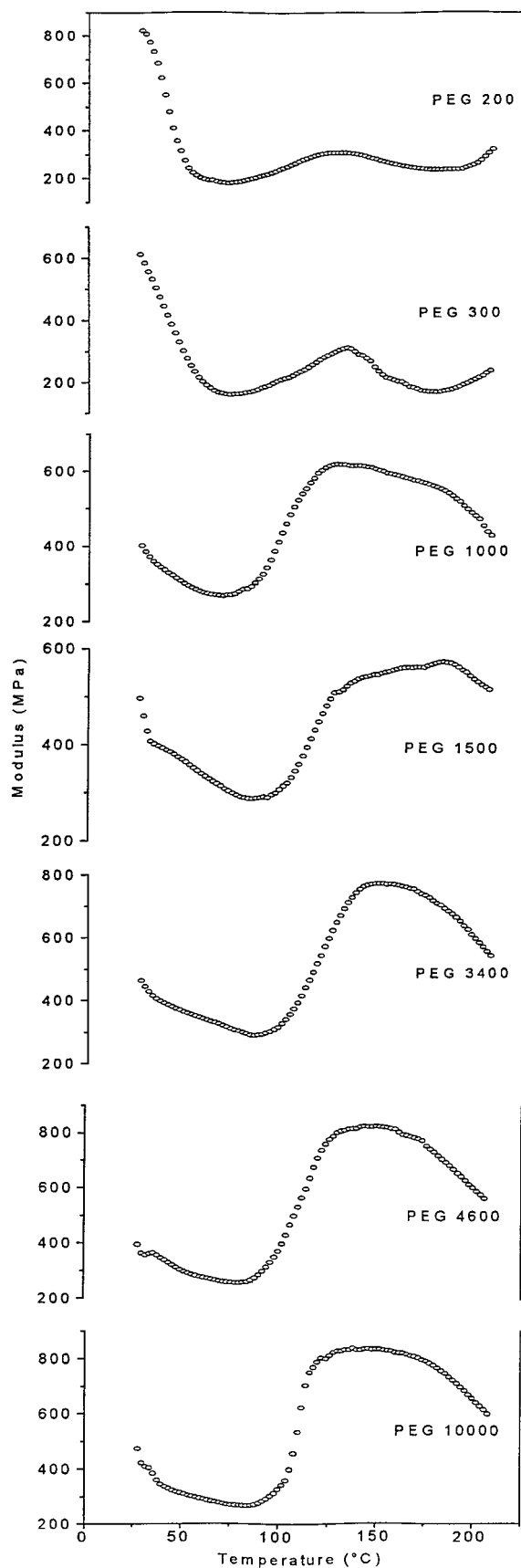
needed for entanglement between the PEG 600 and the PEG 900. In reality, the results in Table II are more significant, as in all the graphs reported (Figs. 1 and 2), entanglement and its concurrent increase in joint modulus occur at temperatures at which most of the water has already been lost. The results in Table II indicate that at 100% concentration the weight average m value of the polymer is greater of the critical m_c value needed for entanglement between the PEG 1000 and the PEG 1500. It is then between these two values of M_w which a change in slope should be observed in Fig. 3, as indeed is the case. The change in slope in the graph of relative E_{Young} as a function of M_w (Fig. 3) indicate then that there is a change in molecular level behavior at $M_w \pm 1500$, this being obtained experimentally. The calculations, as indicated above, support this. As the experimental values of m_w have been obtained through the application of the regression equation, $m = 0.919 \, \alpha f - 0.579$ derived[2] from the general equation $f = km/(\alpha E)$,[1,2] it can be concluded that this equation is also valid for entanglement networks.

The above means, for instance, that the values of parameters in the affine theory of rubber elasticity[11,12] equation $G_N^\circ = (\rho/M_e)RT$ correlating the apparent molecular weight M_e of linear segments between entanglement nodes (which has already been shown to be directly related[2] to the value of m for polycondensates) with the network density ρ and the value of the rubber plateau modulus G_N° can then be modified to as a function of m. To have a general equation it is necessary to distinguish between the value of m of the bonds connecting each repeating unit as $m_{e,\text{external}}$ ($=\mathrm{DP}_e$ in the cases presented) and the value of $m_{e,\text{internal}}$ to the repeating unit ($=2 \, \mathrm{DP}_e$ in the case of PEG, different according to the internal structure of the repeating unit for other polymers). In the simplest form then, as DP $= m_{\text{external}}$ and $M_e = M_0 \mathrm{DP}_e$, then $M_e = M_0 m_{e,\text{external}}$

$$G_N^\circ = [\rho/(M_0 m_{e,\text{external}})]RT$$

and hence parameters such as G_N° and ρ can be obtained with considerably more ease by simple TMA experiments and the use of the $f = km/(\alpha E)$ equation. It must be stressed that the values of m reported in Tables I and II are the total values of m ($=m_{\text{external}} + m_{\text{internal}}$). This modified equation of the affine theory of rubber elasticity can also explain the dependence of the average m of the system from the temperature. The above equation of the affine theory of rubber elasticity has been checked with other authors' data[11,13] for polybutadiene and found to be correct. With the specimens at hand, namely joints of beech wood bonded by a thin glue-line of PEG, as the value of ρ is that of the whole joint and

Figure 1   TMA curves of the variation of the relative modulus as a function of temperature of beech wood joints bonded with PEGs of different M_w.
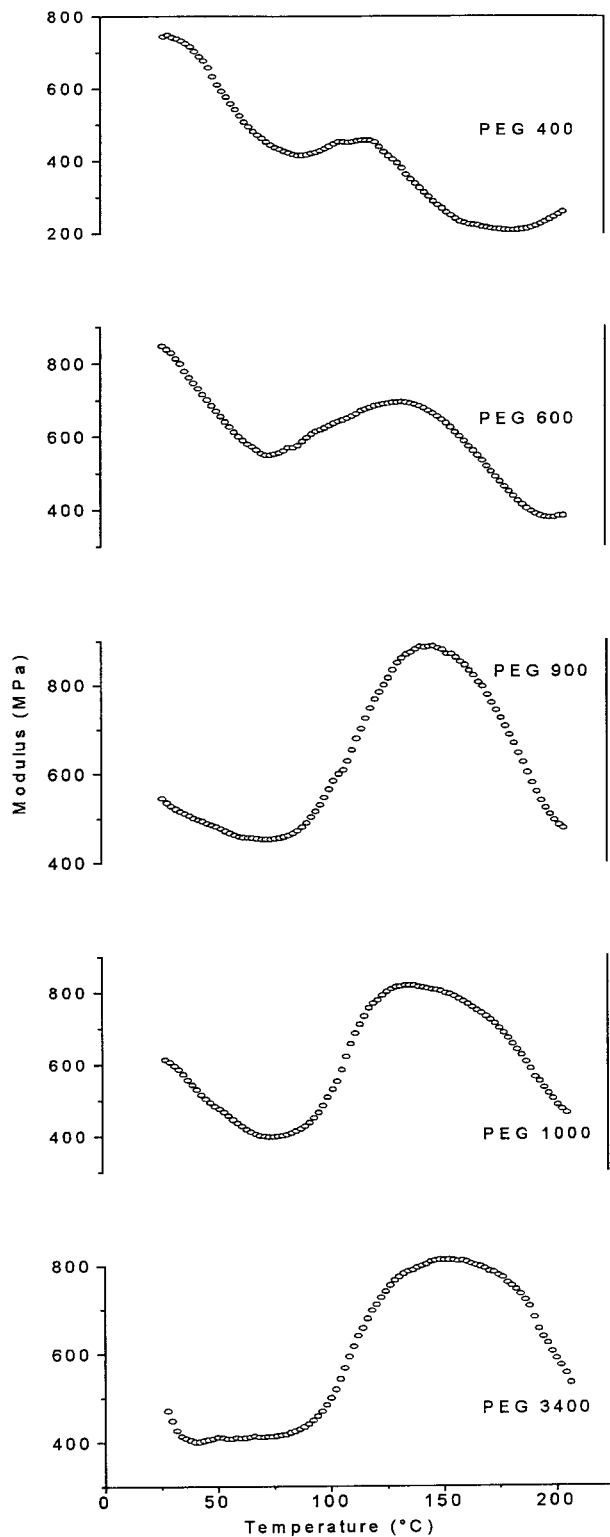
Figure 3 TMA-derived variation of relative modulus as a function of PEG M_w of PEG-bonded beech wood joints.

is hence always dominated by the density of the substrate, and is always between 400 and 450 kg/m^3, the use of the above equation based only on $m_{e,\text{external}}$ gives incorrect results, but it gives correct results if instead the total system m_{min} (as shown in Table II) is used to obtain the equation $G_N^\circ = [\rho/(M_0 m_{e,\text{total}})]RT$.

In Figure 3 are indicated the total curve of the maximum value of $1/f$ ($1/f \sim E_{\text{Young}}$) as a function of the M_w of the PEGs. While the total curve can be described by the regression equation $1/f = 0.0043$ log $M_w - 0.0151$ with a coefficient of correlation $r = 0.94$, the two regions with PEGs of different behavior can be described by the two linear relationships $1/f = 9.8 \times 10^{-6} M_w + 0.0059$ with coefficient of correlation $r = 0.99$ in the M_w range 200–1000, and $1/f = 4.33 \times 10^{-7} M_w + 0.0197$ with coefficient of correlation $r = 0.99$ in the M_w range 3400–10,000. The intersection of the two straight lines is at $M_w = \pm 1400$, indicating that it is around this value of M_w, thus in the range 1000–1500 M_w, that the behavior of the PEG changes, as can be foreseen from the calculated values of m and m_c and the experimental values of m_{min} indicated in Table II.

In conclusion, the general applicability of the equation $f = km/(\alpha E)$ to all kinds of networks, cross-linked[1,2] and entanglement networks, renders this simple equation a further good tool for the interpretation of the characteristics and of the behavior of all types of polymer networks.

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Figure 2 TMA curves of the variation of the relative modulus as a function of temperature of beech wood joints impregnated with PEGs of different M_w.
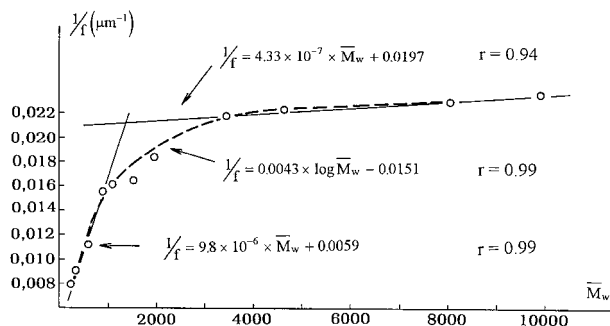
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