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DEPARTMENT OF MECHANICAL ENGINEERING AND MECHANICS
SCHOOL OF ENGINEERING
OLD DOMINION UNIVERSITY
NORFOLK, VIRGINIA 23508

INVESTIGATION OF PARAMAGNETIC RESPONSE OF METALLIC EPOXIES

By

Robert L. Ash, Principal Investigator

and

Hoshang Chegini, Research Assistant

Final Report
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INVESTIGATION OF PARAMAGNETIC RESPONSE OF METALLIC EPOXIES

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Robert L. Ash[1] and Hoshang Chegini[2]

SUMMARY

The paramagnetic properties of epoxies which were impregnated with metal ions were examined as the primary task in this research. A major conclusion of this work was that the quality control of the epoxies was insufficient to permit reliable evaluation. Subsequently, a new set of specimens are being prepared.

As an additional task, the research assistant has investigated a new method for estimating heats of combustion for saturated hydrocarbons. The results of that investigation have shown that the empirical approach developed by Singh and Sprinkle is a promising method for on-line measurements.

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[1] Chairman/Eminent Professor, Department of Mechanical Engineering, Old Dominion University, Norfolk, Virginia 23508.
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I. ELECTRON PARAMAGNETIC RESPONSE CHARACTERIZATION OF METAL CONTAINING EPOXIES

Several types of epoxies are currently being used for aerospace application because of their versatility, processability, chemical resistance, low density, and low cost. Since pure polymers do not meet all the requirements needed for aerospace applications, research efforts have been directed toward the modification of these materials (Ref. 1).

One of these modifications is the incorporation of metal ions into these resin systems. Important changes can occur in the properties of these polymeric materials when small quantities of metallic ions are introduced into the systems. Such changes as increases in mechanical strength and increase in moisture resistance are reported in Refs. 2-6, although the reasons for these changes are not fully understood. In order to obtain more information on the electronic structure and the coordination of the metal ions in these polymer matrices, the magnetic properties of the systems have been investigated. Studies were performed for MY-720* epoxy matrices containing Fe, Ni, Co, and Cr metal ions in various concentration ratios. A set of sixteen $Me(acac)_x$** modified epoxy specimens were sent to Virginia Polytechnic Institute for magnetic susceptibility measurements. The magnetic susceptibility can be calculated from the expression (Ref. 7):

$$X_g = \beta \frac{w}{W}$$

where w is net change of sample mass in the magnetic field and W is the mass of the sample out of field. Analysis of standard material allows determination of β values for any particular magnetic field strength. The

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*MY-720 epoxy resin is a product of Narmco Materials, Inc.
**$Me(acac)_x$ is modified epoxy specimen where Me represents the metal ion in acetylacetonates (acac).

analysis of data did not provide us with an acceptable solid conclusion. As a result repeated measurement became necessary. Two sets of identical specimens were sent to Virginia Commonwealth University and Virginia Tech. Unfortunately the analysis of the new sets of data suggested nonuniformality of metal ion distribution in the specimens. Progress in this work has been stopped until a new set of specimens are fabricated.

II. A NEW METHOD TO DETERMINE HEATS OF COMBUSTION OF GASEOUS HYDROCARBONS (Ref. 8)

The heat of combustion of hydrocarbons are presently determined (Ref. 9) by using a constant volume bomb calorimeter. These measurements can be very accurate (<1%). However, calorimetric measurements cannot be used on-line, and require information about the thermal properties of the combustion products of the test sample. The method reported here is direct, on-line, and does not require any prior knowledge of the exact composition of test sample. Since the heat of combustion of the test gas depends on its effective hydrocarbon content, measurement of the amount of oxygen needed for complete combustion can provide us with thermal content of the test gas. NASA has recently developed an oxygen-monitoring-and-control system for the Langley 8-foot high temperature tunnel (Ref. 10). It is based on Y_2O_3-stabilized ZrO_2 electrochemical sensor. The system is capable of maintaining oxygen concentration in the combustion product gases at 20.9 ± 1.0 percent.

The essential chemistry of the hydrocarbon combustion process in oxygen-enriched air is represented by the following equation:

$$\ell(\text{Air}) + m(O_2) + n(C_xH_y) \rightarrow \ell(\text{Air}) + nx(CO_2) + \frac{n}{2} y\,(H_2O)$$

$$\underline{\text{Input channel}} \qquad \underline{\text{Output channel}}$$

$$+ \left[m - n\left(\frac{4x + y}{4}\right)\right](O_2) + \text{Heat} \qquad (1)$$

where C_xH_y represents the hydrocarbon in the reaction. The hydrocarbon flowrate can be controlled and measured by thermal mass flowmeters (Ref. 11). This equation assumes that the added oxygen in the input channel was equal to the amount needed for complete combustion of the hydrocarbon. The mole fraction of oxygen in the output channel of equation (1) is given by the following equation:

$$P(O)_2 = \frac{0.2095\,\ell + \left[m - n\left(\frac{4x + y}{4}\right)\right]}{\ell + nx + \frac{n}{2} y + \left[m - n\left(\frac{4x + y}{4}\right)\right]} \qquad (2)$$

If the mole fraction of oxygen in the output channel is the same as in the reference gas (air), then

$$0.2095 = \frac{0.2095\,\ell + \left[m - n\left(\frac{4x + y}{4}\right)\right]}{\ell + nx + \frac{n}{2} y + \left[m - n\left(\frac{4x + y}{4}\right)\right]} \qquad (3)$$

Simplifying equation (3) yields

$$\frac{m}{n} = \frac{4x + 1.2095y}{4(1 - 0.2095)} = \alpha \qquad (4)$$

calculated values of m/n for some of the pure saturated hydrocarbons in standard and nonstandard air are summarized in Table 1.

Table 1. Summary of m/n-Values for Selected Saturated Hydrocarbons for $P(O_2)$ = 0.2042 and 0.2095.

Hydrocarbon	Chemical Formula	m/n - Value		Hydrocarbon	Chemical Formula	m/n - Value	
		$P(O_2)$ = 0.2042	$P(O_2)$ = 0.2095			$P(O_2)$ = 0.2042	$P(O_2)$ = 0.2095
Methane	CH_4	2.770	2.795	Hexane	C_6H_{14}	12.836	12.945
Ethane	C_2H_6	4.783	4.825	Heptane	C_7H_{16}	14.849	14.975
Propane	C_3H_8	6.796	6.855	Octane	C_8H_{18}	16.862	17.005
Butane	C_4H_{10}	8.809	8.855	Nonane	C_9H_{20}	18.875	19.035
Pentane	C_5H_{12}	10.823	10.915	Decane	$C_{10}H_{22}$	20.888	21.065

If the test gas is not a pure single hydrocarbon, but is a mixture of two or more hydrocarbons, equation (4) can be used directly to calculate m/n values for the effective test hydrocarbon where the X and Y values for the mixture can be obtained from:

$$X = \sum_{i=1}^{n} f_i X_i$$

$$Y = \sum_{i=1}^{n} f_i Y_i \qquad (5)$$

Here, f_i represents the mole fraction of each hydrocarbon in the test gas. For example, for a test gas containing equal mole fractions of CH_4 and C_2H_6, the equivalent hydrocarbon would be $C_{1.5}H_5$.

Because m/n-values for various test gases containing saturated hydrocarbons are related to their chemical composition, they can serve as the basis for direct determination of their heats of combustion. Table 2 summarizes the heat of combustion of several pure saturated hydrocarbons.

Table 2. Summary of Heats of Combustion of Selected Saturated Hydrocarbons

Hydrocarbon	m/n $P(O_2) = 0.2095$	Heat of Combustion KCal/Mode	Heat of Combustion / m/n
CH_4	2.795	212.80	76.14
C_2H_6	4.825	372.82	77.27
C_3H_8	6.855	530.61	77.40
C_4H_{10}	8.885	687.65	77.39
C_5H_{12}	10.915	845.10	77.43
C_6H_{14}	12.945	1002.55	77.45

III. EXPERIMENTAL VERIFICATION OF THEORETICAL PROCEDURE

The experimental plan involved measuring m/n values for the following kinds of test gas samples:

1. Pure, saturated gaseous hydrocarbons (methane, ethane, propane, and butane, etc.)
2. Binary mixtures of selected saturated hydrocarbons (i.e., no non-combustible components)
3. Binary mixtures containing a saturated hydrocarbon and an inert gas.
4. Gaseous mixtures containing several saturated hydrocarbons and selected noncombustible impurities.

It should be noted that n in the parameter m/n represents the vol-

ume flow rate of the test gas. We have used a positive displacement dry test meter for measuring the volumetric flowrate (n) of the test gases. Results of heat of combustion are summarized in Tables 3, 4, and 5 for various test gases.

Table 3. Summary of Experimental and Theoretical m/n-Values for Selected Hydrocarbons in Air [$P(O_2)$ = 20.42%].

Test Hydrocarbon	Hydrocarbon Flowrate (n), Sccm	Equalizing Oxygen Flowrate (m), Sccm	Carrier Air Flowrate (ℓ), Sccm	m/n-Value	
				Experimental	Theoretical
CH_4	71.80±0.72	200.80±1.00	500.0	2.797±0.042	2.770
C_2H_6	45.85±0.46	214.67±1.00	500.0	4.682±0.070	4.783
C_3H_8	29.18±0.30	199.71±1.00	500.0	6.843±0.103	6.796
C_4H_{10}	24.20±0.24	213.00±1.00	500.0	8.801±0.132	8.809

From the data summarized in Tables 3 and 4, it is apparent that the calculated and the experimental values of m/n for various types of mixtures are in reasonably good agreement. As has been indicated earlier, the m/n-values for the mixtures can be used to infer their heats of combustion. Using the reported heat of combustion values for saturated hydrocarbons listed in Table 2, the following relationship has been derived between m/n and the heat of combustion values expressed in kilocalories per mole (Ref. 11). Based on a fourth order least square fit the following equation was obtained.

$$\text{Heat of combustion [Kcal/mole]} = a_0 + a_1(m/n) + a_2(m/n)^2\ a_3(m/n)^3 + a_4(m/n)^4 \qquad (6)$$

where $a_0 = -23.2134$

$a_1 = +91.2088$

$a_2 = -2.9745$

$a_3 = +0.3032$

$a_4 = -0.0117$

A comparison between the heat of combustion values calculated on the basis of their experimentally observed m/n-values and known chemical composition is given in Tables 3, 4, and 5. It is apparent that they are in reasonably good agreement.

Table 4. Summary of Experimental and Theoretical m/n-Values for Various Test Gas Mixtures $P(O_2) = 0.2042$

Test Gas Mixture (V/o)	Mixture Flowrate (n), Sccm	Equalizing Oxygen Flowrate, (m) Sccm	Carrier Air Flowrate, (ℓ) Sccm	m/n Value	
				Experimental	Theoretical
(a) Binary Mixtures					
0.5 CH_4 + 0.5 C_2H_6	96.00±0.83	362.3±1.0	500.0	3.774±0.043	3.770±0.044
0.5 CH_4 + 0.5 C_3H_8	68.70±0.75	326.4±1.0	500.0	4.751±0.066	4.783±0.065
0.5 CH_6 + 0.5 C_4H_{10}	56.18±0.75	322.0±1.0	500.0	5.732±0.092	5.789±0.094
0.5 C_2H_6 +0.49 C_4H_{10}	52.58±0.53	353.0±1.0	500.0	6.713±0.087	6.740±0.030
0.5 CH_4 + 0.5 N_2	100.30±1.23	153.5±1.0	500.0	1.530±0.028	1.517±0.034
0.5 CH_4 + 0.5 CO_2	100.40±1.01	153.3±1.0	500.0	1.527±0.025	1.515±0.031
0.5 C_2H_6 + 0.5 N_2	99.80±1.10	252.2±1.0	500.0	2.526±0.038	2.516±0.026
0.5 C_2H_6 + 0.5 CO_2	99.90±0.84	253.0±1.0	500.0	2.531±0.031	2.514±0.023
0.5 C_3H_8 + 0.5 N_2	99.90±1.05	353.3±1.0	500.0	3.536±0.040	3.524±0.021
0.5 C_3H_8 + 0.5 CO_2	100.00±0.78	354.3±1.0	500.0	3.542±0.037	3.521±0.018

Table 4. (continued)

Test Gas Mixture (V/o)	Mixture Flowrate (n), Sccm	Equalizing Oxygen Flowrate, (m) Sccm	Carrier Air Flowrate,(ℓ) Sccm	m/n Value	
				Experimental	Theoretical
(b) Complex Mixtures					
C_2H_6(44.63%) + C_3H_8 (25.88%) + C_4H_{10} (10.81%) + CO_2 (5.09%) + N_2(13.59)	39.7±0.4	199.0±1.0	500.0	5.014±0.075	4.894±0.083
CH_4 (53.04%) + C_2H_6 (26.09%) + C_3H_8(16.42%) + CO_2 (1.43%) + N_2(1.01%)	49.9±0.5	198.0±1.0	500.0	3.968±0.060	3.975±0.034
CH_4(50.84%) + C_2H_6(17.12%) + C_3H_8 (24.87%) + CO_2(3.34%) + N_2(3.83%)	50.3±0.5	193.0±1.0	500.0	3.837±0.057	3.936±0.046
CH_4(51.51%) + C_2H_6(21.24%) + C_3H_8(23.82%) + CO_2(1.74%) + N_2(1.69%)	49.2±0.5	199.5±1.0	500.0	4.055±0.061	4.070±0.036

Table 5. Comparison Between the Calculated and Measured Values of Heats of Combustion for Various Gas Mixtures.

Mixture Composition	Heat of Combustion, KCal/Mole	
	Experimental	Calculated
0.5 CH_4 + 0.5 C_2H_6	292.6±3.4	292.2±3.9
0.5 CH_4 + 0.5 C_3H_8	369.5±5.2	371.1±5.2
0.5 CH_4 + 0.5 C_4H_{10}	446.3±7.4	449.2±2.2
0.5 CH_4 + 0.5 N_2	110.6±2.2	109.0±2.8
0.5 CH_4 + 0.5 CO_2	110.4±2.2	109.4±2.6
0.5 C_2H_6 + 0.5 N_2	193.0±3.1	192.2±2.2
0.5 C_2H_6 + 0.5 CO_2	193.4±2.6	192.0±1.8
0.5 C_3H_8 + 0.5 N_2	274.3±3.8	273.3±1.6
0.5 C_3H_8 + 0.5 CO_2	274.7±3.0	273.0±1.4
C_2H_6(44.63%) + C_3H_8(25.88%) + C_4H_{10}(10.81%) + CO_2(5.09%) + N_2(13.59%)	390.1±11.7	380.6±9.9
CH_4(53.04%) + C_2H_6(26.09%) + C_3H_8(18.42%) + CO_2(1.43%) + N_2(1.01%)	307.7±7.8	308.3±8.0
CH_4(50.84%) + C_2H_6(17.12%) + C_3H_8(24.87%) + CO_2(3.34%) + N_2(3.83%)	297.4±5.6	305.4±8.0
CH_4(51.51%) + C_2H_6(21.24%) + C_3H_8(23.82%) + CO_2(1.74%) + N_2(1.69%)	311.5±8.0	315.9±8.3

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where w is net change of sample mass in the magnetic field and W is the mass of the sample out of field. Analysis of standard material allows determination of β values for any particular magnetic field strength. The

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$$+ \left[m - n\left(\frac{4x + y}{4}\right)\right](O_2) + \text{Heat} \qquad (1)$$

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$$P(O)_2 = \frac{0.2095\,\ell + \left[m - n\left(\frac{4x + y}{4}\right)\right]}{\ell + nx + \frac{n}{2}\,y + \left[m - n\left(\frac{4x + y}{4}\right)\right]} \qquad (2)$$

If the mole fraction of oxygen in the output channel is the same as in the reference gas (air), then

$$0.2095 = \frac{0.2095\,\ell + \left[m - n\left(\frac{4x + y}{4}\right)\right]}{\ell + nx + \frac{n}{2}\,y + \left[m - n\left(\frac{4x + y}{4}\right)\right]} \qquad (3)$$

Simplifying equation (3) yields

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CH_4	71.80±0.72	200.80±1.00	500.0	2.797±0.042	2.770
C_2H_6	45.85±0.46	214.67±1.00	500.0	4.682±0.070	4.783
C_3H_8	29.18±0.30	199.71±1.00	500.0	6.843±0.103	6.796
C_4H_{10}	24.20±0.24	213.00±1.00	500.0	8.801±0.132	8.809

From the data summarized in Tables 3 and 4, it is apparent that the calculated and the experimental values of m/n for various types of mixtures are in reasonably good agreement. As has been indicated earlier, the m/n-values for the mixtures can be used to infer their heats of combustion. Using the reported heat of combustion values for saturated hydrocarbons listed in Table 2, the following relationship has been derived between m/n and the heat of combustion values expressed in kilocalories per mole (Ref. 11). Based on a fourth order least square fit the following equation was obtained.

$$\text{Heat of combustion [Kcal/mole]} = a_0 + a_1(m/n) + a_2(m/n)^2\ a_3(m/n)^3 + a_4(m/n)^4 \qquad (6)$$

where $a_0 = -23.2134$

$a_1 = +91.2088$

$a_2 = -2.9745$

$a_3 = +0.3032$

$a_4 = -0.0117$

A comparison between the heat of combustion values calculated on the basis of their experimentally observed m/n-values and known chemical composition is given in Tables 3, 4, and 5. It is apparent that they are in reasonably good agreement.

Table 4. Summary of Experimental and Theoretical m/n-Values for Various Test Gas Mixtures $P(O_2) = 0.2042$

Test Gas Mixture (V/o)	Mixture Flowrate (n), Sccm	Equalizing Oxygen Flowrate, (m) Sccm	Carrier Air Flowrate, (ℓ) Sccm	m/n Value	
				Experimental	Theoretical
(a) Binary Mixtures					
0.5 CH_4 + 0.5 C_2H_6	96.00±0.83	362.3±1.0	500.0	3.774±0.043	3.770±0.044
0.5 CH_4 + 0.5 C_3H_6	68.70±0.75	326.4±1.0	500.0	4.751±0.066	4.783±0.065
0.5 CH_6 + 0.5 C_4H_{10}	56.18±0.75	322.0±1.0	500.0	5.732±0.092	5.789±0.094
0.5 C_2H_6 +0.49 C_4H_{10}	52.58±0.53	353.0±1.0	500.0	6.713±0.087	6.740±0.030
0.5 CH_4 + 0.5 N_2	100.30±1.23	153.5±1.0	500.0	1.530±0.028	1.517±0.034
0.5 CH_4 + 0.5 CO_2	100.40±1.01	153.3±1.0	500.0	1.527±0.025	1.515±0.031
0.5 C_2H_6 + 0.5 N_2	99.80±1.10	252.2±1.0	500.0	2.526±0.038	2.516±0.026
0.5 C_2H_6 + 0.5 CO_2	99.90±0.84	253.0±1.0	500.0	2.531±0.031	2.514±0.023
0.5 C_3H_8 + 0.5 N_2	99.90±1.05	353.3±1.0	500.0	3.536±0.040	3.524±0.021
0.5 C_3H_8 + 0.5 CO_2	100.00±0.78	354.3±1.0	500.0	3.542±0.037	3.521±0.018

Table 4. (continued)

Test Gas Mixture (V/o)	Mixture Flowrate (n), Sccm	Equalizing Oxygen Flowrate, (m) Sccm	Carrier Air Flowrate,(ℓ) Sccm	m/n Value	
				Experimental	Theoretical
(b) Complex Mixtures					
C_2H_6(44.63%) + C_3H_8 (25.88%) + C_4H_{10} (10.81%) + CO_2 (5.09%) + N_2(13.59)	39.7±0.4	199.0±1.0	500.0	5.014±0.075	4.894±0.083
CH_4 (53.04%) + C_2H_6 (26.09%) + C_3H_8(16.42%) + CO_2 (1.43%) + N_2(1.01%)	49.9±0.5	198.0±1.0	500.0	3.965±0.060	3.975±0.034
CH_4(50.84%) + C_2H_6(17.12%) + C_3H_8 (24.87%) + CO_2(3.34%) + N_2(3.83%)	50.3±0.5	193.0±1.0	500.0	3.837±0.057	3.936±0.046
CH_4(51.51%) + C_2H_6(21.24%) + C_3H_8(23.82%) + CO_2(1.74%) + N_2(1.69%)	49.2±0.5	199.5±1.0	500.0	4.055±0.061	4.070±0.036

Table 5. Comparison Between the Calculated and Measured Values of Heats of Combustion for Various Gas Mixtures.

Mixture Composition	Heat of Combustion, KCal/Mole	
	Experimental	Calculated
0.5 CH_4 + 0.5 C_2H_6	292.6±3.4	292.2±3.9
0.5 CH_4 + 0.5 C_3H_8	369.5±5.2	371.1±5.2
0.5 CH_4 + 0.5 C_4H_{10}	446.3±7.4	449.2±2.2
0.5 CH_4 + 0.5 N_2	110.6±2.2	109.0±2.8
0.5 CH_4 + 0.5 CO_2	110.4±2.2	109.4±2.6
0.5 C_2H_6 + 0.5 N_2	193.0±3.1	192.2±2.2
0.5 C_2H_6 + 0.5 CO_2	193.4±2.6	192.0±1.8
0.5 C_3H_8 + 0.5 N_2	274.3±3.8	273.3±1.6
0.5 C_3H_8 + 0.5 CO_2	274.7±3.0	273.0±1.4
C_2H_6(44.63%) + C_3H_8(25.88%) + C_4H_{10}(10.81%) + CO_2(5.09%) + N_2(13.59%)	390.1±11.7	380.6±9.9
CH_4(53.04%) + C_2H_6(26.09%) + C_3H_8(18.42%) + CO_2(1.43%) + N_2(1.01%)	307.7±7.8	308.3±8.0
CH_4(50.84%) + C_2H_6(17.12%) + C_3H_8(24.87%) + CO_2(3.34%) + N_2(3.83%)	297.4±5.6	305.4±8.0
CH_4(51.51%) + C_2H_6(21.24%) + C_3H_8(23.82%) + CO_2(1.74%) + N_2(1.69%)	311.5±8.0	315.9±8.3

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INVESTIGATION OF PARAMAGNETIC RESPONSE OF METALLIC EPOXIES

By

Robert L. Ash[1] and Hoshang Chegini[2]

SUMMARY

@ ABS

The paramagnetic properties of epoxies which were impregnated with metal ions were examined as the primary task in this research. A major conclusion ~~of this work~~ was that the quality control of the epoxies was insufficient to permit reliable evaluation. Subsequently, a new set of specimens ~~are~~ LS being prepared.

← As an additional task, ~~the research assistant has investigated~~ is investigated a new method for estimating heats of combustion for saturated hydrocarbons. The results of that investigation have shown that the empirical approach ~~developed by Singh and Sprinkle~~ is a promising method for on-line measurements.

@ DBA Author

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[1] Chairman/Eminent Professor, Department of Mechanical Engineering, Old Dominion University, Norfolk, Virginia 23508.
[2] Research Assistant, Department of Mechanical Engineering, Old Dominion University, Norfolk, Virginia 23508.