

Ultrasonic characterization of the curing of powder coating films based on their $\tan(\delta)$

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Abstract—The aim of this study was to establish a relationship between the mechanical properties of a powder coating, extracted using ultrasonic analyses, and the extent of its curing. This study was necessitated by the fact that most current methods either focus on in-process temperature monitoring or on laboratory analysis of powder samples and not on post-curing characterization of industrial samples. Working towards the objective the study involved investigating powder coating films by employing transmission mode ultrasound to extract the dimensionless material descriptor, $\tan(\delta)$. It has been demonstrated that trends observed in the mechanical properties of the coatings extracted by processing the ultrasonic signal corresponded to those experimentally extracted using mechanical testing.

I. INTRODUCTION

Powder coatings are dry polymer based surface coatings that are sprayed onto the object surface using an electrostatic gun that charges each particle and then, in most cases, is cured by heating the object in a convection oven. In the oven cross-linking of the polymer chains progresses with curing time and the extent of cross-linking determines the mechanical properties, described by elastic moduli, of the coating.

Testing for curing of powder coatings has traditionally been achieved using in-process temperature monitoring methods. Various in situ cure monitoring methods have been studied [1] [2] [3]. Cure characterization has also been achieved using Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Thermal Analysis (DMTA) [4] [5] [6]. Some studies have employed ultrasound to study curing [7] [8]. In all these cases the experiments were performed in a laboratory setting while the powder was being cured. These methods don't address the problem of post-curing characterization of coatings that are finished products. The eventual goal of this study is to be able to characterize these cured coatings on their substrates. Working towards this goal, as an intermediate step, this paper presents methods and models to characterize substrate-free polymeric films using ultrasound.

II. THEORY

Dynamic Mechanical Analysis (DMA) is one methodology used to determine elastic moduli for the characterization of

coatings [9]. Elastic moduli can as well be determined from the multispectral ultrasonic parameters of attenuation and phase velocity [10]. The dimensionless quantity, $\tan(\delta)$, can be used to compare differently cured films and is defined in the next section. In order to determine the velocity and attenuation inside the polymeric films, two models were used as described in the following sections. The first model is a simple Time-of-Flight based transmission mode model. The second model compensates for the first model's inability to account for the case wherein the system is unable to resolve multiple reflections within the polymeric film layer.

A. Calculation of Elastic Moduli

There are two experimental protocols that can be used to calculate the elastic moduli of materials. One involves tensile testing without any oscillations. The second involves oscillatory testing wherein two frequency dependent moduli are calculated viz. the storage modulus and the loss modulus. Together they describe the viscoelastic properties of a material. Since the polymer is a viscoelastic material the latter protocol is to be used in testing. The storage and loss moduli are given by Equations 1 and 2 respectively [10].

$$L' = \frac{\rho V(\omega)^2 \left[1 - \left(\frac{\alpha(\omega)V(\omega)}{\omega} \right)^2 \right]}{\left[1 + \left(\frac{\alpha(\omega)V(\omega)}{\omega} \right)^2 \right]^2} \quad (1)$$

$$L'' = \frac{2\rho V(\omega)^2 \left(\frac{\alpha(\omega)V(\omega)}{\omega} \right)}{\left[1 + \left(\frac{\alpha(\omega)V(\omega)}{\omega} \right)^2 \right]^2} \quad (2)$$

ρ is the density of the viscoelastic material, $V(\omega)$ is the frequency dependent phase velocity and $\alpha(\omega)$ is the frequency dependent attenuation within the sample. $\tan(\delta)$, a measure of the loss in the medium, can be used to compare cured films. It is given by,

$$\tan(\delta) = \frac{L''(\omega)}{L'(\omega)} \quad (3)$$

B. Transmission Mode Model 1: Velocity obtained from Time-of-Flight(TOF). No multiple reflections.

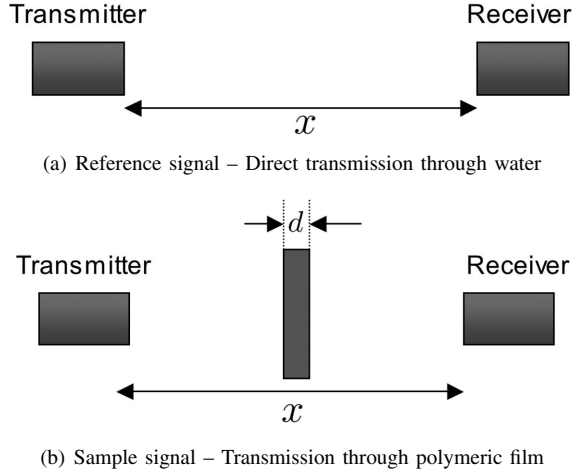


Fig. 1. Transmission mode experiments

In the first model, the TOF of an ultrasonic wave through the sample can be used to determine the velocity of sound in the sample. The set up consists of two transducers in a transmit-receive configuration set apart a fixed distance from each other. First a direct transmission signal through the coupling medium (air or water) has to be acquired (Figure 1(a)). The TOF of the peak, $t_R(\omega)$, is obtained from the time-frequency domain using the Wigner transform of the signal. Next, $t_S(\omega)$, has to be determined from the TOF of the wave through the sample of thickness d (Figure 1(b)). Assuming no multiple reflections within the film sample, the velocity in the sample is given by,

$$V_S(\omega) = \frac{d}{\Delta t(\omega) + \frac{d}{V_R}} \quad (4)$$

where $\Delta t(\omega) = t_S(\omega) - t_R(\omega)$. V_R is the velocity of sound in the coupling medium and this can be determined empirically from a separate experiment. The attenuation, $\alpha_S(\omega)$, can be calculated from the peak heights of the direct and through-sample signals using the equation,

$$\alpha_S(\omega) = \left(-\frac{1}{d}\right) \cdot 20 \log_{10} \left(\frac{H_S(\omega)}{H_R(\omega)} \right) \quad (5)$$

where $H_S(\omega)$ is the peak height of the signal through the sample and the coupling medium and $H_R(\omega)$ through the coupling medium only.

C. Transmission Mode Model 2 : Considering multiple reflections in coating

Model 1 does not account for the case wherein the system is unable to resolve multiple reflections inside the polymeric film layer. Model 2 is designed to take this shortcoming of Model 1 into consideration and appropriately compensate for the multiple reflections within the layer. The entire system is assumed to be linear and shift invariant allowing us to model the transfer function of the system as a multiplication

between the individual transfer functions of the components of the system. A direct transmission reference signal has to be acquired and used to deconvolve the system response from the response obtained when the polymeric film sample is present. The attenuation and phase velocity can be derived from the magnitude and phase spectra of the deconvolved signal.

The spectrum of the direct transmission signal can be written as,

$$F_R(\omega, x) = |F_0(\omega_0) e^{-\alpha_R(\omega)x} | e^{i(k'_R(\omega)x + \phi_0)} \quad (6)$$

$$P_T(\omega) \cdot P_R(\omega) \cdot D_R(\omega, z) \cdot T_R \quad (7)$$

where $\alpha_R(\omega)$ is the frequency dependent attenuation of the coupling medium, $P_T(\omega)$ and $P_R(\omega)$ are the transmitting and receiving transducer responses and $D_R(\omega, z)$ is the diffraction effect. T_R is the transmission through the coupling medium. k'_R is the wavenumber of the signal in the coupling medium.

If a material sample is placed in between the two transducers then the frequency spectrum can be written as,

$$F_S(\omega, x) = |F_0(\omega_0) e^{-\alpha_R(\omega)(x-d) - \alpha_S(\omega)d} | \quad (8)$$

$$e^{i(k'_R(\omega)(x-d) + k'_S(\omega)d + \phi_0)} \cdot P_T(\omega) \quad (9)$$

$$P_R(\omega) \cdot D_S(\omega, z) \cdot T_S \quad (10)$$

where $\alpha_S(\omega)$ is the frequency dependent attenuation of the sample of thickness d . T_S is the transmission through the sample immersed in the coupling medium. k'_S is the wavenumber of the signal in the sample. Dividing magnitudes of Equation 8 by Equation 6 we get,

$$\frac{|F_S(\omega, x)|}{|F_R(\omega, x)|} = e^{\alpha_R(\omega)d - \alpha_S(\omega)d} \cdot \frac{|T_S|}{|T_R|} \cdot \frac{|D_S(\omega, z)|}{|D_R(\omega, z)|} \quad (11)$$

For thin samples we assume that the change in the diffraction effect will be negligible and thus the last term in the equation can be cancelled out.

The reference signal is deconvolved from the sample signal via pseudo-inverse filtering to obtain, $a(\omega) = A(\omega)e^{i\Delta\phi}$, where $\Delta\phi(\omega) = \phi_S(\omega) - \phi_R(\omega)$ is the deconvolved unwrapped phase spectrum. The magnitude $A(\omega)$ is a result of the transmission coefficients and the attenuation as the wave passes through the various materials. In the case of the sample being only the polymer coating we have,

$$A(\omega) = e^{\alpha_R(\omega)d - \alpha_S(\omega)d} \cdot \frac{|T_S|}{|T_R|} \quad (12)$$

The attenuation in the sample, $\alpha_S(\omega)$, is then given by,

$$\alpha_S(\omega) = -\left(\frac{1}{d}\right) \cdot \ln \left(\frac{A(\omega)|T_R|}{|T_S|} \right) + \alpha_R(\omega) \quad (13)$$

d is the thickness of the sample. $\alpha_R(\omega)$ is the attenuation in the coupling medium. If the coupling medium used is water the attenuation is comparably negligible and consequently the reference attenuation term $\alpha_R(\omega)$ can be omitted. The sample phase velocity, $V_S(\omega)$, is given by,

III. EXPERIMENTAL RESULTS

A. Sample Preparation

The samples were created using a polyester based powder obtained locally and coated in the laboratory to have a greater degree of control over the experiments. Three curing times were chosen – 1 minute, 3 minutes and 5 minutes, corresponding to a degree of curing of 66%, 96% and 100%. The curing schedule, shown in Figure 3, was determined by performing a thermal analysis of the powders using a Differential Scanning Calorimeter (DSC)(MODEL: Texas Instruments TA-DSC 2010). The data obtained from the DSC were used to determine the parameters in the Arrhenius equation (ASTM Standard E2041-03 [13]) in order to determine the curing factor. From the analysis a non-linear curing-time curve at 215°C was generated and it was found that the polymer was 100% cured in 5 minutes.

$$V_S(\omega) = \frac{1}{\frac{\Delta\phi(\omega)}{\omega d} + \frac{\Delta t}{d} + \frac{1}{V_R(\omega)} + \frac{\phi_m(\omega)}{\omega d}} \quad (14)$$

Δt is the time difference in the signal centroids of the sample and reference signals. $\phi_m(\omega)$ is the additional phase introduced by the multiple reflections within the coating layer. The calculation of the transmission coefficient due to multiple reflections within the polymeric film is dealt with in the next section.

1) *Multiple reflections model to determine transmission coefficients:* Multiple reflections within plate-like structures lead to the modification of the resultant transmission coefficient for waves traversing through the sample medium. The transmission coefficient can be modeled as the interference of the direct wave passing through the layered system and the sum of the waves arising due to multiple reflections within the layered structure [11] [12].

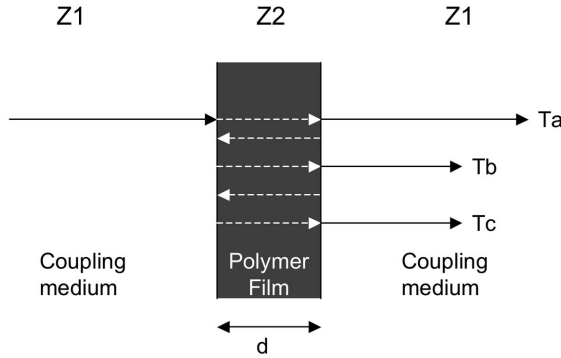


Fig. 2. Multiple reflections model

The total transmission coefficient is obtained by summing the individual coefficients ($T_S = T_a + T_b + T_c + \dots$). T_a is the direct through transmission signal without any internal reflection. T_b , T_c , etc. are the transmission coefficients due to internal reflections.

$$T_a = T_{12}T_{21} \quad (15)$$

$$T_b = T_{12}R_{21}R_{21}T_{21}e^{i2kd} \quad (16)$$

$$T_c = T_{12}R_{21}R_{21}R_{21}R_{21}T_{21}e^{i4kd} \quad (17)$$

where k is the frequency dependent wave number for the polymeric material. The subscripts 1 and 2 refer to the coupling medium and the polymeric film respectively.

Substituting the values, rewriting and using the formula for a geometric progression, we get the total transmission coefficient as,

$$T_S = \frac{(1 - R_{12}^2)}{1 - R_{12}^2 e^{i2kd}} \quad (18)$$

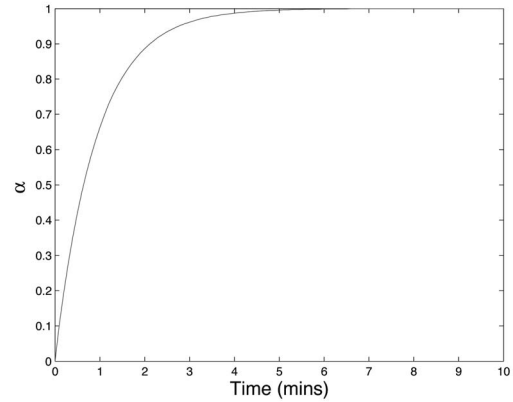


Fig. 3. Curing factor, α , v/s time for polyester at 215°C

The samples were created by cleaning the substrate (block of *Teflon*[®]), coating the substrate using an electrostatic spray gun and then heating them in an oven for the various cure times at 215°C . The polymer film was then peeled off the substrate after curing. All substrates were preheated in the oven to reach an equilibrium temperature. For the DMA analysis, a piece of cloth was coated and cured. The sample thicknesses were measured using a Coordinate Measuring Machine (CMM). Thicknesses were $314.4 \mu\text{m}$, $342.4 \mu\text{m}$ and $222.6 \mu\text{m}$ for the film. The variation in the thickness of the coatings was due to the entire coating process being a manual operator-driven one.

B. Transmission Mode Results - Model 1

The experiment was conducted in transmission mode as described earlier (Figure 1) using two 2 MHz Panametrics immersion transducers excited with a short pulse. The $\tan(\delta)$ plots for the cured polymeric films, calculated using Equations 1, 2 and 3, have been compiled together in Figure 4. It can be seen from the plot that the samples are indistinguishable from each other using this model and the standard deviation of the results is also very high.

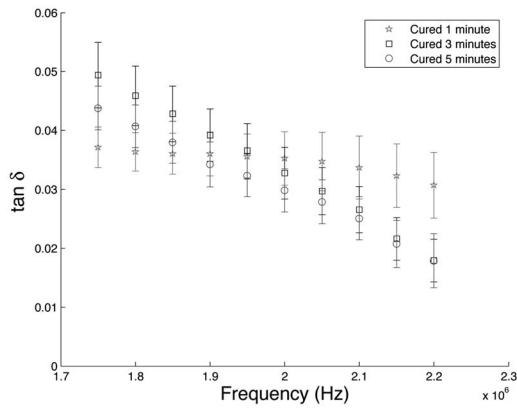


Fig. 4. Multispectral $\tan(\delta)$ in film (No multiple reflections, TOF)

C. Transmission Mode Results - Model 2

The average velocity inside a fully-cured bulk sample of the polymeric material was found to be 2273 m/s. The thickness of the films being in the 200 μm to 350 μm range means that the reflections from the two surfaces of the layer are not resolvable. The second model compensated for this shortcoming of the investigative system. The same experimental data used in Model 1 were used for analysis using the second model. In this case, the 5 minute cured film sample can be clearly differentiated from the 1 minute cured film based on the $\tan(\delta)$ value (Figure 5). The curing extent of the 3 minute cured film was closer to that of the 5 minute film than the 1 minute film and this is reflected in their $\tan(\delta)$ values. $\tan(\delta)$ decreased with increased curing time indicating that the polymer became more rigid upon curing due to increased cross-linking of the polymer chains. It has been noted in literature that at high frequencies the storage modulus, L' , increases, leading to the decrease in $\tan(\delta)$ as also seen in the plot [14]. Model 2 proved to be more robust than Model 1 and provided results with a significantly lower standard deviation.

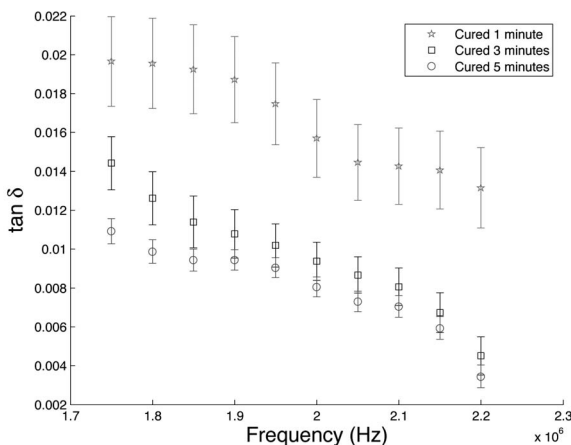


Fig. 5. Multispectral $\tan(\delta)$ in film (Multiple reflections)

IV. CONCLUSION

The extent of curing of a polymer-based powder coating determines its mechanical properties. These mechanical properties in turn affect any investigative ultrasonic signal employed. This relationship has been quantitatively demonstrated in this paper. The parameter, $\tan(\delta)$, was extracted and used in discriminating between polymeric films cured for different times. Two models were proposed to extract this parameter and the model that considered multiple reflections within the coating film provided better results. Additionally, for comparison with the ultrasonic analyses, DMA was performed on the polymer coated onto a cotton fiber cloth. The DMA results qualitatively agreed with the ultrasonic results, albeit, in a different frequency range. As in the ultrasonic case, the $\tan(\delta)$ for the cured sample was lower than that of the uncured samples. The effects of coatings on metallic substrates need to be evaluated under the multiple-reflections model presented in Section II-C.

REFERENCES

- [1] A. Cutolo, S. Calabro, G. Cantoni, V. D. Vita, M. Buonocore, L. Giordano, G. Nicolais, A. Breglio, and A. Cusano, "In situ measurement of the thermoset resin degree of curing using embedded fiber optic," in *SPIE Conf. on Fiber Opt. Sens. Tech. and Apps.*, vol. 3859, 1999, pp. 106–112.
- [2] L. Fei and Y. Chun, "Cure monitoring of epoxy resin and silica optical fiber and odr," in *SPIE Conf. on Fiber Opt. Sens. Tech. and Apps.*, vol. 3860, no. 382-389, 1999.
- [3] G. A. George, "New approaches to the characterization of the cure of epoxy resins for advanced composite materials," *Mats. For.*, vol. 9, no. 4, pp. 224–236, 1986.
- [4] R. Mafi, S. Mirabedini, M. Attar, and S. Moradian, "Cure characterization of epoxy and polyester clear powder coatings using differential scanning calorimetry (dsc) and dynamic mechanical thermal analysis (dmta)," *Progress in Org. Coatings*, vol. 54, no. 3, pp. 164 – 169, 2005. [Online]. Available: <http://dx.doi.org/10.1016/j.porgcoat.2005.06.006>
- [5] E. G. Belder, H. J. J. Rutten, and D. Y. Perera, "Cure characterization of powder coatings," *Progress in Org. Coatings*, vol. 42, pp. 142–149, 2001. [Online]. Available: <http://dx.doi.org/10.1016/j.porgcoat.2005.06.006>
- [6] J. B. Henderson, W. D. Emmerich, E. Kaisersberger, S. C. Hagen, and E. Wassmer, "Characterization of the curing and high-temperature decomposition behaviour of a thermosetting polymer," *Proc. ANTEC 89*, pp. 781–784, May 1989.
- [7] H. T. Hahn, "Application of ultrasonic technique to cure characterization of epoxies," *Proc. Symp. on Nondestructive Methods of Mats.*, pp. 315–326, April 1983.
- [8] F. Lionetto, F. Montagna, and A. Maffezzoli, "Ultrasonic dynamic mechanical analysis of polymers," *Appl. Rheol. (Switzerland)*, vol. 15, no. 5, pp. 326 – 35, 2005.
- [9] D. J. David and A. Misra, *Relating materials properties to structure*. Technomin Publishing Company, Inc, 1999.
- [10] F. Lionetto and A. Maffezzoli, "Relaxations during the postcure of unsaturated polyester networks by ultrasonic wave propagation, dynamic mechanical analysis, and dielectric analysis," *J. Poly. Sci. B, Poly. Phys. (USA)*, vol. 43, no. 5, pp. 596 – 602, 2005/03/.
- [11] L. M. Brekhovskikh, *Waves in Layered Media*. Academic Press, 1980.
- [12] A. Lavrentyev and S. Rokhlin, "Anomalous attenuation effect on reflectivity of an ultrasonic wave from a thin layer between dissimilar materials," *J. Acoust. Soc. Am. (USA)*, vol. 101, no. 6, pp. 3405 – 14, 1997/06/.
- [13] *ASTM E2041-03 Standard Method for Estimating Kinetic Parameters by Differential Scanning Calorimeter Using the Borchardt and Daniels Method*. West Conshohocken, PA: ASTM International, 2003, vol. 14.02.
- [14] L. H. Sperling, *Introduction to Physical Polymer Science*. John Wiley and Sons Ltd., 1992.