Infrared Photoacoustic and Dynamic Mechanical Spectroscopy of Sheet-Molded Compounds

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SYNOPSIS

Chemical and physical characteristics of sheet-molded compounds were investigated using infrared and mechanical spectroscopies. Fourier transform infrared spectroscopy with photoacoustic detection facilitated surface analysis for determination of composition, depth profile, and thermal exposure effects. Dynamic mechanical spectroscopy utilized torsion, tension, and flexure modes to evaluate temperature and frequency-dependent viscoelastic properties.

INTRODUCTION

Sheet-molded compounds (SMCs) (glass fiber reinforced thermoset plastics) are becoming increasingly important as structural materials for automotive, aerospace, and general industrial applications. Typically, these structures are assembled using adhesives rather than mechanical fasteners. The chemical and physical characteristics of SMCs and adhesives are similar such that the bonded structure often exhibits synergistic properties. Consequently, an investigation was conducted to study the chemical and physical characteristics of SMCs that might provide insight for the design of adhesives with compatible properties, specifically, the chemical features associated with the surface that ultimately influences adhesion and the physical aspects associated with the bulk material that contribute to the strength of the bonded structure.

Fourier transform infrared spectroscopy with photoacoustic detection facilitated the investigation of chemical properties related to the surface. The determination of composition, depth profile, and thermal exposure effects was of interest. Traditional methods of infrared spectral analysis have utilized transmission and reflection sampling techniques.[1,2] Photoacoustic detection allows for examination of the surface without alteration and minimal sample preparation.

Mechanical spectroscopy was used to evaluate viscoelastic properties of the bulk material. Mechanical characterization has been the subject of extensive study and includes strength, failure, fracture, and fatigue analyses.[3] Temperature-dependent dynamic modulus was determined in torsion, tension, and flexure modes. Frequency-dependent dynamic modulus was measured in torsion mode to construct master curves (time–temperature superposition) and evaluate damping attributes.

Several samples of commercially available SMCs were studied for comparison. Preliminary testing was performed to design appropriate experimental conditions for infrared and mechanical measurements. This included thermal analysis (differential scanning calorimetry, thermomechanical analysis, and thermogravimetry) and electromechanical testing (tensile and flexure strength).

EXPERIMENTAL

Sample Preparation

SMC materials included three commercially available blends identified as A, B, and C. Samples were prepared in compliance with procedures described by the Automotive Composites Consortium.[4] All specimens for each SMC manufacturer were ob-

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tained from a single test plaque (30 × 30 cm). Geometry and corresponding dimensions for test specimens are described below.

Infrared Spectroscopy

Infrared absorption spectra were obtained with a Fourier transform infrared spectrometer (Perkin-Elmer 1750 and 1760-X) using photoacoustic detection (MTEC 200). The cosmetic surface of plaques, or that which typically appears upon use, was chosen for all observations. Test specimens were prepared as discs (10 mm diameter × 2.5 mm thickness) and examined without conditioning or surface alteration. A carbon black (Mogul L, Cabot Corp.)/

potassium bromide (Spectra-Tech Inc.) pellet (1 : 10 wt/wt) was prepared with dimensions similar to sample specimens for background spectra. Spectrometer mirror velocity of 0.1 cm/sec was selected for all measurements unless otherwise specified. The detector cell was purged with helium and spectrometer cabinet with nitrogen. Spectra are the result of 256 symmetric interferogram coads at 2 cm^{-1} resolution unless indicated otherwise. Spectrometer and detector amplifier gains were adjusted to 8 and 64, respectively.

Qualitative compositional analysis of SMC was studied by identification and assignment of chemical functionality consistent with commercially available fillers, resins, and additives. The photoacoustic cell
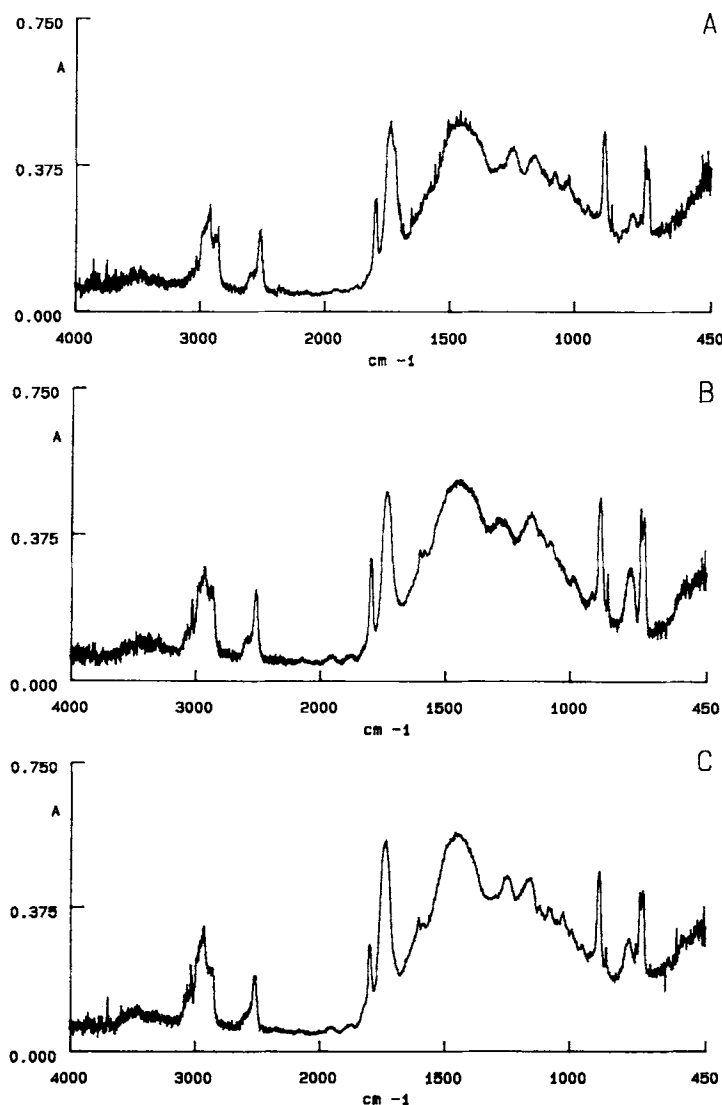

Figure 1   Infrared photoacoustic spectra of SMC blends A, B, and C.
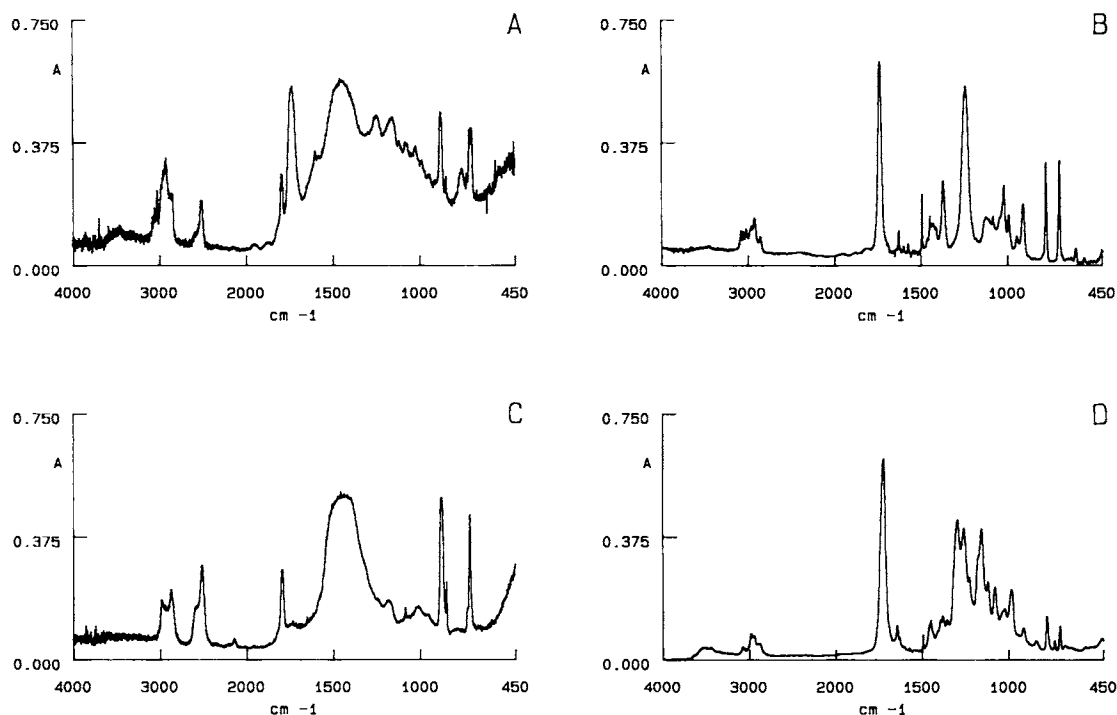
Figure 2 Infrared photoacoustic spectra of SMCs and components. (A), blend C; (B), additive [poly(vinyl acetate)]; (C), filler (calcium carbonate); (D), resin (unsaturated polyester).

Table I Absorption Frequencies of SMC, Resin, Additive, and Filler

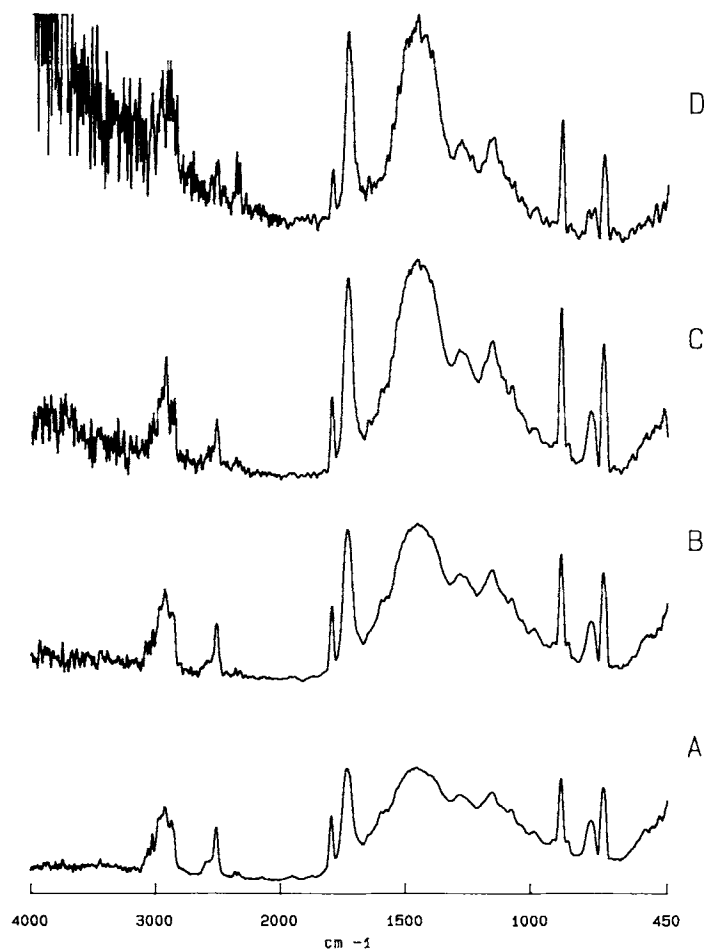| Assignment (Organic)	SMC	Resin	Additive	Filler	Assignment (Inorganic)
OH stretch	3,480 cm^{-1}	3,504 cm^{-1}			
CH stretch	3,207			2,979 cm^{-1}	
	2,925 cm^{-1}				
	2,854	2,878	2,828 cm^{-1}		
	2,516			2,518	CO_3^{-2} (crystalline)
	1,797			1,795	
CO=O stretch	1,734	1,723	1,740		
C=C stretch	1,601	1,642			
	1,445	1,453		1,446	
			1,372		
Co stretch	1,245	1,294	1,243		CO_3^{-2} antisymmetric stretch
CH$_2$ and CH$_3$		1,255			(amorphous)
deformation	1,155	1,155			
	1,075	1,078			
	1,020		1,021		
		980	911		
	878			876	
	848			847	
CH deformation	756	779	776		CO_3^{-2} (crystalline)
	713			708	
	700	702	698		

Figure 3 Infrared photoacoustic spectra of SMC (blend B) at various spectrometer mirror velocities. (A), 0.1 cm/s; (B), 0.2 cm/s; (C), 0.5 cm/s; (D), 1.0 cm/s.

was equipped with multisampling accessories[5] for transmission, reflectance, and direct photoacoustic measurements to accommodate liquid, powder, and solid samples, respectively.

Depth profile studies were performed to evaluate the relationship between thermal diffusion length and composition. Spectrometer mirror velocities of 0.1, 0.2, 0.5, and 1.0 cm/s were used. The total coads acquired at each mirror velocity were progressively increased by a factor of two (128, 256, 512, and 1,024).

Thermal exposure effects were studied to determine volatility, residual cure, and decomposition. SMC samples (3 mm diameter) were subjected to various temperatures (100, 200, 550, and 1,000°C) in a thermogravimetric analyzer (Perkin–Elmer TGS 2) and transferred directly to the photoacoustic cell. In addition, samples were studied by differential scanning calorimetry (Perkin–Elmer DSC-2).

Mechanical Spectroscopy

Temperature-dependent modulus in torsion was determined with a dynamic analyzer (Rheometrics RDA 700) using torsion rectangular fixtures. A controlled sinusoidal strain (0.1%) was imposed at constant frequency (10 rad/s). Rectangular solids (50 × 12 × 2.5 mm) were studied without conditioning. Experiments were performed in "autotension" mode to accommodate thermal expansion. Data was acquired in a temperature range of −25–275°C at a rate of 2°C/min. Frequency dependent modulus (0.1–100 rad/sec) was measured at constant temperature between 0 and 250°C (25°C increments). Samples were conditioned (60 min at 200°C) to ensure complete cure and consistent thermal history. Each sample was exposed to a thermal soak (30 min at set temperature) prior to measurement.
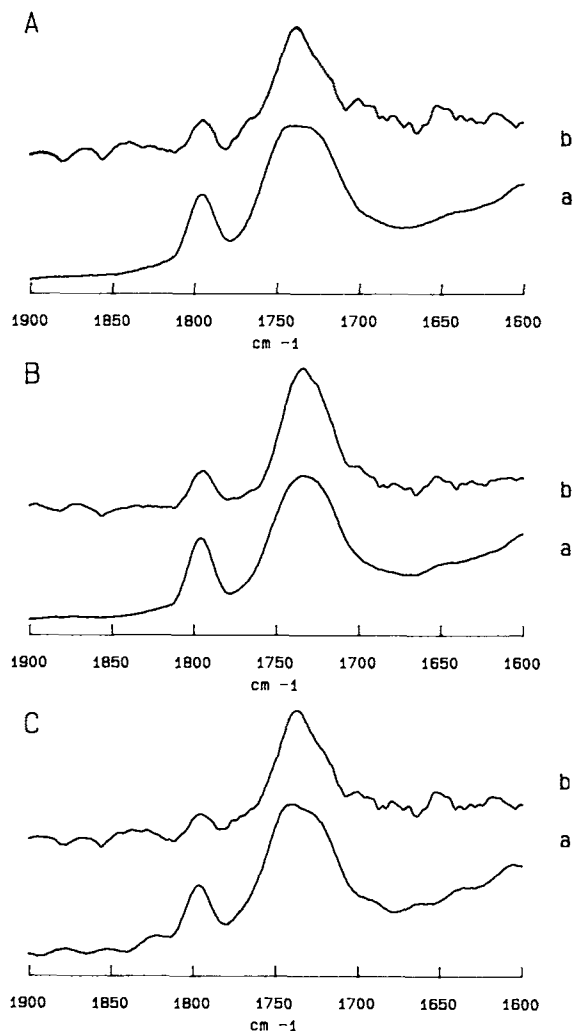
Figure 4   Infrared photoacoustic spectra of SMC blends A, B, and C at (a) 0.1 and (b) 1.0 cm/s.

Table III   Temperature-Dependent Weight Loss and Calcium Carbonate Content of SMC Blends A, B, and C Determined by Thermogravimetry

| | Weight Loss (%) | | | | $CaCO_3$ |
Blend	100°C	200°C	550°C	1,000°C	Content
A	0.06	0.31	26.0	48.2	50.4
B	0.05	0.40	24.5	46.0	48.6
C	0.06	0.37	28.6	47.6	43.3

D 638) were measured without conditioning. Deformation was periodically terminated (10°C increments) and gage length adjusted to compensate for thermal expansion. Temperature range and rate similar to torsion testing were selected using an environmental chamber (Applied Test Systems).
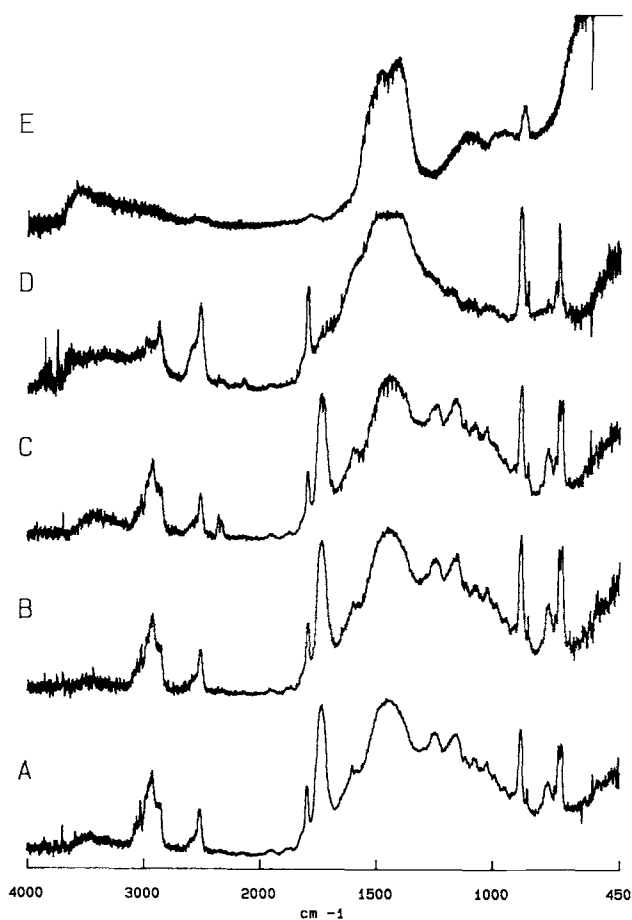
Temperature-dependent modulus in tension was examined with a servohydraulic tester (Instron 1350) equipped with prototype fixtures. A controlled sinusoidal strain (0.1%) was imposed at constant frequency (1.6 Hz). Type I geometry solids (ASTM

Table II   Depth Profile Absorption Intensity Ratio (1,797/1,734 cm^{-1}) at Various Scan Velocities for SMC Blends A, B, and C

| | Absorption Intensity Ratio | | | |
Blend	0.1 cm/s	0.2 cm/s	0.5 cm/s	1.0 cm/s
A	0.55	0.42	0.34	0.28
B	0.60	0.49	0.41	0.27
C	0.40	0.32	0.26	0.19

Figure 5   Infrared photoacoustic spectra of SMC (blend C) following thermal exposure. (A), 25°C; (B), 100°C; (C), 200°C; (D), 550°C; (E), 1,000°C.
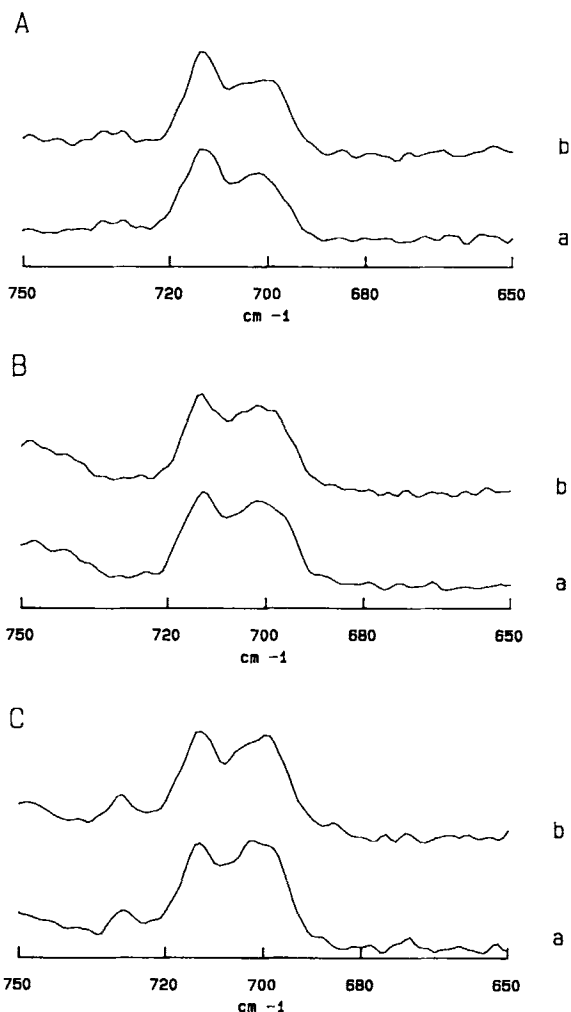
A

B

C

Figure 6 Infrared photoacoustic spectra of SMCs (blends A, B, and C) (a) prior to and (b) following thermal exposure (45 min at 200°C).

Temperature-dependent modulus in flexure was determined with a dynamic mechanical analyzer (Du Pont 982) using a vertical clamp assembly. A sinusoidal controlled strain (0.05 mm displacement) was imposed at resonant frequency (variable). Rectangular solids (70 × 11.5 × 2.5 mm) were studied without conditioning with temperature range and rate similar to torsion and tension testing.

RESULTS AND DISCUSSION

Infrared Spectroscopy

Infrared photoacoustic spectra of SMC are shown in Figure 1. Comparison of the three blends indicates

similar spectral characteristics. Assignment of chemical functionality and the nature of origin of absorption is achieved by comparison of these spectra to commercially available SMC components. Examples of filler (calcium carbonate), resin (unsaturated polyester), and low-profile additive [poly(vinyl acetate)] are shown in Figure 2. Prominent absorption frequencies are listed in Table I with corresponding chemical functionality.[6] Of particular interest are the contributions from calcium carbonate appearing at 2,518, 1,795 (CO_3^{-2} stretch), 1,446 (CO_3^{-2} antisymmetric stretch), 876, 847, and 708 cm^{-1}. Resin absorptions prevalent in SMCs include those at 3,480 (O—H stretch), 1,734 (C=O stretch), 1,500–1,000 (C—O stretch and C—H$_1$ deformations), and 1,000–700 cm^{-1} (C—H deformations). Similar carbonyl, carbon—oxygen, and carbon—hydrogen absorptions are apparent from the low-profile additive. Identification and unambiguous assignment of chemical functionality from infrared spectra of SMCs is difficult due to the complex nature of these materials.

Infrared photoacoustic spectra illustrating depth profile scans are shown in Figures 3 and 4. Signal-to-noise ratio deteriorates directly proportional to mirror velocity[7]; consequently, spectra were subjected to a smoothing function (Savitzky/Golay). Thermal diffusion length is inversely proportional to mirror velocity[8]; however, quantitative assessment of sampling depth is not possible since only approximate values for sample density, specific heat, and thermal diffusivity are available. Qualitative interpretation of results is possible by comparison of absorption intensity ratio attributable to calcium carbonate and resin or additive (1,797/1,734 cm^{-1}). This information is listed in Table II. As thermal diffusion length decreases, the apparent relative concentration of calcium carbonate diminishes, consistent with the manner in which these composites are manufactured. In addition, the ratio for each

Table IV   DSC Results and Absorption Intensity Ratio (713/700 cm^{-1}) of SMC Blends A, B, and C

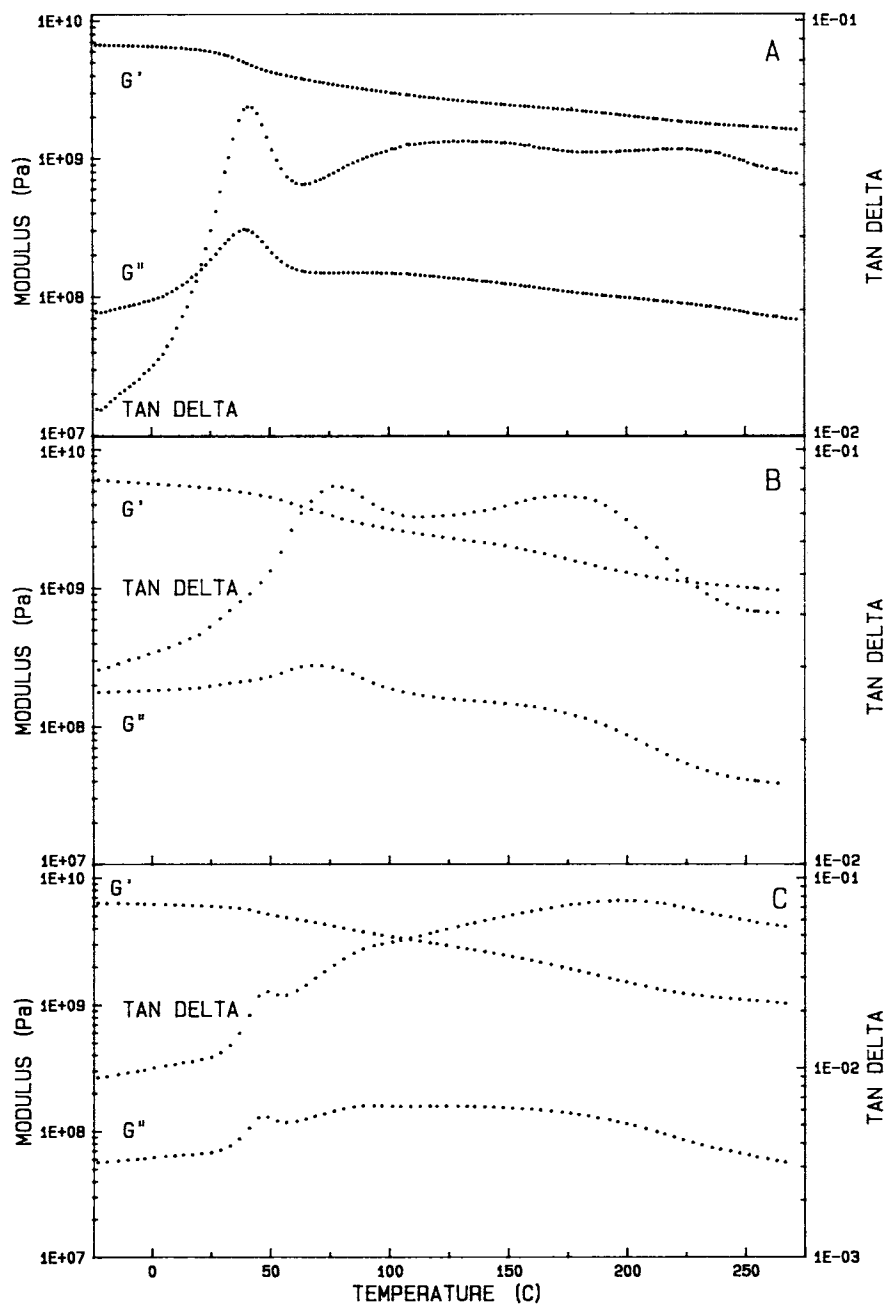| Blend	Exotherm		Absorption Intensity Ratio	
	Onset (°C)	Enthalpy (cal/g)	Before	After
A	152	−3.1	1.07	1.15
B	136	−5.1	1.30	1.31
C	136	−2.7	0.93	1.00

Figure 7 Temperature-dependent mechanical spectra in torsion of SMC blends A, B, and C.

blend at 1.0 cm/sec velocity is in direct agreement with total calcium carbonate concentration (see Table III).

Infrared photoacoustic spectra obtained after sample thermal exposure are shown in Figures 5 and 6. Temperature-dependent weight loss and thermodynamic data are listed in Tables III and IV as determined by thermogravimetry and differential scanning calorimetry, respectively. Following exposure at 100°C, no apparent spectral change is observed in conjunction with minimal weight loss (0.06%), indicating low volatility. After 200°C exposure, a minor spectral change occurs when examining the absorption intensity ratio for resin or additive and filler (713/700 cm^{-1}). The latter absorption may be attributable to styrene monomer present in resin and additive components.

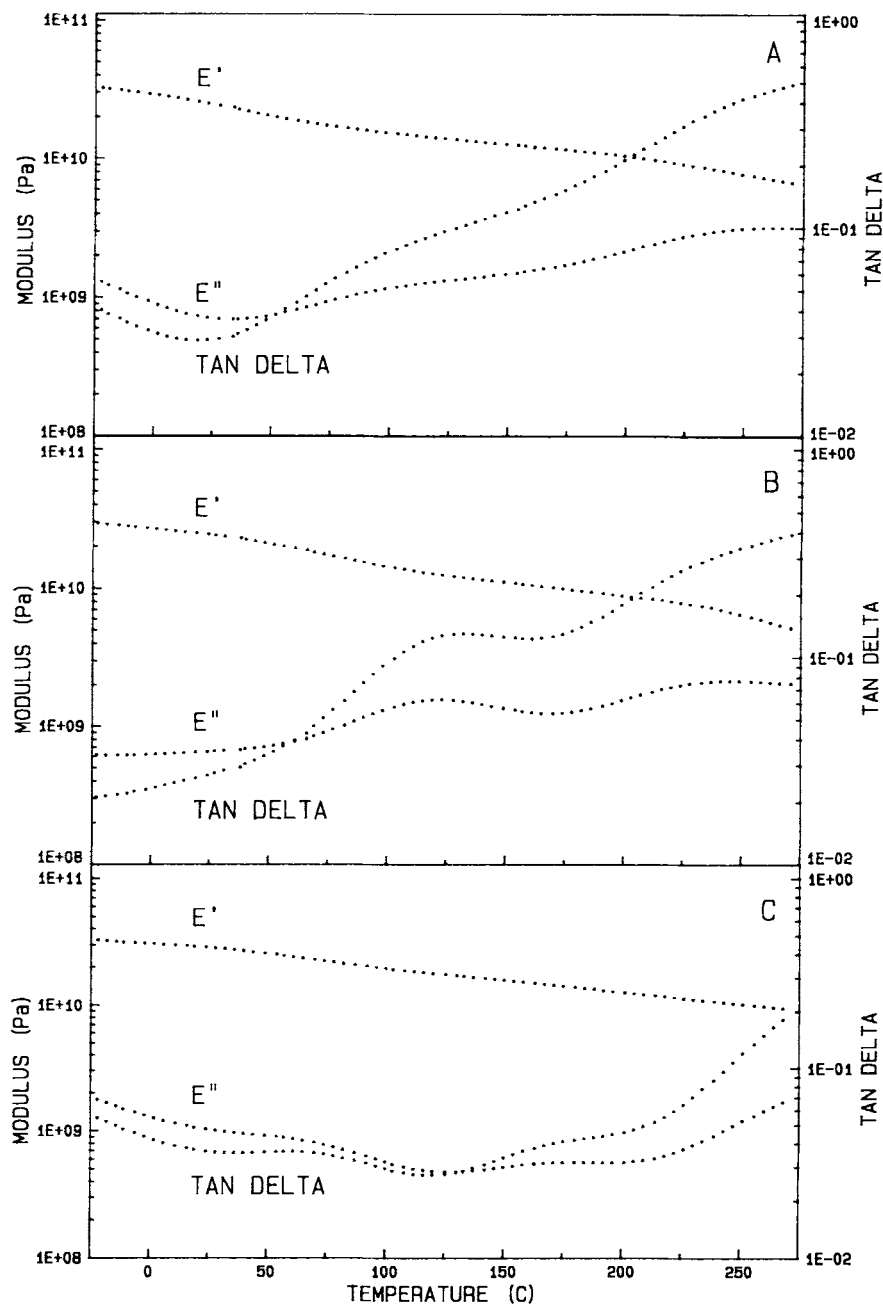Accordingly, this observation may be the result

Figure 8   Temperature-dependent mechanical spectra in tension of SMC blends A, B, and C.

of residual cure of resin as shown from DSC measurement or volatilization as determined from TGA (0.36% weight loss). Upon exposure at 550°C, a dramatic weight loss occurs, corresponding to thermal decomposition of organic components. The resultant spectrum resembles that of calcium carbonate. Finally, after 1,000°C exposure the spectrum exhibits characteristics of thermal decomposition products and amorphous glass.

Mechanical Spectroscopy

Temperature-dependent dynamic mechanical spectra in torsion, tension, and flexure are shown in Figures 7, 8, and 9, respectively. Corresponding complex modulus (25°C) and tangent delta (maxima) are listed in Table V.

Mechanical spectra in torsion include profiles of storage (G') and loss (G'') modulus and tangent delta
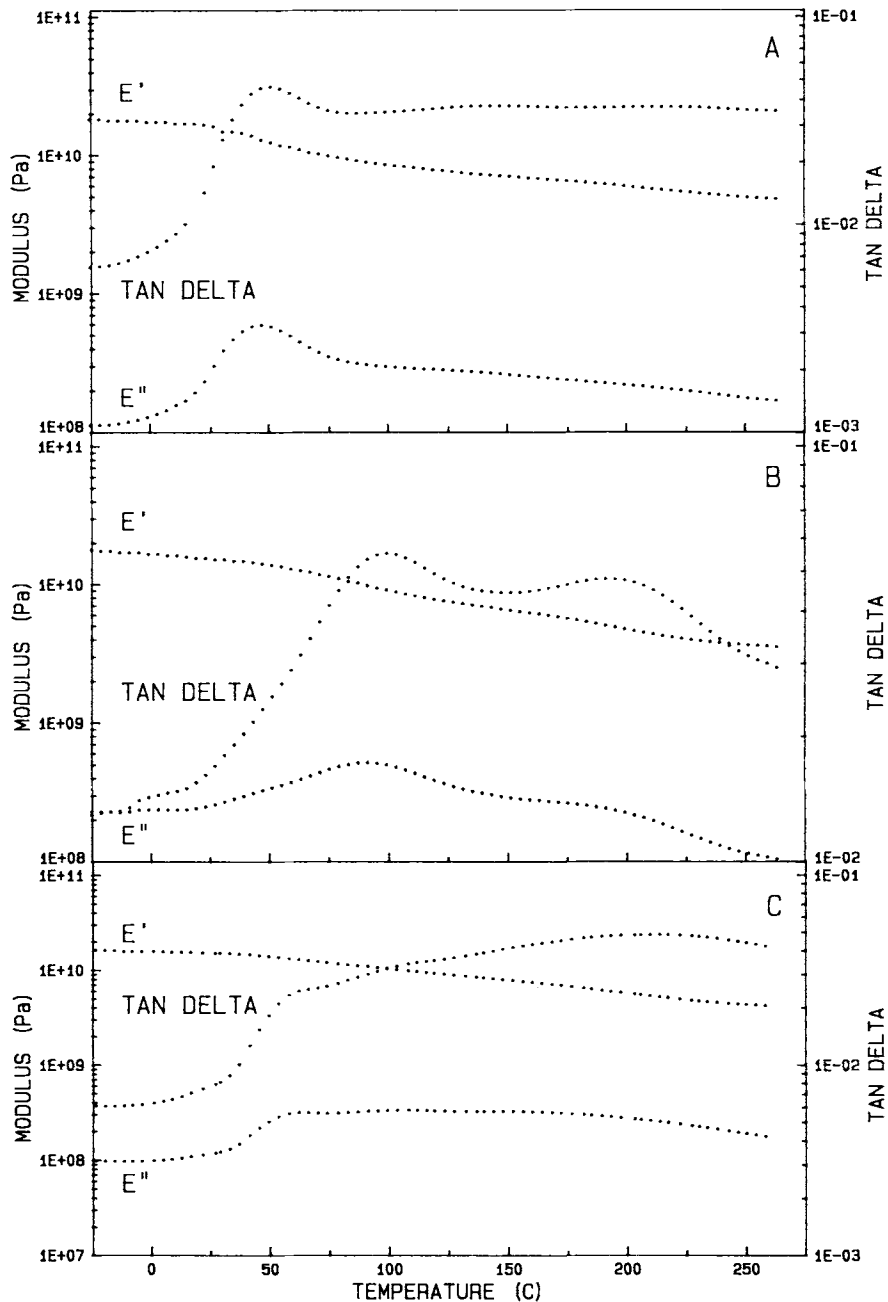
Figure 9   Temperature-dependent mechanical spectra in flexure of SMC blends A, B, and C.

(G''/G'). Each blend exhibits complete mapping of glass and rubber plateaus and transition zone in the temperature range of interest as indicated by storage modulus. Distinguishing features are apparent from comparison of tangent delta that show multiple transitions. For example, blends A and C are characterized by three tangent delta maxima while blend B shows two. Maxima are typically associated with glass transitions and may arise from distinct non-

homogeneous polymer matrices including thermoset resins and thermoplastic additives.

Mechanical spectra in tension also include profiles of storage (E') and loss (E'') modulus and tangent delta (E''/E'). Again, complete mapping is apparent from storage modulus behavior. However, all three blends exhibit two tangent delta maxima. These maxima are shifted relative to one another as is the case with torsion tangent delta maxima
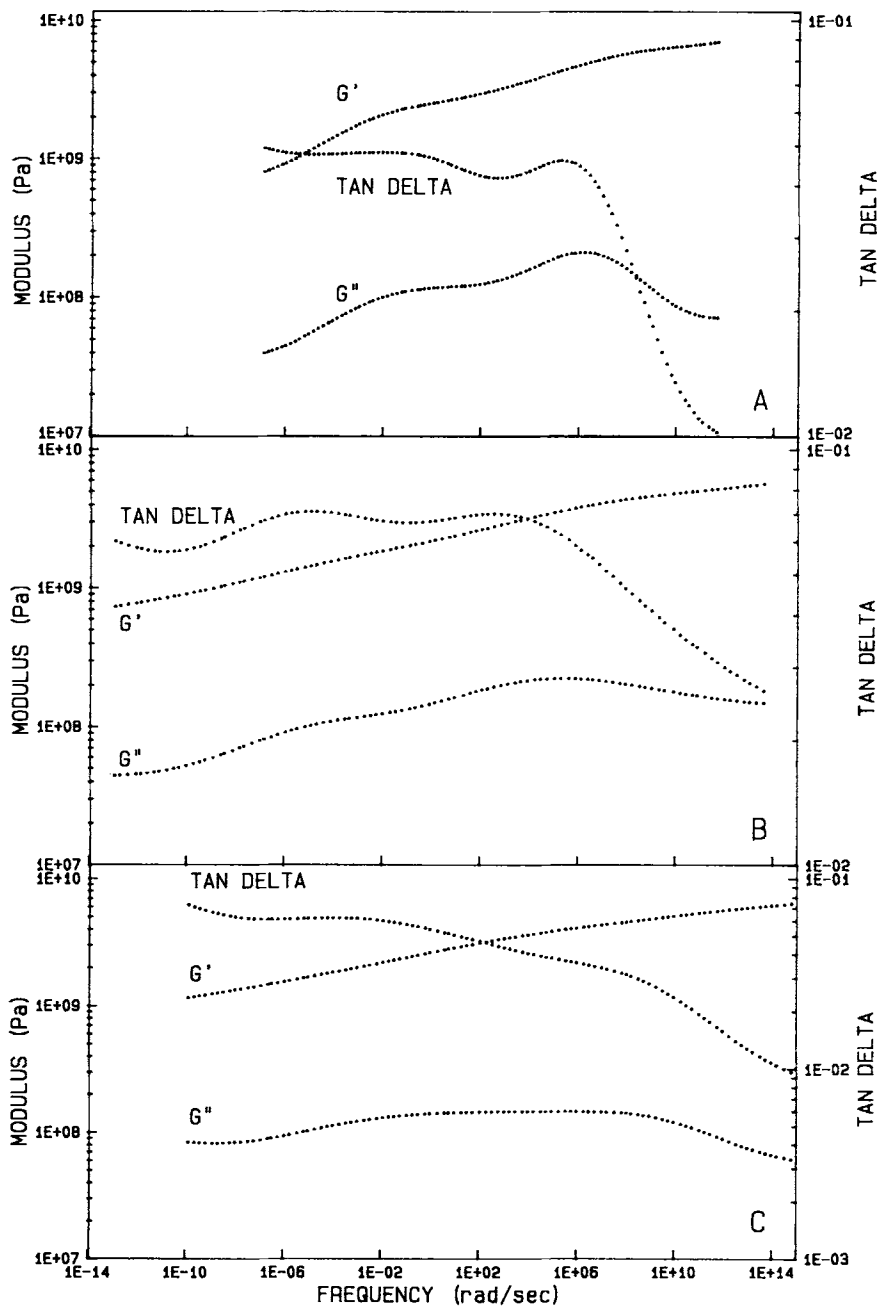
Figure 10   Frequency-dependent mechanical spectra in torsion of SMC blends A, B, and C.

and also exhibit distinct form. Mechanical spectra in flexure of storage (E') and loss (E'') modulus and tangent delta (E''/E') show complete mapping of viscoelastic behavior. Blends A and C are characterized by three tangent delta maxima while blend B shows two prominent transitions.

Comparison of torsion, tension, and flexure temperature-dependent viscoelasticity for a particular blend is indicative of anisotropic laminate behavior.

Similar mechanical spectra in each mode are typically demonstrated by isotropic materials. The anisotropy may be attributable to type and orientation of glass fiber reinforcement. Of particular interest is the appearance of three transitions in torsion and flexure and only two in tension for blends A and C. The interaction of polymer, filler, and reinforcement and test axis orientation may account for this observation. It should be noted that comparison of

Table V Complex Modulus (25°C) and Tangent Delta (max) in Torsion, Tension, and Flexure for SMC Blends A, B, and C

	Blend A	Blend B	Blend C
Complex modulus			
G^* (torsion)	5.97E+09 Pa	5.24E+09 Pa	5.94E+09 Pa
E^* (tension)	2.43E+10 Pa	2.43E+10 Pa	2.85E+10 Pa
E^* (flexure)	1.64E+10 Pa	1.53E+10 Pa	1.51E+10 Pa
Tangent delta (°C)			
Torsion	42	77	48
	135	176	89
	223		199
Tension	94	128	72
	254	254	170
Flexure	51	99	62
	143	191	117
	220		214

discrete values of complex modulus [$G^* = (G'^2 + G''^2)^{1/2}$ and $E^* = (E'^2 + E''^2)^{1/2}$] indicates indistinguishable properties between blends for a particular mode (see Table V). However, each mode for a particular blend exhibits a different value confirming the assignment of anisotropic behavior.

Frequency-dependent mechanical spectra in torsion are shown in Figure 10. Master curves were constructed using an "autoshift" routine based upon storage modulus. In this manner, horizontal and vertical shift factors (a_T and T/T_0) are weighted equally for each sample to accommodate comparison. Spectra include complete mapping of storage and loss modulus and tangent delta at reference temperature ($T_0 = 125°C$). The form of these spectra, showing a transition from rubber-to-glass plateau as a function of frequency, closely resembles temperature-dependent viscoelastic behavior. Consequently, the first criterion for application of the method of reduced variables is fulfilled.[9] The initial glass transition for blends A and C, observed in

temperature-dependent spectra, is absent in frequency-dependent spectra and may be the result of sample conditioning (60 min at 200°C). Calculation of WLF constants (C_1^0 and C_2^0), activation energy (E_a), and loss modulus area ($A_{G''}$) are listed in Table VI. The WLF [log $a_T = -C_1^0 (T - T_0)/C_2^0 + (T - T_0)$] and Arrhenius [$E_a = Rd \ln a_T/d(1/T)$] equations were applied for these calculations. A plot of $T - T_0/\log a_T$ vs. $T - T_0$ yielded WLF constants ($T = 125–250°C$). Empirical and theoretical shift factors were in agreement, thus fulfilling the second criterion for application of time–temperature superposition. A plot of log a_T vs. $1/T$ (0–250°C) yielded a linear relationship fulfilling the third criterion. Accordingly, activation energy, pertaining to viscoelastic flow in the temperature range of interest, was derived. Damping attributes were evaluated by comparison of loss modulus area and are related to energy dissipation as heat from vibrational perturbation. However, this observation may not correlate directly with sound damping due to the frequency range resulting from reduced variables.[10]

Table VI Time–Temperature Superposition Results in Torsion for SMC Blends A, B, and C

	Blend A	Blend B	Blend C
WLF constant c_1^0	5.0	15.1	9.7
($T_0 = 125°C$) c_2^0	10.8	56.9	26.9
Activation energy ($T_0 = 125°C$) (Kj/mol)	440.8	370.3	351.3
Loss modulus area ($T_0 = 125°C$)	1.2	1.1	1.0

CONCLUSION

The feasibility of surface analysis by infrared photoacoustic spectroscopy of SMCs has been investigated. Although results of this study are preliminary, utility of the technique for qualitative determination of composition, depth profile, and thermal exposure effects has been demonstrated. In addition, evaluation of viscoelastic properties of SMC by multimodal dynamic mechanical spectroscopy has shown the application of such methods for characterization of anisotropic materials.

Future work concerns investigation of adhesive formulations and bonded structures with these techniques to assist the design of systems with compatible properties.

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