

This article was downloaded by:

On: 22 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

### Simple Approach for Quantifying the Thermodynamic Potential of Polymer-Polymer Adhesion

Boxin Zhao<sup>a</sup>; Lulu Bursztyn<sup>a</sup>; Robert Pelton<sup>a</sup>

<sup>a</sup> McMaster Centre for Pulp and Paper Research, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada

**To cite this Article** Zhao, Boxin , Bursztyn, Lulu and Pelton, Robert(2006) 'Simple Approach for Quantifying the Thermodynamic Potential of Polymer-Polymer Adhesion', *The Journal of Adhesion*, 82: 2, 121 – 133

**To link to this Article:** DOI: 10.1080/00218460600559508

**URL:** <http://dx.doi.org/10.1080/00218460600559508>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Simple Approach for Quantifying the Thermodynamic Potential of Polymer–Polymer Adhesion

**Boxin Zhao**  
**Lulu Bursztyn**  
**Robert Pelton**

McMaster Centre for Pulp and Paper Research, Department of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada

*The free energies of mixing a series of water-soluble polymers with cellulose were calculated using the UNIFAC (universal functional group activity coefficients) algorithm, and the results were correlated with measurements of polymer/cellulose adhesion. The more negative the minimum free energy of mixing, the greater the measured adhesion. Adhesion was quantified by single-lap shear test in which regenerated cellulose films were laminated with aqueous polymer. The results are relevant to the use of adsorbed water-borne polymers to strengthen cellulose fiber–fiber bonds in paper. The calculations did not anticipate the exceptional strength-enhancing properties of carboxymethyl cellulose, nor did they predict molecular-weight effects. Nevertheless, the approach may have utility as a general tool to relate polymer chemistry to adhesion performance.*

**Keywords:** Adhesion prediction; Cellulose/polymer interactions; Polymer adhesion; UNIFAC (universal functional group activity coefficients); Water-borne adhesive

### INTRODUCTION

One the largest uses of water-borne adhesives is in paper manufacture. Virtually every printing and packaging paper, including the paper on which this work is printed, contains one or more of a wide variety of polymers, including starch, polyacrylamide, and carboxymethyl cellulose [1]. The role of these polymers is to strengthen paper by increasing the adhesion between cellulose fibers. From an adhesion-science

Received 12 September 2005; in final form 7 December 2005.

Address correspondence to Robert H. Pelton, McMaster Centre for Pulp and Paper Research, Department of Chemical Engineering, JHE-136, McMaster University, Hamilton, Ontario L8S 4L7, Canada. E-mail: peltonrh@mcmaster.ca

perspective, paper adhesion is unusual because only a very small quantity ( $\sim 10 \text{ mg/m}^2$ ) of the paper-strength-enhancing polymer (*i.e.*, the adhesive) is confined between two porous and rough cellulose fiber surfaces. Furthermore, in the early stages of the joint formation, both the cellulose substrate and the adsorbed adhesive layer are water swollen, giving an opportunity for adhesive diffusion (mixing) into the substrate. Thus, unlike typical applications for pressure-sensitive adhesives and other industrial adhesives, cohesive failure of the adhesive is not an issue because there is no distinct adhesive layer and partial mixing of the adhesive with the substrate is a possibility. The goal of this article is to describe a computational approach to relate polymer composition to adhesive joint formation with a specific substrate. Although our interests have focused on water-soluble polymer adhesion to cellulose, we believe that our approach has general applicability in linking polymer chemistry to adhesive joint strength.

There have been a number of semiempirical theoretical attempts to relate adhesion to adhesive properties, and these are summarized in an excellent review by Berg [2]. Arguably, the greatest efforts have been in applying acid/base/surface energy concepts to predict molecular adhesion. Borch [3] has reviewed the use of these approaches for adhesion to paper and has applied them to predict adhesion to hydrophobically modified (*i.e.*, sized) paper surfaces [4].

The diffusion theory of adhesion has also formed the basis of predictive approaches. Because cellulose fiber–fiber bonds in paper are first formed when the fibers are wet, McKenzie [5] proposed that water-swollen hemicellulose polymers on the wood-pulp fiber surfaces interdiffuse to give a strong adhesive joint, an example of the diffusion mechanism of adhesion. A key concept in the diffusion mechanism is that the polymers at the interface must be compatible to mix. Thus, compatible polymers will give strong adhesion whereas incompatible polymers will not. The role of fiber surface polymer compatibility was demonstrated by preparing and testing papers from mixtures of two types of cellulose fibers [6]. One fiber type had dextran, a linear water-soluble carbohydrate, grafted on the fiber surface. The other fiber type had hydrophobically modified dextran grafted on the surface. Although the hydrophobic dextran was also water soluble, it was incompatible with the native dextran, and thus aqueous mixtures of the two types of dextrans were biphasic (*i.e.*, insoluble in each other). We showed that the weakest paper corresponded to samples with the highest concentration of bonds between incompatible fibers [6].

Although the diffusion mechanism was formulated to explain welded polymer interfaces where significant polymer interpenetration occurs, Miller and coworkers have argued that the tendency to mix

could be used to predict the properties of joints spanning much shorter distance scales than polymer welds, such as silane-enhanced joints between glass and polymer [7]. Furthermore, they showed that the universal functional groups contributions method (UNIFAC) could be used to estimate the free energy of mixing between two materials knowing only the functional-group composition of each material. UNIFAC was originally proposed by Fredenslund and Praetisiz to calculate liquid activity coefficients [8]. Using UNIFAC, intermolecular forces are calculated by summing the contributions of the functional groups. The data for the empirical UNIFAC approach comes from liquid vapor equilibria, which are rather sensitive to intermolecular forces. UNIFAC has been encoded into a number of commercial chemical-process modeling software packages.

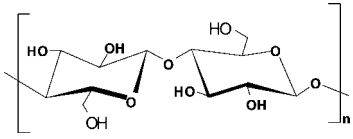
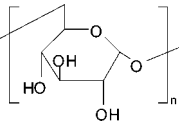
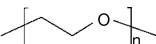
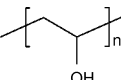
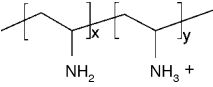
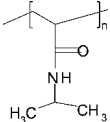
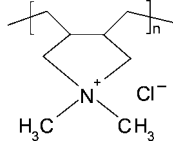
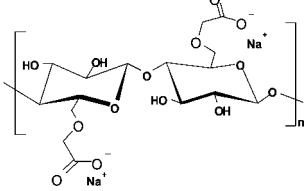
Inspired by Berg's work, we believe that UNIFAC may serve as a general approach to rank the effectiveness of polymeric adhesives for a specific substrate. Herein, we report a comparison of shear strengths of regenerated cellulose films laminated with polymers as functions of the estimated (UNIFAC) free energy of mixing between the polymer adhesive and cellulose. Our hypothesis is that the more negative the free energy of mixing, the more compatible the adhesive and the cellulose, which in turn should give stronger adhesion. In many respects our goals and our experiments mirror the classic 1948 study by McLaren, who attempted to correlate polymer polarity with adhesion to cellulose [9].

## EXPERIMENTAL

Seven water-borne polymers (see Table 1) were chosen as representatives of three categories of polymers: hydrophilic *versus* hydrophobic, charged *versus* noncharged, and simple structure *versus* complicated structure. They were dextran (average Mw = 464 k, Sigma-Aldrich, Toronto, ON), carboxymethyl cellulose (sodium salt Mw = 700 K, DS 0.9, Aldrich), poly(diallyldimethylammonium chloride) (Mw = 400–500 k, Aldrich), poly(ethylene oxide) (Mw = 200 k and 1000 k, Dow (Union Carbide) Canada, Montreal, QU), poly(vinyl alcohol), 87–89% hydrolyzed, Mw = 13–23 k, Aldrich), poly(n-isopropylacrylamide) (Mw ≈ 500 k, homemade), and polyvinylamine (Mw = 450 k, 96% hydrolyzed, BASF, Ludwigshafen, Germany). These polymers were dissolved in Milli-Q water at various concentrations.

Regenerated cellulose films were cut from commercial SpectraPor membrane tubing (diameter of 76 mm) with a molecular weight cutoff of 12,000–14,000 (Spectrum Laboratory Inc., Rancho Dominguez, CA).

**TABLE 1** Polymers, Their Structural Units, and UNIFAC Functional Groups

Polymer	Polymer structural unit	UNIFAC functional groups
Cellulose		1CH <sub>2</sub> , 3CH, 2CH, 1OH (primary), 2OH (secondary)
Dextran		1CH <sub>2</sub> , 3CH, 3OH (secondary), 2CHO
PEO		1CH <sub>2</sub> -O, 1CH <sub>2</sub>
PVA		1CH <sub>2</sub> , 1CH, 1OH (secondary)
PVAm		1CH <sub>2</sub> , 1CHNH <sub>2</sub>
PNIPAM		2CH <sub>3</sub> , 1CH <sub>2</sub> , 1CH, 1CONHCH <sub>2</sub>
PDADMAC		4CH <sub>2</sub> , 1CH <sub>3</sub> , 2CH, 1CH <sub>3</sub> N
CMC		3CH, 2CHO, 1CH <sub>2</sub> O, 1CH <sub>2</sub> COO, 2OH (secondary)

PEO, polyethylene oxide; PVA, polyvinyl alcohol; PVAm, polyvinyl amine; PNIPAM, poly(*n*-isopropylacrylamide); PDADMAC, poly(diallyldimethyl ammonium chloride); and CMC, carboxymethyl cellulose.

Cellulose strips 10 mm wide by approximately 50 mm long were cut from the SpectraPor membrane tube with the long axis of the strip corresponding to the diameter axis of the tube. The films were marked so

that the inner surfaces of the original dialysis tubing were used for the adhesion measurements. The cellulose strips were rinsed with Milli-Q water to remove the preservatives and plasticizer. After rinsing, the films were soaked for  $\sim 24$  h and rinsed again before use. Laminates were prepared by the following procedure.

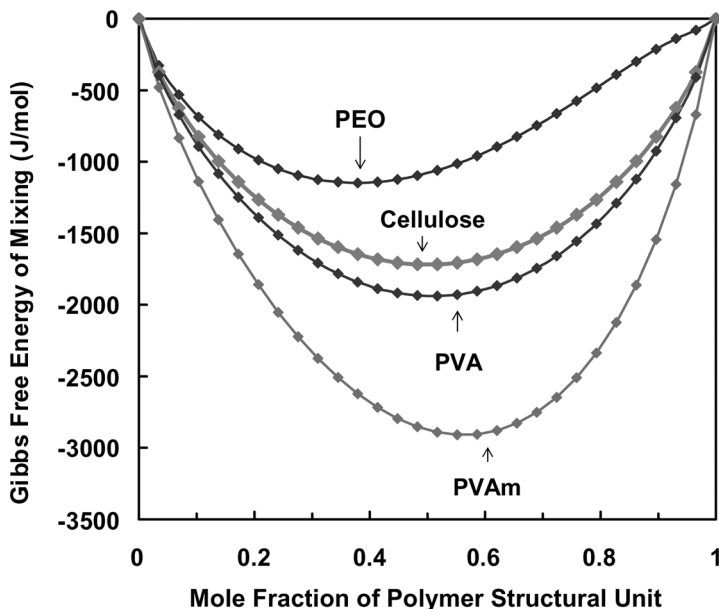
Two cleaned, wet cellulose strips were placed on a polished stainless-steel plate, and the excess solution was blotted with Whatman filter paper. The first strip of the laminate was then placed, face up, on a blotting paper, and  $1.5\ \mu\text{l}$  of polymer solution was carefully placed at one end of the film. The second film was placed to give a lap joint with an area of  $3\ \text{mm} \times 10\ \text{mm}$ . Preliminary experiments were conducted to demonstrate that  $1.5\ \mu\text{l}$  polymer solution could fully cover the contact area without significant leakage of polymer from the joint. Finally, the laminate was placed between two sheets of blotting paper beneath a 45-lb weight and allowed to dry overnight at room temperature.

Shear tests were performed with an extension velocity of  $10\ \text{mm}/\text{min}$  using an Instron 4411 (Instron Corp., Canton, MA) material tester with Series IX software located in a constant temperature ( $23^\circ\text{C} \pm 1$ ) and humidity ( $50\% \pm 2$ ) room. A 50-N load cell was used in all experiments. The maximum force required to separate the laminated films was recorded as a measure of the adhesion strength and was normalized by the film width as Newtons/meter.

## RESULTS

The Gibbs free energy of mixing for polymer pairs at  $25^\circ\text{C}$  was calculated as a function of concentration using Aspen Plus Version 12.1 (Aspen Technology, Inc., Cambridge, MA), which provides both the algorithm and the database. The functional group assignments for each polymer are listed in Table 1. Note that this calculation did not include water, which is known to be important in the early stages of fiber/fiber bonding. Figure 1 shows the free energy of mixing for four polymer pairs including cellulose with itself. The more negative the free energy of mixing, the greater thermodynamic driving force for mixing. Polyvinylamine (PVAm) and poly(vinyl alcohol) (PVA) gave a more negative mixing energy than did cellulose with itself. By contrast, polyethylene oxide (PEO) showed less favorable mixing with cellulose.

Results for the remaining polymer pairs are summarized in Figure 2. The curves for the two most hydrophobic polymers, poly(*N*-isopropylacrylamide) (PNIPAM) and poly(diallyldimethyl ammonium chloride) (PDADMAC), were well above the reference cellulose curves. In particular, the PDADMAC curve showed positive free energies of mixing for most of the mole fraction range; apparently, it was not compatible with

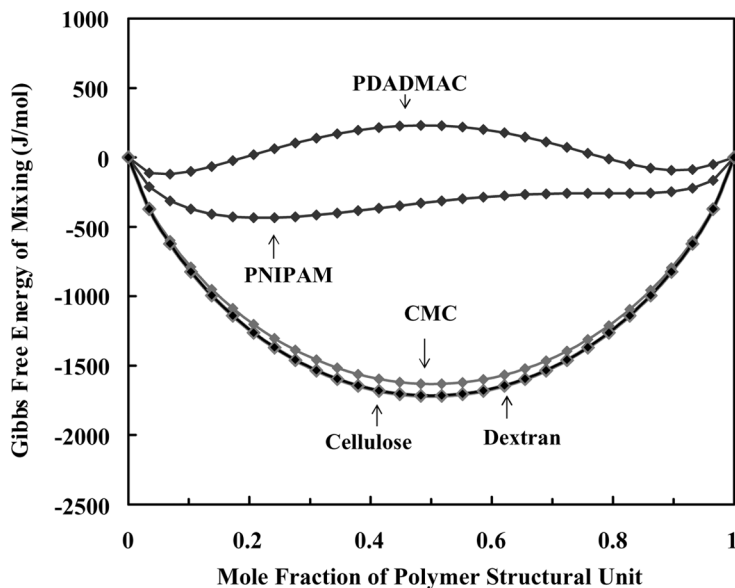


**FIGURE 1** Gibbs free energy of mixing for polyethylene oxide (PEO), polyvinyl alcohol (PVA), and polyvinyl amine (PVAm) with cellulose, and cellulose with itself.

hydrophilic cellulose. The three carbohydrate pairs (cellulose/cellulose, dextran/cellulose, CMC/cellulose) have similar mixing free energy curves, reflecting the similarities in the distribution of functional groups; see Table 1.

To compare the calculations with the shear-strength measurements, the minimum points of the free energy curves were extracted and listed in Table 2. The thermodynamic driving force for mixing followed the order PDADMAC < PNIPAM < PEO < CMC < cellulose, dextran < PVA < PVAm. Furthermore, the mole fractions corresponding to the minimum free energy of mixing showed the same trends.

Cellulose lap joints with polymeric adhesive were prepared, and the shear strength was measured as a function of the coverage of polymer in the joint. In previous work, we have shown that the strength of wet cellulose laminates can be measured by peeling [10]; however, the dry laminates employed in this work were too brittle for peeling. Although the mechanics of single-lap-joint failure involves a complex mixture of peel and shear, the results were reproducible, and the testing geometry is a reasonable model for in-plane fiber–fiber bond failure in paper. No cohesive failure of the cellulose substrates was observed.



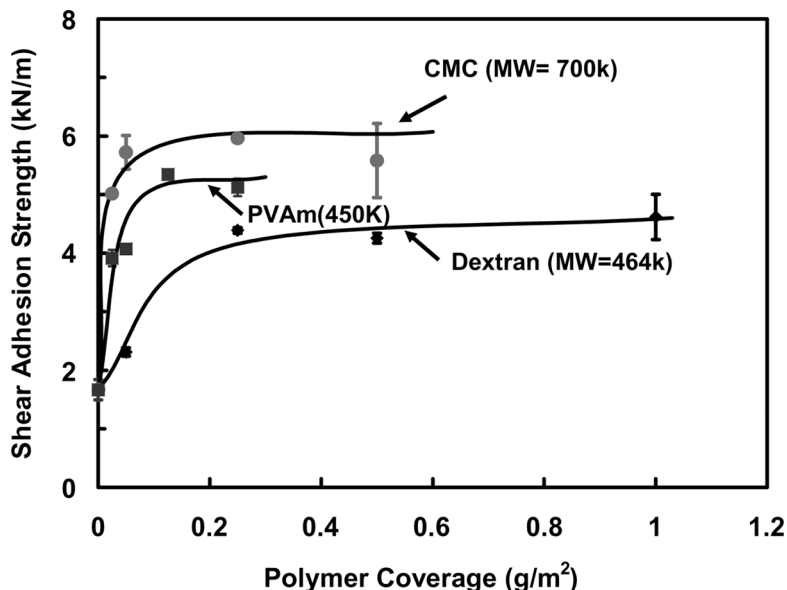
**FIGURE 2** Gibbs free energy of mixing for polydiallyldimethyl ammonium chloride (PDADMAC) and poly(*n*-isopropylacrylamide) (PNIPAM), CMC, dextran with cellulose, and cellulose with itself.

Figure 3 shows the results for the three highest strength polymers plotted as functions of polymer coverage (mass of polymer per square meter of joint). Note that the failure force is divided by the sample width, giving a measure of practical adhesion. From 0 to  $0.1 \text{ g/m}^2$  polymer coverage, joint strength increased with polymer coverage,

**TABLE 2** Gibbs Free Energy of Mixing Calculated *via* UNIFAC and the Corresponding Molar Fraction of the Structural Unit of Polymers

Polymers	$G_{\min}$ (J/mol)	Molar fraction for $G_{\min}$
PDADMAC	-120.9	0.07
PNIPAM	-435.4	0.2
PEO	-1146.7	0.38
CMC	-1631.3	0.5
Dextran	-1714.3	0.5
Cellulose	-1716.8	0.5
PVA	-1938.3	0.5
PVAm	-2908.4	0.55



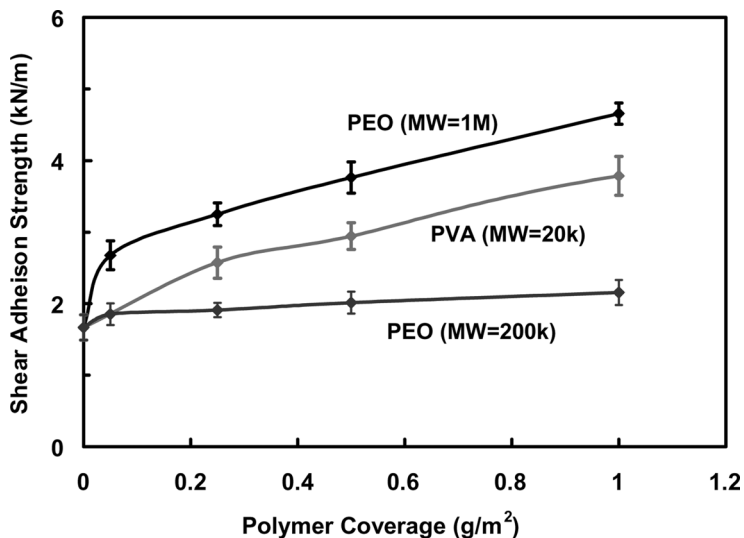


**FIGURE 3** Shear adhesion strength as function of coverages of carboxyl methylcellulose (CMC), polyvinylamine (PVAm), and dextran. Error bars represent measurement standard errors.

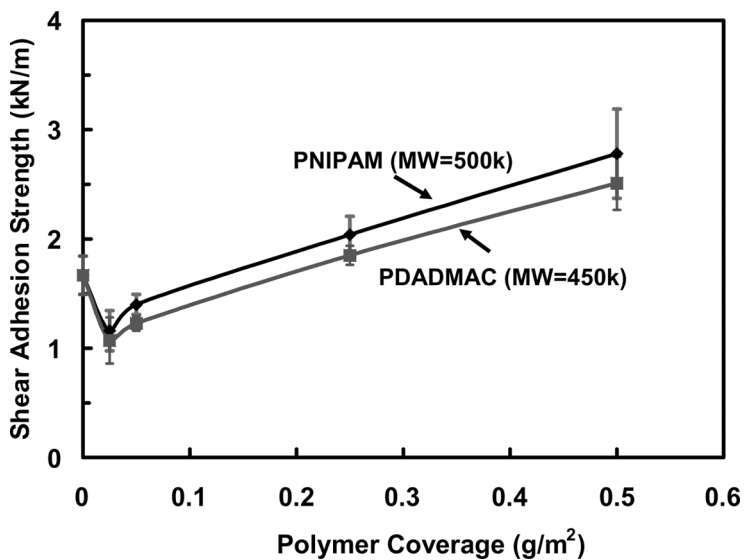
whereas adhesion was constant for coverages greater than  $0.2 \text{ g/m}^2$ . CMC not only gave the strongest joint but achieved its maximum with the lowest coverage.

Figure 4 shows the results for two PEOs and PVA. The very high-molecular-weight PEO did increase strength, whereas the intermediate-molecular-weight PEO did not influence shear adhesion. Note that polymer molecular weight is not accounted for in the UNIFAC calculations. The low-molecular-weight PVA gave modest adhesion improvements.

Figure 5 shows results for two hydrophobic polymers—the nonionic PNIPAM and the cationic PDADMAC. At low coverage, the polymers reduced adhesion between the cellulose films, whereas at higher coverage the shear strength was modestly greater than the cellulose control. The initial reduction of adhesion reflects the incompatibility of the hydrophobic polymers with cellulose. Adhesion did increase modestly at the highest polymer coverage, perhaps indicating a gasket effect (*i.e.*, increased molecular contact between rough surfaces). Note that PDADMAC is frequently used in the paper-making process as a coagulant.



**FIGURE 4** Shear adhesion strength as function of polymer coverages for polyethyleneoxide (PEO) and poly(vinyl alcohol) (PVA). Error bars are measurement standard errors.



**FIGURE 5** Shear adhesion strength as function of polymer coverages for poly(diallyldimethyl ammonium chloride), (PDADMAC), and poly(N-isopropylacrylamide) (PNIPAM).

In an effort to rank the polymers and to facilitate comparison with the calculations, results were extracted at coverages of  $50 \text{ mg/m}^2$  and  $250 \text{ mg/m}^2$  and are compared in Figure 6. Except for dextran, the rankings were the same for the two polymer coverage values.

Figure 7 shows the  $50 \text{ mg/m}^2$  laminate shear strengths versus the minimum (*i.e.*, the most negative) free energy of mixing. With the exception of CMC, the shear strength increases with the calculated tendency of the polymers to mix with cellulose. CMC is an obvious outlier in Figure 7, giving much higher adhesion than the others. Laine and coworkers have demonstrated that fibers treated with CMC at high temperature give exceptionally strong paper, perhaps suggesting specific interactions between CMC and cellulose [11].

In relating measured shear strengths to mixing free energies, we assume that measured shear strengths reflect mainly the properties of the polymer/cellulose interface and not dissipative mechanisms within the polymer layer. The fact that very high-molecular-weight PEO (1M) produced significantly stronger bonds than PEO (200k)

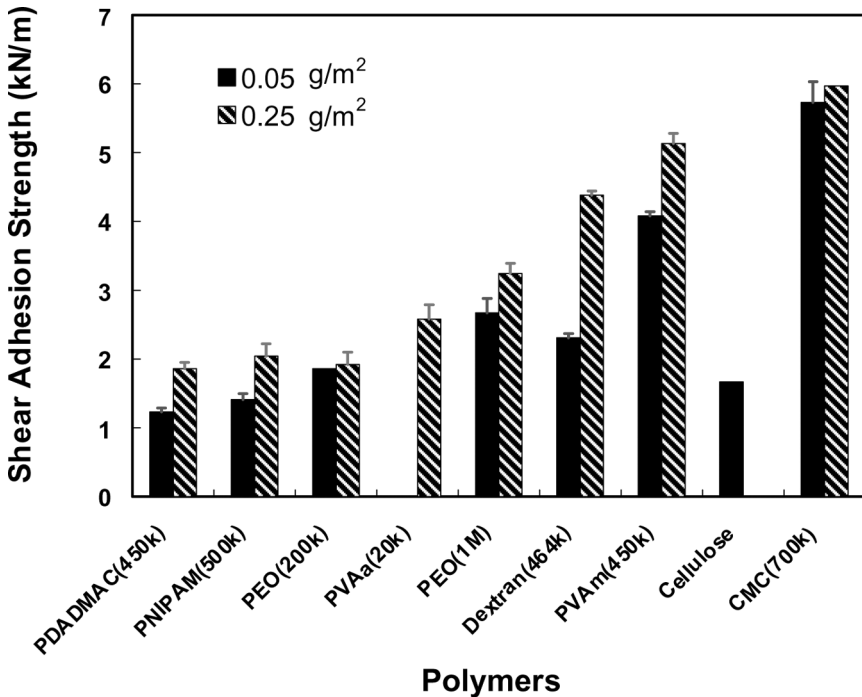
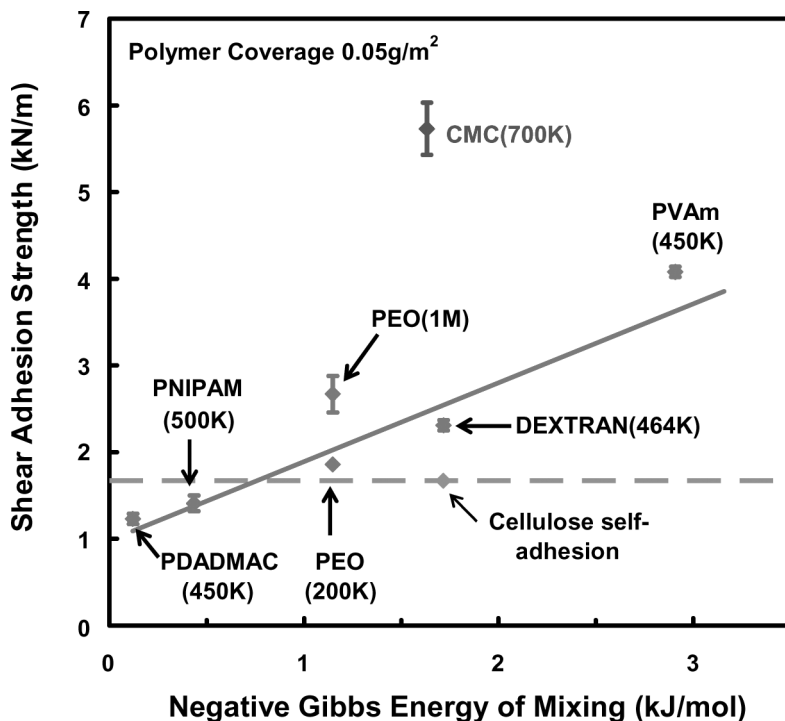


FIGURE 6 Polymer ranking by adhesion strength.



**FIGURE 7** Correlation of the minimum Gibbs free energy of mixing of polymer with cellulose and the lap-shear strength of regenerated cellulose films laminated with polymer.

suggests that the cohesive interactions were also contributing to the measured shear strengths.

## DISCUSSION

Sharpe's essay [12] makes the compelling argument that interfacial forces often drive the formation of an adhesive joint by the development of an interphase. Furthermore, the mechanical properties of the resulting joint are sensitive to the mechanics of the measurement, and thus, the resulting joint strength may not necessarily scale with the interfacial forces driving joint formation. The use of group contribution methods to estimate the free energy of mixing and, thus, the propensity to form a joint is an ingenious idea first proposed by Miller, Knowlton, and Berg to explain the role of coupling-agent structure on the properties of glass composites [7]. Our results suggest that

this approach can be applied to the general adhesion between any polymer pair. Knowledge of polymer structure alone allows for a crude ranking of potential adhesives for a substrate based on the minimum free energy of polymer/substrate mixing. Of course, our results also highlight the limitations of this approach; there is no accounting for molecular weight, viscoelastic properties, and cooperative interactions. Thus, the calculations do not anticipate the role of PEO molecular weight or the exceptionally high adhesion with CMC. On the other hand, deviations from the thermodynamic rankings may have diagnostic value in that large deviations point to the existence of specific interactions.

The next step to improve this analysis is to include the effect of water so that the propensity to mix can be estimated as a function of water content during drying. In the absence of water, most of these polymers have a high glass transition temperature and would not be expected to interdiffuse.

## CONCLUSIONS

The key conclusions from this work are as follows:

1. The free energy of mixing a polymeric adhesive and a polymeric substrate is an indicator of the thermodynamic potential for adhesion.
2. The minimum Gibbs free energies of polymers with cellulose gave the same ranking as the adhesion measurements except for CMC, which was predicted to have much lower adhesion than was observed.
3. The free energy of mixing approach may serve as a general tool to relate polymer chemistry to its adhesion performance.

## ACKNOWLEDGMENT

The authors acknowledge BASF Canada and Science and Engineering Research Canada for funding this work.

## REFERENCES

- [1] Pelton, R. H., *Appita* **57**, 181–190 (2004).
- [2] Berg, J. C., Semi-empirical strategies for predicting adhesion, in *Adhesion Science and Engineering*, A.V. Pocius (Ed.) (Elsevier, New York, 2002), Vol. 2, pp. 1–75.
- [3] Borch, J., *J. Adhes. Sci. Technol.* **5**, 523–541 (1991).
- [4] Borch, J., *Tappi* **65**, 72–73 (1982).

- [5] McKenzie, A. W., *Appita* **37**, 580–583 (1984).
- [6] Pelton, R. H., Zhang, J., Wågberg, L., and Rundlöf, M., *Nordic Pulp Paper Res. J.* **15**, 400–406 (2000).
- [7] Miller, A. C., Knowlton, M. T., and Berg, J. C., *J. Adhes. Sci. Technol.* **14**, 1471–1484 (2000).
- [8] Fredenslund, A., Jones, R. L., and Prautisiz, J. M., *AICHE J.* **21**, 1086–1099 (1975).
- [9] McLaren, A. D., *J. Polym. Sci.* **3**, 652–662 (1948).
- [10] Kurosu, K. and Pelton, R., *J. Pulp Paper Sci.* **30**(8), 228–232 (2004).
- [11] Laine, J., Lindström, T., Nordmark, G. G., and Risinger, G., *Nordic Pulp Paper Res. J.* **15**, 520–526 (2000).
- [12] Sharpe, L. H., *J. Adhes.* **67**, 277–289 (1998).