

Effect of relative humidity on the curing and dielectric properties of polyurethane-based composites

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Abstract: Isocyanate groups present in the pre-cure mix of polyurethane-based composites are highly moisture sensitive. Binding of water with isocyanate groups occurs at the expense of cross-linking in the cure process. Consequently, the dielectric properties of the resulting material may alter due to i) the presence of bound water in the material and ii) changes in the dielectric properties of the polymer due to reduced cross-linking. In this work, polyurethane-based composite samples were cured in various controlled relative-humidity environments, created using saturated salt solutions. The dielectric constant of the materials was measured as a function of cure time, in the frequency range of 0.5 to 18 GHz. In this way the relationship between relative humidity during cure, and dielectric properties of the resulting composites, is demonstrated.

Introduction

Of principle importance in the production of composite materials for particular electromagnetic applications, such as for shielding or absorption of electromagnetic radiation, is tight control of the complex permittivity and permeability of the final product. Some commonly-used matrix materials are highly moisture-sensitive, and variations in environmental relative humidity (RH) may affect the way in which the matrix cures. Broadband measurements of complex permittivity and permeability were conducted in the frequency range 0.5 to 18 GHz, on a polyurea/polyurethane hybrid dielectric matrix with approximately spherical ferromagnetic particles dispersed throughout. The effect of water uptake on the electromagnetic properties of the composite was examined as a function of time during the curing process of the polymer material, for various values of relative humidity in the range from 0 to 90%. Humidity control was achieved through the use of desiccators containing various saturated salt solutions.

Complex permittivity and permeability were measured using the coaxial transmission/reflection method for determination of S-parameters, utilizing a vector network analyzer. Conversion of S-parameters to complex permittivity and permeability was accomplished using the well-known Nicholson-Ross-Weir algorithm [1, 2]. The complete method, including

a discussion of uncertainty analysis, is presented by Baker-Jarvis [3].

It was determined that, during the curing process, water uptake into the polymer matrix alters the dielectric properties of the material. This behavior is attributed to the polar nature of the water molecule, and manifests itself as an increase in the magnitude of the real permittivity of the composite as a function of increasing relative humidity and time. Little change in the permeability was observed. These observations demonstrate explicitly that the bulk electromagnetic properties of composites containing moisture-sensitive polymer matrices depend upon humidity control in material preparation.

Composite material fabrication and curing

The composite material studied consists of a polyurea/polyurethane hybrid polymer binder initially in the form of two precursors. When mixed together these exothermically react to form the final polymer matrix. The polymer precursors were supplied by ARC Technologies, Inc [4]. The first precursor is composed of an aromatic urethane polymer, medium density isocyanate, and propylene carbonate. The second of the polymer precursors, composed of diethyltoluenediamine and polyether amine, is initially loaded with roughly spherical ferromagnetic particles with diameter in the micrometer size range, shown in Figure 1.

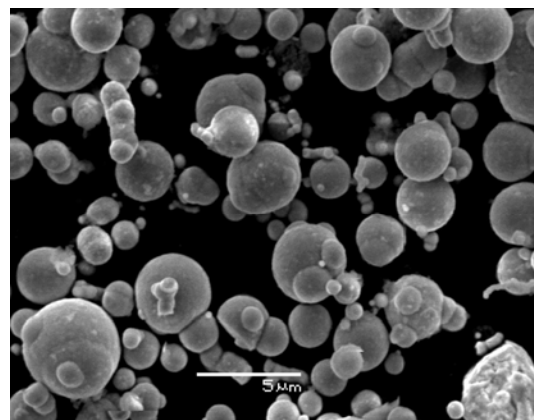


Figure 1: SEM micrograph showing the size distribution and approximate spherical shape of the ferromagnetic filler particles.

The filler particles were dispersed as evenly as possible throughout the second precursor by physical agitation, prior to combining with the first precursor to create the mixed composite. Once the precursors were thoroughly combined, the material was pressed between two aluminum plates into sheets nominally 1 mm thick. This thickness of sample material was chosen such that the singular behavior of the Nicholson-Ross-Weir algorithm, for sample length equal to multiples of one half of a wavelength in the material, could be avoided. After pressing, the sheet material was placed under vacuum to remove residual air bubbles, and then placed in a controlled RH environment.

By placing the prepared composite sheets in an environment in which the relative humidity is controlled, the amount of water absorbed by the composite can be varied. This phenomenon has been observed by Ludwig and Urban for polyurethane coatings, and is attributed to the presence of isocyanate groups in the pre-cure mixture [5]. The isocyanate groups are highly reactive to water, which is absorbed at the expense of cross-linking in the cure process. The real and imaginary parts of the permittivity of water can be represented by the Debye equation:

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + \omega^2 \tau^2}, \quad \epsilon'' = \frac{(\epsilon_s - \epsilon_{\infty})\omega\tau}{1 + \omega^2 \tau^2}$$

Where ϵ_{∞} is the high frequency limiting relative permittivity, ϵ_s is the static permittivity, and τ is the relaxation time [6]. At 25 degrees Celsius and 1 GHz, ϵ' is determined to be $78.16 + i3.79$, demonstrating a high dielectric constant due to the polar nature of the water molecule [7, section 6-15]. At 10 GHz, ϵ' is reduced whereas ϵ'' increases such that the dielectric constant is $62.81 + i29.93$. It is expected that absorption of water into the curing composite will have a strong effect upon the dielectric properties of the material, due both to the reduction in cross-linking and the presence of bound water with relatively high dielectric constant.

Controlled RH environments were created by placing saturated salt solutions in isolated desiccators. The RH was determined from the empirical formula:

$$RH = A \exp(B/T)$$

where T is the temperature in Kelvin, and A and B are empirical constants specific to the particular saturated salt solution utilized [7, section 15-25]. To produce an environmental RH of $84 \pm 2\%$, a KCl solution was used in which A and B are 49.38 and 159 respectively. One set of measurements was taken in ambient RH. This was determined to be 27% by averaging the RH

conditions in the laboratory over the course of the 8 day curing process. 0% RH was produced by anhydrous calcium sulfate crystals, also placed in an isolated desiccator.

Microwave frequency permittivity and permeability measurements

Method and results

Electromagnetic parameters of the materials were measured, over the frequency range 0.5 to 18 GHz, by placing samples in a section of transmission line and measuring the S-parameters as described in references [1-3]. The transmission line utilized was a 7mm coaxial line attached to a low-loss, beadless, air-line sample cell connected to an Anritsu 37347C vector network analyzer. The sample holder and pertinent parameters are shown schematically in Figure 2.

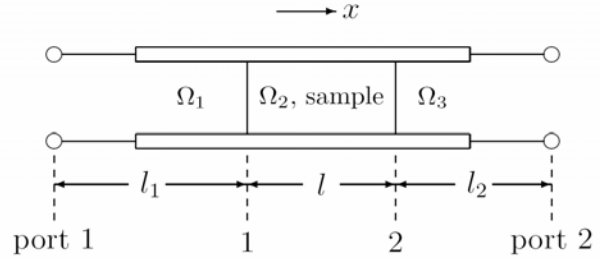


Figure 2: Schematic diagram of sample cell and sample placement. Ports 1 and 2 terminate at the vector network analyzer interface while l is the sample length, and l_1 and l_2 are the reference plane positions. The Ω_i represent the three distinct regions of the boundary value problem.

Placement of the sample within the sample cell essentially breaks the transmission line down into three distinct regions. Permittivity and permeability determination becomes a boundary value problem. The complex permittivity and permeability of the sample were determined from the measured reflection and transmission coefficients according to the method described by Nicholson-Ross-Weir [1, 2]. This algorithm allows one to determine the permittivity and permeability explicitly, but suffers from some instability. In particular, the solutions for both the permittivity and permeability are unstable at integral multiples of one-half wavelength in the sample material. Also, calculated values for the permittivity and permeability are highly sensitive to the position of the sample within the sample cell (parameters l_1 and l_2). All of this leads to significant system uncertainty and the need for careful sample preparation and placement during measurement.

7 mm coaxial samples were prepared from the sheet composite material at days 1, 2, 4, and 8 of cure. Material cured in the 0% RH environment was not suitable for sample preparation until day 63 of cure. This was due to the sheet material remaining soft until this stage of curing – a mechanical outcome of the effect of ambient RH on the curing process. Five samples were created for each measurement, with the results averaged after analysis to reduce random uncertainty. The samples were created from the sheet composite material by punching with a custom-made punch adhering to strict tolerances for the inner and outer diameter. The inner diameter was specified by measuring the diameter of the inner conductor of the sample holder at several points along its length. For this measurement a Fowler Ultra Digit Mark IV micrometer was used, with systematic uncertainty 1 μm . The diameter of the inner conductor was found to be 3.034 ± 0.002 mm. The outer diameter was taken as given by the manufacturer of the sample cell: 7.000 ± 0.004 mm. A strict tolerance on the inner and outer diameter of the samples (nominally ± 5 μm [8]) is necessary to reduce or eliminate any air gaps between the sample and sample cell for inner and outer radii, which can lead to under-measurement of ϵ' [9]. The resulting samples exhibit a good fit within the coaxial sample-holder for both the inner and outer radii, minimizing air-gap uncertainty. The length of each sample, parameter l , was measured using the digital micrometer.

Observation and interpretation

Measured values of the real relative permittivity demonstrate a strong dependence upon the environmental relative humidity, even from the beginning of the curing process. Figure 3 shows a comparison of measured values for the real relative permittivity and permeability of the polymer composite for samples cured in 84% and 27% RH, for frequencies 1 and 10 GHz, as a function of cure time. Notice the significant difference in values for ϵ' at the different RH values, as well as the slight rise in ϵ' for the 27% RH samples as curing progresses. The 84% RH samples clearly, after one day, have a higher real permittivity than the 27% RH samples. The value of ϵ' for the samples cured in 84% RH also appears relatively flat as a function of cure time, indicating that electromagnetic property development is substantially complete even on day 1. The 27% RH samples show a rise in real relative permittivity as a function of cure time, indicating that property development is continuing at least through day 4. A thorough error analysis is still in progress, thus the uncertainties shown in Figure 3 are derived from scatter in values measured on different 7mm samples taken from the same sheet. This is likely to under-estimate

the true uncertainty. In contrast, the real relative permeability of the composite is not strongly influenced by the RH of the curing environment, or the cure time. Measurements made on the samples from the 0% RH environment at day 63 yield a real relative permittivity of 9.7 ± 0.1 at 1 GHz, and 8.6 ± 0.1 at 10 GHz. The real relative permeability was found to be 3.1 ± 0.1 at 1 GHz, and 1.8 ± 0.1 at 10 GHz. Even after 63 days of curing, the real relative permittivity for the sample cured in 0% RH remains lower than that seen for the 27% RH sample at day 8, as anticipated. The real relative permeability values are similar to those measured on day 8 for the samples cured in 27% RH.

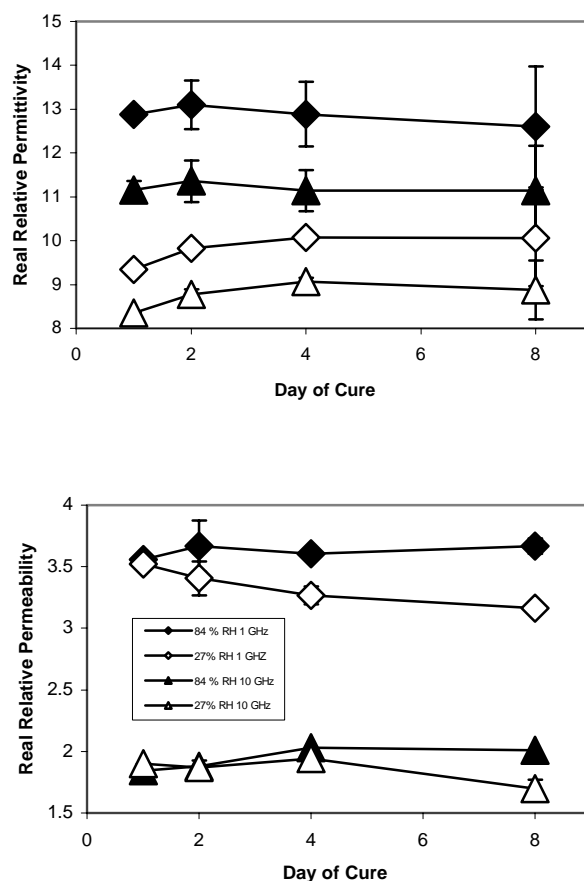


Figure 3: Real relative permittivity and permeability as a function of the day of cure for 27% (open symbols) and 84% (filled symbols) RH samples, measured at 1 (diamonds) and 10 (triangles) GHz.

Figure 4 shows the experimentally-measured real parts of permittivity and permeability over the frequency range 0.5 to 18 GHz for the 84% RH samples. These curves are averages of measurements on several samples at each day of cure. The oscillations visible in ϵ' are largely due to residual mismatches that occur,

after system calibration, when the sample cell is reconnected to the test-port cables between measurements. Another source of error arises from sensitivity to the uncertainty in the sample position within the co-axial sample cell and variations in microstructure and/or surface quality from sample to sample. Notice the strong relaxation in the real permeability due to the magnetic filler particles.

Conclusion and future work

The electromagnetic properties of the polyurea/polyurethane-based composites studied here are strongly influenced by the presence of water vapor during the curing process, as evidenced by the significant difference in the real relative permittivity of samples cured in different RH environments. This difference is caused primarily by water uptake into the polymer matrix which alters the dielectric properties of the composite material due to its strong polar nature and high value of real relative permittivity. Furthermore, examination of the complex permeability over curing time shows that the magnetic properties of the material are not influenced to as great a degree as the dielectric properties by the relative humidity of the curing environment. Future work will include making measurements on the unfilled (particle free) polymer as a function of cure time in various RH environments.

Acknowledgements

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References

- [1] A. M. Nicholson and G. Ross, "Measurement of the intrinsic properties of materials by time domain techniques," *IEEE Trans. Instrum. Meas.*, vol. IM-19, pp. 377-382, Nov. 1970.
- [2] W. B. Weir, "Automatic measurement of complex dielectric constant and permeability at microwave frequencies," *Proc. IEEE*, vol. 62, pp. 33-36, Jan. 1974.
- [3] J. Baker-Jarvis, "Transmission / reflection and short-circuit line permittivity measurements," *NIST Technical Note* 1341, 1990.
- [4] ARC Technologies, Inc. (<http://www.arc-tech.com/>)
- [5] B. W. Ludwig and M. W. Urban, "Quantitative determination of isocyanate concentration in crosslinked polyurethane coatings," *J. Coatings Technology*, vol. 68, pp. 93-97, June 1996.
- [6] C. A. Balanis, *Advanced Engineering Electromagnetics*, p. 84, New York: John Wiley and Sons, 1989.
- [7] D. R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, 82nd edition, Boca Raton: CRC Press, 2002.
- [8] I. J. Youngs, "NAMAS-accredited microwave permittivity/permeability measurement system," *IEE Proc.-Sci. Meas. Technol.*, vol. 143, pp. 247-253, Jul. 1996.
- [9] E. J. Vanzura, J. R. Baker-Jarvis, J. H. Grosvenor and M. D. Janezic, "Intercomparison of permittivity measurements using the transmission/reflection method in 7-mm coaxial transmission lines," *IEEE Trans. Microwave Theory and Techniques*, vol. 42, pp. 2063-2070, Nov. 1994.

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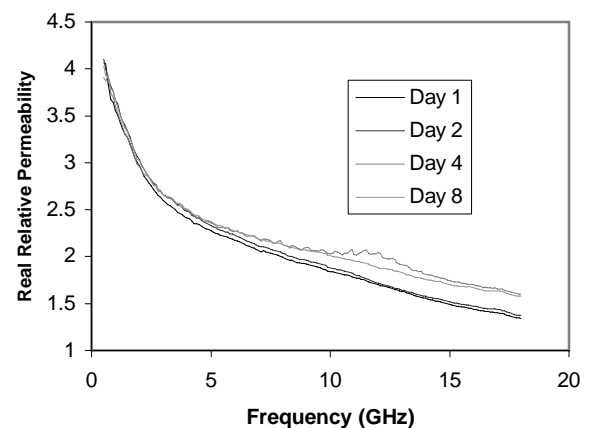
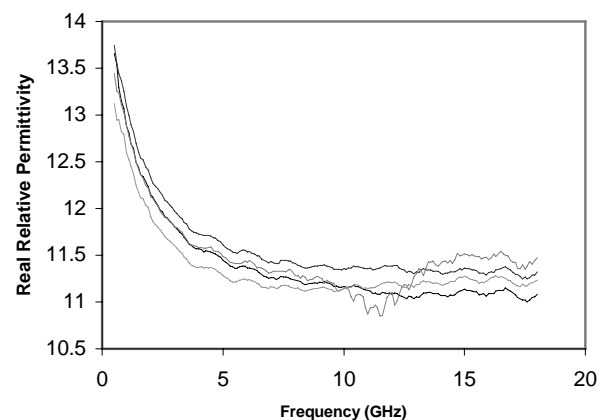


Figure 4: Real relative permittivity and permeability as a function of frequency for samples cured in 84% RH. Measurements are made at days 1, 2, 4 and 8 of cure.