Inverse Gas Chromatography for the Determination of the Dispersive Surface Free Energy and Acid–Base Interactions of a Sheet Molding Compound. I. Matrix Material and Glass

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ABSTRACT: Sheet molding compound is a material composed of a polyester thermosetting matrix with a thermoplastic, an inorganic filler, a metal oxide, reinforcement fibers, and material performance enhancers embedded in the crosslinked matrix. To achieve the optimum mechanical properties required for the composite material, the surface free energy of the polyester composite needs to be understood. In this study, the composite matrix and glass reinforcement fibers are compared with respect to their surface free energy and acid–base characteristics on the basis of inverse gas chromatography measurements. The inverse gas chromatography results for the matrix and glass are compared to previous results found for sized and unsized cellulosic fibers. The inverse gas chromatography data are used to assess chemical modifications performed on the biobased fibers to predict improvements in the fiber/matrix interaction, and this provides inferences on the overall composite cohesion. Our results show first that any fiber reinforcement system for the polyester composite material has to be acidic to promote good adhesion as the matrix system is very basic and second that the individual dispersive surface energies of the components of the matrix interact in a weighted average to determine the overall surface energy of the composite. Also, a commercial glass reinforcement sized for polyester has been found to have a lower interaction parameter than literature values for cellulosic fibers. This finding suggests that cellulosic fibers might have an advantage in competing with a conventional glass-fiber reinforcement system in fiber/matrix bonding for sheet molding compound composites. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3519–3524, 2008

Key words: biofibers; chromatography; compatibilization; composites; surfaces

INTRODUCTION

Background

Natural-fiber-reinforced composites have gained increased attention over the past decade as competitive materials for the replacement of petroleum-derived materials.[1] Natural fibers have the advantages of lower weight, lower cost, and ease of processing in comparison with synthetic fibers.[2] However, natural fibers have a lower Young's modulus than synthetic fibers. Therefore, to compete with a completely synthetic composite, the cohesion, solubility, and chemical bonding of a natural-fiber-based composite must be maximized. One of the variables to be considered when an organic composite is being designed is the London dispersion component of the surface free energy along with the acid–base characteristics of both the matrix material and the reinforcing fiber. The surface free energy of polyester,[3] polystyrene,[4] and the inorganic component calcium carbonate ($CaCO_3$) have been reported,[5] but the materials interacting within sheet molding compound (SMC) have not been studied.

Glass fibers have been used as reinforcements for many years in SMC. As such, glass fibers have received considerable scientific characterization. Recently, Feuillade et al.[6] presented a thorough study of glass fibers in which the techniques of Fourier transform infrared spectroscopy, pyrolysis, gas chromatography, mass spectrometry, X-ray photoelectron spectroscopy, static secondary-ion mass spectrometry, dynamic secondary-ion mass spectrometry, and contact-angle analysis were performed on glass fibers. Of interest to

the study presented in this work was the contact-angle analysis done with column wicking. The surface energies determined for two types of glass fibers were 29.37 and 26.57 mJ/m^2. Park and Kim[7] also used wicking experiments to determine the total surface energy of polyester-sized glass fibers to be approximately 38 mJ/m^2. In the following study, inverse gas chromatography (IGC) results are used to determine the dispersive surface energies of a commercial glass-fiber reinforcement. A future article will provide an IGC analysis of various lignocellulosic fibers.

IGC background for the determination of acid–base interactions

The Lewis acid–base theory is critical to the IGC analysis of fiber/matrix acid–base interactions. IGC uses probe liquids to determine the acid–base character of the solid packed in the column. The retention times of both the carrier gas and the probe gas are recorded. These retention times are related to thermodynamic quantities that can be used to ascertain the acid–base character of the solid phase. The retention time of a probe is measured and then used in the following relationship:

$$V_g = \frac{273.15}{T_c} \times \frac{1}{w} \times Q(T_r - T_i) \qquad (1)$$

where V_g is the volume of carrier gas required to elute a zone of solvent vapor, T_c is the column temperature, w is the mass of adsorbent packed into the column (g), Q is the corrected flow rate of the helium gas, and T_r and T_i are the retention times of the probe and inert gas. The retention time measured by IGC is the net retention volume (the volume of carrier gas required to elute a zone of solute vapor) per gram of adsorbent, and it is determined with eq. (1). From the retention volume, the Gibbs free energy of the system can be determined.[8] The following relationship shows how the net retention volume is related to the Gibbs free energy:

$$-\Delta G = RT (\text{Ln } V_g) + C \qquad (2)$$

where ΔG is the change in Gibbs free energy due to adhesion, R is the universal gas constant, T is the temperature, and C is equal to $RT \text{Ln}(p_o/A\pi_o)$ (where p_o is 1 atm and π_o is 3.38×10^{-4} N/m). In eq. (2), the Gibbs free energy is related to the retention volume. The constant C is treated as a constant for most applications and can be determined by linear regression. The Gibbs free energy is also related to the work of adhesion (W_a) through the following expression:

$$-\Delta G = NaW_a \qquad (3)$$

where N is Avogadro's number and a is the surface area of the absorbed probe molecule. Combining eqs. (2) and

(3) leads to an equation that is useful for relating the net retention volume of gas to the Gibbs free energy of adsorption. However, first W_a needs to be related to the fundamental forces of interaction. W_a is related to the polar and dispersive forces by the following expression:

$$W_a = (1 + \cos \theta)\gamma_L = 2(\gamma_L^d \gamma_S^d)^{1/2} + 2(\gamma_L^p \gamma_S^p)^{1/2} \qquad (4)$$

where θ is the contact angle with surface for liquid probe, γ_L^d is dispersive surface energy of liquid phase, γ_S^d is the London dispersion component of the surface free energy of the solid, γ_L^p is polar surface energy of liquid phase, γ_S^p is polar surface energy of solid phase, and γ_L is liquid phase total surface energy. In eq. (4), the London component and the polar surface free energy for the liquid and the solid are related in a geometric mean functionality to W_a. By the use of probe liquids that are nonpolar in nature, the polar part of the geometric function disappears, and W_a becomes

$$W_a = 2 \times (\gamma_S^D \times \gamma_L^D)^{1/2} \qquad (5)$$

This allows the net retention volume to be related directly to the surface free energies. By the rearrangement of eqs. (2), (3), and (5), the following expression is derived:

$$RT (\text{Ln } V_G) = 2N(\gamma_S^D)^{1/2}a(\gamma_L^D)^{1/2} + C \qquad (6)$$

Through the plotting of $RT \text{Ln } V_G$ versus $a(\gamma_L^d)^{1/2}$, a linear relationship is found, and the slope of the linear curve allows the calculation of γ_S^d. This is known as the Schultz–Lavielle method.[9,10] Another method, proposed by Donnet et al.,[11] uses a polarization technique and plots a polarization index, $(h\upsilon_L)^{1/2}\alpha_{0,L}$ (where h is Planck's constant, υ_L is the electronic frequency of the probe, and $\alpha_{0,L}$ is the deformation polarizability of the probe), versus $RT \text{Ln } V_G$. Both the Schultz–Lavielle and polarization methods of IGC analysis have been used in the literature and compared.[11,12]

After the IGC analysis is performed with the nonpolar probes, polar probes are analyzed. With the polar probes, both the dispersive and polar forces are present. After measurements are made with the polar probes, a plot of $RT \text{Ln } V_G$ versus $(h\upsilon_L)^{1/2}\alpha_{0,L}$ (in the case of the polarization approach) is generated with the nonpolar alkane probes and the polar probes.

The vertical distance of the data point corresponding to a polar probe from the nonpolar line is the graphical representation of the acid–base Gibbs free energy of adsorption. With the experiments run at different temperatures, the acid–base Gibbs free energy of acid-base absorption (ΔG_{AB}) is measured, and the parameter is related to the acid–base enthalpy of adsorption (ΔH_{AB}) by the following expression:

$$\Delta G_{AB} = \Delta H_{AB} - T\Delta S_{AB} \qquad (7)$$

where ΔS_{AB} is entropy of acid-base ineraction. From this equation, ΔH_{AB} can be determined through the plotting of ΔG_{AB} versus T, which produces a straight line, the intercept of which is ΔH_{AB}.

Gutmann's approach of using electron donors and acceptors for the enthalpy of acid–base interactions can now be applied:

$$-\Delta H_A^{AB} = K_a DN + K_b AN \qquad (8)$$

where ΔH_A^{AB} is enthalpy of acid-base interaction. AN and DN are the acceptor and donor numbers related to chemical references. DN was defined as the negative of the enthalpy of formation for the chemical made by the acid–base reaction with antimony pentachloride. The corresponding electrophilicity of a chemical species was determined from the ^{31}P-NMR shifts induced by triethyl phosphine oxide, a basic probe. K_a and the K_b are constants that show how the solid differs from the references used with the standards.[13]

EXPERIMENTAL

In this study, a polyester-based SMC material was crosslinked by compression molding at the Advanced Engineering Wood Composites Center of the University of Maine, ground with a mortar and pestle, thermally conditioned, and examined by IGC. An experimental method was developed to determine both the London dispersion component of the surface free energies and the Gutmann parameters K_a and K_b for the material.

Sample preparation

The SMC material used for the experiments was composed of a dicyclopentadiene-modified polyester resin with a molecular weight of 12,000 (28.10%), polystyrene with a molecular weight of 250,000 (13.08%), polyethylene powder (0.97%), styrene (6.27%), butylated hydroxytoluene as an inhibitor (0.02%), a compatibilizer (0.48%), a 5% parabenzoquinone solution (0.15%), black pigment (0.05%), zinc stearate (2.42%), and $CaCO_3$ (48.45%; Hubercarb w4).

The SMC was crosslinked at 150°C for 30 min. This time at this temperature was enough to cause the styrene to react with the polyester without the addition of any initiator. After crosslinking, the material was placed in double-lined plastic bags and hammered into coarse particles. The coarse particles were ground to a powder with a mortar and pestle. The ground polymer was screened first by a 45-mesh screen and then by a 60-mesh screen for a maximum particle size of 60 mesh. The powder sample was heated for 3 days at 150°C to drive off volatiles. IGC columns were packed, and the samples were conditioned at 150°C in a gas chromatography oven with 15 sccm of helium until the flame ionizing detector recorded a background signal of less than 5 pA at 30°C.

Chopped-strand glass fibers (Owens Corning brand 973), a conventional reinforcing system designed by Owens Corning Corp. (Granville, OH) specifically for SMC use, were also analyzed with IGC analysis. The glass fibers were commercially sized to enhance medium-solubility resin compatibility with either polyester or vinyl ester resins. The strands were packed "as is" with lengths over 1 in. into the IGC column. The glass fibers were conditioned at 103°C for 24 h with 10 sccm of helium until the flame ionizing detector recorded a background signal of less than 5pA at 30°C.

IGC measurements

Experiments were conducted with two available IGC instruments. One IGC instrument consisted of a Hewlett–Packard HP 6850 gas chromatograph (Santa Clara, CA) equipped with an automatic injector, and the second instrument was a fully automated Surface Measurements Systems SMS IGC (Alperton, UK) with head-space temperature control. For the IGC column into which the particle samples were packed, the HP 6850 used Teflon tubing with a 2.5-mm inner diameter, whereas the SMS IGC used custom silane-treated glass tubes. The SMC materials were analyzed with either the HP 6850 (at 65, 75, 85, 100, 110, and 120°C) or the SMS IGC (at 30, 35, 40, 100, 110, and 120°C). The glass fibers were analyzed with the SMS IGC at temperatures of 30, 35, and 65°C. The thermodynamic nature of the IGC theories allowed for different temperatures, masses, and flow rates to be used in determining the surface energy and acid–base characteristics of different materials for comparison [eqs. (1)–(3)].

Vapors of HPLC-grade polar and nonpolar probes were sampled by a microsyringe, an infinite dilute concentration of the probe was injected into the packed column, and the retention time was measured with a flame ionization detector. An infinitely dilute sample of methane was also injected to determine the dead time in the column. The probe retention time and the methane retention time were entered into eq. (1) with the mass of the packed material in the column. Values of the retention time were used for calculating γ_S^d, K_a, and K_b for the polyester material. Calculations were done with an Excel spread sheet and packaged software from SMS. To calculate K_a and K_b, eq. (8) was written in the $y = mx + b$ form, and AN* (energy/mol) was used instead of AN, which is a unitless value:

$$-\frac{\Delta H_A^{AB}}{4.184 \ AN^*} = \frac{DN}{AN^*}K_a + k_b \qquad (9)$$

Values of DN and AN were found in the literature and are reported in Table I for the probes used in IGC.

TABLE I
Physical Constants for the Probes Used in the IGC Experiments[12]

Probe	$\alpha_0(h\nu)^{0.5}$ $\times 10^{49}$ C$^{3/2}$ m^2 V$^{-1/2}$	DN (kcal/mol)	AN* (kcal/mol)	Specific characteristic
n-Hexane	9.2	—	—	Nonpolar
n-Heptane	10.3	—	—	Nonpolar
n-Octane	11.4	—	—	Nonpolar
n-Nonane	12.5	—	—	Nonpolar
n-Decane[a]	13.6	—	—	Nonpolar
n-Undecane[a]	14.7	—	—	Nonpolar
Acetone	5.8	17	2.5	Amphoteric
Chloroform	7.8	—	4.8	Acidic
Tetrahydrofuran	6.8	20	0.5	Basic
Ethyl acetate	7.9	17.1	1.5	Amphoteric

[a] The values were calculated by extrapolation as Donnet et al.[11] did for *n*-nonane.

Temperatures of 30, 35, 40, 65, 75, 85, 100, 110, and 120°C were used for determining γ_S^d. However, only at the temperatures of 100, 110, and 120°C were meaningful and well-correlated values for K_a and K_b determined for the SMC material.

RESULTS AND DISCUSSION

Large temperature ranges were explored for the polyester-based material. In Figure 1, a linear response to the temperature can be seen for γ_S^d. Results for γ_S^d also demonstrated slightly higher values for the SMC material (47 J/m^2 at 30°C; Fig. 1) in comparison with previous literature for pure polyester (44 mJ/m^2 at 30°C; Table II)[3] and polystyrene (39 mJ/m^2 at 30°C; Table II).[14] The higher γ_S^d value of the SMC material is thought to be contributed by CaCO$_3$, a component of considerable proportion in the matrix material. Keller and Luner[15] reported that preconditioning of the (precipitated) CaCO$_3$ samples at different temperature levels (100–300°C) would result in a huge range of 55–250 mJ/m^2 (at 100°C column temperature) for γ_S^d values because of the influence of physisorbed and chemisorbed water on the surfaces within the pore structure of the sample. At a preconditioning temperature of 120°C, which approximated the temperature (150°C) used for preconditioning our samples, the γ_S^d value of (precipitated) CaCO$_3$ was 58 mJ/m^2 when extrapolated to the test (column) temperature of 30°C (Table II). With a composition of 28.1% polyester, 20% polystyrene, and 48.5% CaCO$_3$, the rule of mixture provides for the SMC matrix a γ_S^d value of 50 mJ/m^2, which closely agrees with the experimental value of 47 mJ/m^2 (30°C; Fig. 2) from our study.

From the slope and intercept of the data in Figure 3, K_a and K_b were determined. In this investigation, the polar characteristics of the solid material could be determined only at higher temperatures because of the adsorption of the probes into the polymer matrix. These higher temperatures levels (100, 110, and

120°C), together with a higher flow rate of 30 mL/min for the carrier gas, were required to facilitate the movement of the probes through the column[16] so that meaningful K_a and K_b values could be calculated. However, at higher temperatures, Santangelo et al.[17] reported a glass transition of approximately 100°C for polystyrene, and this may lead to some bulk adsorption phenomena beyond what is expected with IGC. Keller and Luner,[5] who worked with CaCO$_3$ using IGC, also found that the basic characteristic of CaCO$_3$ was so strong that acidic probes could not be used because of the reaction (adsorption) with CaCO$_3$. Despite the potential impact of bulk adsorption on our findings, the high coefficient of determination for the regression is an indication that the IGC theory is valid under the protocol (e.g., temperatures of 100, 110, and 120°C) that we adopted.

K_a of the SMC material was found to be 0.40, and K_b was 2.23. Previously, polystyrene has been reported to have K_a and K_b values of 0.06 and 0.35[4]
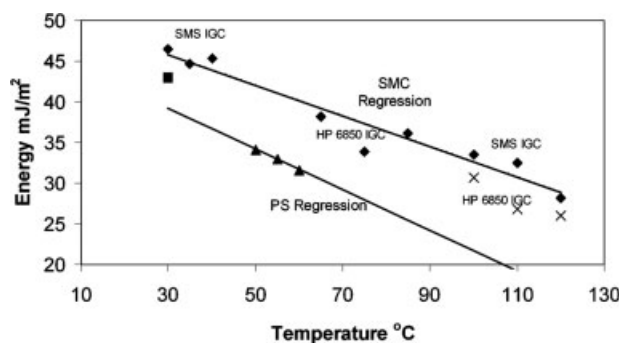

Figure 1 Dispersive energy for (◆) the SMC material, (▲) polystyrene (PS),[13] (■) polyester,[3] and (×) the SMC material repeated at a high temperature. Three temperatures were run per experiment, and the instruments used are listed by the data: SMC IGC was used for 30, 35, 40, 100, 110, and 120°C, and HP 6850 IGC was used for 65, 75, 85, 100, 110, and 120°C. For SMC regression, $R^2 = 0.94$; for PS regression, $R^2 = 0.99$.

TABLE II
Published Data for γ_S^d of the Materials Used in the SMC Matrix

	γ_S^d (mJ/m^2) at various temperatures	R^2	γ_S^d (mJ/m^2) at 30°C (predicted)
Polyester resin[a]	15 (99.85°C), 22 (79.85°C), 32 (59.85°C), 40 (39.85°C)	0.99	44
Polystyrene[b]	31.6 (60°C), 33.0 (55°C), 34.1 (50°C)	0.99	39
Precipitated calcium carbonate[c]	39 (110°C), 41 (100°C), 46 (90°C), 46 (80°C), 48 (70°C)	0.91	58

The values at 30°C were obtained from linear extrapolations.
[a] From ref. 3.
[b] From ref. 13.
[c] From ref. 14.

or 0.28 and 0.46.[18] The very high K_b value for the composite material is thought to be due to the high density of electron-donating oxygens with unshared pairs of electrons available for donor interactions resulting in high basicity[5] in $CaCO_3$ and due to the fact polystyrene with a high π-bonding character has only a K_b value of 0.35–0.46.

This analysis was repeated with chopped-strand glass reinforcement fibers. γ_S^d changed over the temperature range of 40–65°C, with values of 39.8, 41.1, and 41.2 mJ/m^2 at 65, 35, and 30°C, and it was extrapolated to 41.5 mJ/m^2 at 25°C with a 1.00 coefficient of determination. Glass was studied extensively by Dutschk et al.,[19] and their findings indicated that the technique of IGC is "too sensitive to give an unambiguous description of the complex character of heterogeneous fibers"; however, because a rule of mixtures worked with the complicated polyester system and because this glass is sized for polyester, the technique may apply. Park and Kim[7] determined the total surface energy of polyester-sized glass fibers to be approximately 38 mJ/m^2. The value found with IGC is somewhat higher than the value found by Park and Kim but is consistent with IGC values being higher than contact-angle analysis values. In Table II, polyester is reported to have a value of

44 mJ/m^2 and the SMC has a value of 47 mJ/m^2 for the dispersive surface energy. A glass with a dispersive surface energy of 41.5 mJ/m^2 at 25°C should be miscible with the SMC, if we assume that the acid–base surface energies are not too large. The calculated K_a and K_b values were 0.20 and 0.35 with a coefficient of determination of 0.99.

With K_a and K_b for the multicomponent polyester SMC material, the design of the reinforced composite can be concluded with knowledge of K_a and K_b for the fiber reinforcement. Tze et al.[20] reviewed how the acid–base interactions in a composite can be maximized to enhance the mechanical strength of a composite:

$$I_{a-b} = K_{a,f}K_{b,m} + K_{b,f}K_{a,m} \qquad (10)$$

I_{a-b} is known as the interaction parameter, and the subscripts a, b, f, and m refer to the acid, base, fiber, and matrix, respectively. This interaction parameter has been shown to correlate strongly with the shear strength of a carbon-fiber/epoxy interface.[21] K_a and K_b have been determined for various sizing agents with Lyocell fiber reinforcement[20] and have been used to determine the interaction parameter with the SMC material. The K_a and K_b values for the Lyocell
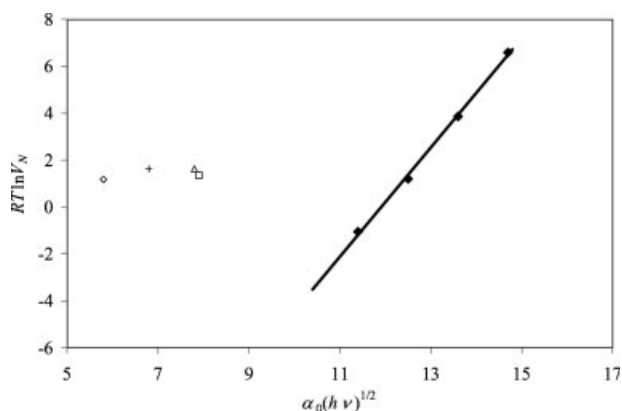

Figure 2 Polarization plot at 100°C used to determine acid–base characteristics of the SMC material with (◆) *n*-alkanes, (□) ethyl acetate, (+) tetrahydrofuran, (△) chloroform, and (◇) acetone.
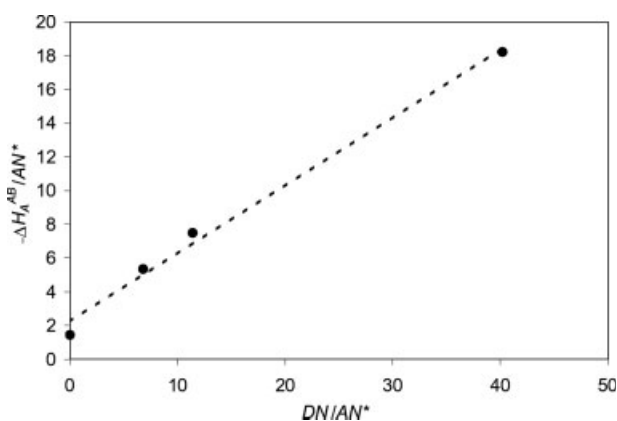

Figure 3 Relationship for determining K_a and K_b with data from the polarization method at 100, 110, and 120°C for the SMC material.

	K_a	K_b	I_{a-b}
SMC material	0.4	2.23	
Polyester-sized glass	0.20	0.35	0.59
Sized cellulose			
Untreated cellulose (Lyocell)[a]	0.36	0.39	0.96
Amino-silanated cellulose[a]	0.33	0.52	0.94
Phenylamino-silanated cellulose[a]	0.32	0.42	0.88
Phenyl-silanated cellulose[a]	0.34	0.43	0.93
Octadecyl-silanated cellulose[a]	0.33	0.27	0.84
SMA-grafted cellulose[a]	0.42	0.57	1.16

[a] From ref. 15.

fiber were determined by Tze et al.[20] previously using the HP 6850 described in the Experimental section with a carrier flow rate of 15 mL/min and temperatures of 25, 35, and 45°C.

From Table III, it is apparent that the only sizing agent that gives a higher interaction parameter in comparison with the untreated fiber is styrene/maleic anhydride (SMA-grafted) for the cellulosic fibers. The reason is apparent because SMA-grafted is the only sizing agent listed that increases the acidic character of the fiber. Because of the high K_b value for the SMC material, any fiber reinforcement in the material will need to have a highly acidic character to promote a good interaction. The polyester-sized glass has a lower interaction parameter than the biobased fibers, and this indicates that the biobased fibers might have an advantage for surface interactions in competing with glass for overall cohesion within an SMC matrix. The glass fibers are sized to promote surface-free energy compatibility (like–like affinity) for polyester and polystyrene matrices, but cellulosic fibers sized to favorable interaction parameter values are likely to bond to SMC materials through enhanced acid–base interactions. The improved fiber/matrix bonding for sized cellulosic fibers will be verified in future studies.

CONCLUSIONS

IGC is a sensitive technique for determining acid–base characteristics of solid materials. Individual components of a material create a weighted average London dispersion component of the surface free energy characteristic for the material. This weighted average includes the interactions of the individual components in the material with each other and follows a simple rule of mixtures. Because the last component to go into an SMC is the reinforcing fibers and the interactions of the fibers with the matrix are critical for proper mechanical reinforcement, the surface free energy for the composite after compounding is needed. K_a and K_b for the SMC material are used to calculate the interaction parameter for the fiber and sizing agents. Any fiber reinforcement to be used with the SMC material should have a highly acidic character to maximize the matrix–fiber interaction. The commercially available polyester-sized glass reinforcement has the lowest interaction parameter in comparison with the sized and unsized cellulosic fibers used in this analysis. Therefore, cellulosic fibers may have an advantage in comparison with glass for surface interactions with the matrix material. The inferred fiber–matrix bonding for SMC composites will be verified in future studies.

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