The Effect of Curing Temperature and Time on the Acoustic and Optical Properties of PVCP

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***Abstract*— Polyvinyl chloride plastisol (PVCP) has been increasingly used as a phantom material for photoacoustic and ultrasound imaging. As one of the most useful polymeric materials for industrial applications, its mechanical properties and behavior are well-known. Although the acoustic and optical properties of several formulations have previously been investigated, it is still unknown how these are affected by varying the fabrication method. Here, an improved and straightforward fabrication method is presented, and the effect of curing temperature and curing time on the PVCP acoustic and optical properties, as well as their stability over time, is investigated. The speed of sound and attenuation were determined over a frequency range from 2 to 15 MHz, while the optical attenuation spectra of samples were measured over a wavelength range from 500 to 2200 nm. The results indicate that the optimum properties are achieved at curing temperatures between 160 °C and 180 °C, while the required curing time decreases with increasing temperature. The properties of the fabricated phantoms were highly repeatable, meaning that the phantoms are not sensitive to the manufacturing conditions provided that the curing temperature and time are within the range of complete gelation–fusion (samples are optically clear) and below the limit of thermal degradation (indicated by the yellowish appearance of the sample). The samples' long-term stability was assessed over 16 weeks, and no significant change was observed in the measured acoustic and optical properties.**

***Index Terms*— Acoustic properties, optical properties, phantoms, photoacoustics, polyvinyl chloride plastisol (PVCP), ultrasound.**

I. Introduction

A. Overview

POLYVINYL chloride plastisol (PVCP) is a suspension of PVC particles in a liquid plasticizer. It is widely available for purchase as a two-part suspension of PVC resin (PVC and copolymers) and plasticizer that keeps the resin in a liquid state at room temperature and forms a plastisol [1]. Upon mechanical mixing and heating between 70 °C and 200 °C (depending on the formulation), the plastic particles dissolve and the mixture turns into a gel of high viscosity. During the process of gelation, the plasticizer penetrates into the PVC grains, swelling them and glueing them together, thus decreasing the relative amount of free plasticizer and forming a homogeneous material [2]. The rate of the gelation process is inversely proportional to the PVC molecular weight and particle size [3]. The gel strength increases with the curing temperature, and the time required for gel formation decreases with the increasing curing temperature. Just above the temperature of gelation, the granular morphology is no longer observable, and the material obtains optimum tensile properties in a process called fusion [4]. On cooling below 60 °C, a flexible, permanently plasticized solid material with elastomeric properties is formed [5].

As an industrial material, PVCP is well-characterized in terms of its mechanical properties and has well-established fabrication methods. Various PVC-based formulations are used with numerous additives that modify the properties and reduce the final cost of the produced articles [6]. However, these formulations are often not widely available for use in the fabrication of tissue-mimicking phantoms and can be expensive, especially if purchased for small production batches. Commercial premixed PVC-plasticizer suspensions can be purchased at low cost as a phthalate-free plastisol base material commonly used for making fishing lures. As this application does not pose any strict requirements on the final product, such as homogeneity and repeatability, several preparation methods for PVCP tissue-mimicking phantoms have been proposed utilizing standard laboratory equipment [7]–[11]. However, these studies have yielded different properties and considerations regarding the suitability of PVCP for applications in photoacoustic and ultrasound imaging. In this article, the properties and the preparation methods for PVCP phantoms are reviewed. A straightforward fabrication method is then introduced, and the effect of fabrication temperature and curing time on the acoustic and optical properties of the material is investigated and their stability over time is presented.

B. Industrial PVCP—Mechanical Properties

The effect of curing temperature and time on the PVCP's mechanical properties (but not acoustic) has already been thoroughly investigated within the scope of its industrial application [12]. Curing conditions commonly used in industry are temperatures ranging from 160 °C to 220 °C and curing times between 6 and 16 min. The optimum properties are

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obtained at 200 °C and 220 °C for curing times of 14 and 10 min, respectively [12]. The tensile strength increases with curing temperature and time, while the elongation at break point is highly sensitive to thermal degradation [13] and is related to the plasticizer structure and molecular weight, which is, in turn, directly linked to chain mobility (high molecular weight results in lower mobility and thus low elongation at break values). The effect of curing temperature and time can also be observed morphologically through microscopic characterization, as well as by studying the color and opacity of the cured samples, which become transparent and acquire a coloration representative of the natural color of the plasticizer used when fully cured [12]. A direct relationship between plasticizer migration and curing temperature and time is known: for lower degrees of curing, the plasticizer is not fully absorbed by the PVC particles and is, thus, free to migrate through the microstructure. The minimum values of migration are obtained at the same curing conditions as the optimum mechanical properties of the samples.

C. Review of Phantom Fabrication Methods

PVCP was first used as a tissue-mimicking material for ultrasound elastography in 2003 [14]. Although no description was given on how the phantoms were prepared, the work provided valuable information on the speed of sound and acoustic attenuation of the material, indicating its tissuelike properties and utility.

The first reported process for the fabrication of PVCP as a phantom for photoacoustic imaging consisted of heating a commercially available plastisol formulation (manufacturer not reported) [7]. The heating was done under partial vacuum in order to eliminate air bubbles. The liquid PVCP was then allowed to cool, reheated, and poured into a mold of the desired shape containing various targets. The use of titanium dioxide (TiO_2) to introduce optical scattering and commercial plastic colors in order to improve absorption was suggested.

The acoustic and optical properties of PVCP were first measured in [8]. The material was also characterized as a potentially suitable tissue-mimicking phantom for use in biomedical photoacoustics, as it is nontoxic, insoluble in water, and can be reused without degradation. The phantoms were prepared by heating a mixture of liquid PVCP and black plastic color (BPC; CI Pigment Black 7) to approximately 200 °C and stirred continuously with a magnetic stirrer. As it is heated, the opaque PVCP-BPC mixture becomes more viscous and translucent, which is when TiO_2 powder was added. The total heating time reported for 300 mL of mixture was 130 min. Upon cooling, the PVCP mixture solidifies and can easily be removed from the glass containers and cut into the desired shape. The properties are summarized in Table I. The reheating of PVCP was reported to alter its optical properties. The speed of sound was insensitive to the addition of colorants during phantom fabrication, but did introduce scattering and increase optical absorption. The provider of the materials was M-F Manufacturing Co., Fort Worth, TX, USA, which is commonly used in all studies reviewed to date, unless stated otherwise. This study reports that the phantoms should be stored away from other plastic materials, as PVCP can react with and dissolve other plastics when in prolonged contact through mutual diffusion. A multilayered PVCP skin phantom [15] has been made using this preparation procedure [8].

The characterization of PVCP mixtures ranging from super-soft to super-rigid enabled their use for the fabrication of a realistic prostate phantom [9]. Phantoms of varying degrees of softness were made by adding 25%–90% softener agent (a plasticizer additive that reduces hardness and increases flexibility), yielding the speed of sound values from 1580 to 1360 $m \cdot s^{-1}$, respectively, thus concluding that the speed of sound of PVCP can be tuned by the addition of the hardener/softener agent. However, it should be noted that the acoustic attenuation was not measured. The mixtures were made using a hot plate set to 450 °C (no information was given on the temperature reached within the PVCP suspension), heated for 20–30 min, and then placed into a vacuum chamber for 1–2 min prior to pouring into an aluminum mold. The mold was preheated to prevent the PVCP from curing too quickly around the walls, which was known to trap the escaping air bubbles. The fabricated PVCP phantoms were left to cool down and were stored in the glass containers [15], at −21 °C.

In 2013, two new fabrication processes were developed. The first one consisted of degassing liquid PVCP suspension at room temperature and then pouring it into the mold and heating in an oven at either 130 °C or 170 °C for plastic and super soft plastic, respectively, for 2 h [10]. The phantom properties were tuned by adding PVC and/or graphite powder. The authors reported that the curing temperature changed all material properties except the speed of sound, but this was not further investigated. The acoustic properties of two formulations can be found in Table I. The phantoms were also characterized thermally, yielding a specific heat capacity between 1.16 and 2.65 $J \cdot kg^{-1} \cdot K^{-1}$ and a thermal conductivity κ from 0.0603 to 0.1243 $J \cdot s^{-1} \cdot K^{-1} \cdot m^{-1}$. The speed of sound was shown to decrease linearly by 20% in the temperature range from 20 °C to 50 °C. Although making the fabrication process easy, this method had several drawbacks, such as bubble formation during heating and graphite particle settling. The properties of PVCP with 2% graphite powder in the temperature range from 20 °C to 45 °C were later measured [16], and two phantoms were made: soft ($\rho = 953 \pm 24$ $kg \cdot m^{-3}$) and hard ($\rho = 972 \pm 24$ $kg \cdot m^{-3}$) with a specific heat capacity of 2.65 ± 0.51 $J \cdot kg^{-1} \cdot K^{-1}$ and a thermal conductivity of 0.091 ± 0.013 $J \cdot s^{-1} \cdot K^{-1} \cdot m^{-1}$. The speed of sound decreased from 1501.5 ± 0.7 $m \cdot s^{-1}$ at 22 °C to 1331.8 ± 0.3 $m \cdot s^{-1}$ at 45 °C, while the acoustic attenuation coefficient changed from 0.46 ± 0.03 to 0.94 ± 0.09 $dB \cdot cm^{-1}$ at the frequency of 1 MHz. The fabrication method still had issues with graphite settling.

The second PVCP fabrication protocol was developed for tuning its optical properties to values relevant for the studies of biological tissue in the near-infrared [11]. The aim of this work was to obtain a standard physical phantom for routine quality control and performance evaluation of photoacoustic imaging instruments. The protocol, called S1, is as follows: upon adding the optical absorbers (BPC) and

scatterers (TiO_2) to liquid PVCP suspension at room temperature, the suspension is sonicated at 40 °C for 10 min; then, it is poured into a flask along with a magnetic stirrer bar, placed in an oil bath preheated to 200 °C, and connected to a vacuum line that is gradually opened until small bubbles are observed in the mixture. During the procedure, the vacuum level should be adjusted to avoid excessive bubbling. After approximately 6 min, the material should reach 130 °C and become viscous; therefore, the stirring speed should be reduced. After two additional minutes, the material should begin to move freely; therefore, stirring should be restored back to its original speed. After 10 min, the stirrer bar should be moved freely, and the material should have reached 180 °C when it is ready for pouring into a mold. Several phantoms were made in the study with varying concentrations of BPC (0% v/v–0.016% v/v for background and 0.064% v/v–0.256% v/v for targets, yielding optical absorption coefficients of 0–0.1 cm^{-1} and 0.26–1.07 cm^{-1}, respectively) and TiO_2 in concentrations of 0–2.5 mg · mL^{-1} for the targets, yielding a reduced optical scattering coefficient of 0.9–6.8 cm^{-1}. The addition of TiO_2 was reported to have no effect on the acoustic attenuation coefficient values. The phantoms were stored in the airtight containers and showed no sign of physical degradation, or bacterial growth during the course of six months. This would make PVCP a suitable candidate for a standard photoacoustic phantom, and however, the material did not satisfy other requirements, such as the ease of preparation and mimicking the ultrasound properties of tissues.

In another study, PVCP's suitability as a potential phantom for photoacoustic vascular imaging was considered due to its stability and longevity [17]. The effect of PVC concentration and the addition of biologically relevant absorbers and scatterers on its acoustic and optical properties were investigated. The phantoms were made following protocol S1 [11]. Hardener agent was added (0% v/v–50% v/v) in order to increase PVC concentration, while 2–0.125 mg · mL^{-1} of TiO_2 and 1% v/v–0.125% v/v BPC were added to tune the reduced scattering coefficient μ_s' and the optical absorption coefficient μ_a respectively. The optical properties were measured in the wavelength range from 500 to 1100 nm, and the ability of PVCP to be tuned to tissue-relevant properties was demonstrated. μ_s' of the PVCP suspension was reported to be less than 0.05 cm^{-1}, making it a good base material, while μ_a exhibited an absorption peaks characteristic of the primary plasticizer bis(2-ethylhexyl) adipate (DEHA), which was reduced with the addition of BPC. The acoustic attenuation coefficient increased from approximately 3 to 5 dB · cm^{-1} at the frequency of 5 MHz with an increasing hardener concentration from 0% to 50%, and however, the speed of sound of PVCP was effectively unalterable. The addition of TiO_2 had no effect on the acoustic properties. The requirement for adequate tunability of the acoustic properties established the ground for further work in which a dual-plasticizer approach for fabricating PVCP phantoms with finely tunable acoustic and optical properties was developed [18]. The plasticizer choice had a great impact on the speed of sound and the acoustic attenuation of PVCP, and four of the most suitable formulations were used for fabrication, with a PVC resin content of 10%–20%. A positive correlation between the speed of sound and the plasticizer density was observed, but none with molecular weight. Glass microspheres were used to tune the acoustic attenuation and ultrasound speckle pattern. The best storage conditions for PVCP phantoms were also thoroughly investigated: encased in a solid chamber and sealed to prevent environmental exposure, and then stored at a low temperature of 2 °C to reduce plasticizer exudation.

The suitability of PVCP as a quantitative photoacoustic imaging (qPAI) phantom has also been assessed [19]. The suspension used was Lure Flex Firm provided by Lure Factors, Doncaster, U.K., a British equivalent to the previously mentioned M-F Manufacturing Co. PVCP was characterized over the wavelength range from 400 to 2000 nm, and the intrinsic absorption peaks were observed at 910, 1190, 1400, and 1720 nm, possibly due to vibrational energy transitions in PVC [20]. The use of various pigments and sulfates as chromophores for multiwavelength photoacoustic imaging phantoms has been thoroughly investigated [21]. The nonlinearity of the optical absorption coefficient was observed at high peak powers typically used in photoacoustic imaging. The Grüneisen parameter was measured to be $\Gamma = 1.01 \pm 0.05$.

In another study, the mechanical and acoustic properties of PVCP were also altered by adding softener, mineral oil, and glass microspheres in order to develop a regression model for the design of formulations with the targeted properties [22]. The optical clarity of the samples was represented by light transmittance at two wavelengths (645 and 532 nm) and increased with the addition of softener, while it decreased with the addition of microspheres and oil, the latter being due to the impediment of cross-linking. The elastic modulus, Shore hardness, and viscoelastic relaxation time constant exhibited a wide range of tunability, whereas the speed of sound and the acoustic attenuation had a large discrepancy with the values of real soft tissues. The regression model was thus applied to the mechanical properties only and validated experimentally with an error <5% within the range of previously measured parameters.

A comprehensive list of the acoustic and optical properties of PVCP phantoms fabricated and characterized in the aforementioned studies and the values obtained in this study are given in Table I.

D. Article Outline

Using the existing methods, it is challenging to produce repeatable phantoms with consistent properties, and thus, PVCP is not the favored choice for a tissue-mimicking material, despite its longevity, stability, and robustness. In this article, an optimized protocol for the fabrication of PVCP phantoms using a commercially available PVC-plasticizer suspension is presented. The effect of curing temperature and time on the acoustic and optical properties of PVCP is then investigated. The fabrication method used is described in Section II, along with the methods employed to characterize the samples. The acoustic and optical properties of the fabricated PVCP

TABLE I
SPEED OF SOUND c, DENSITY ρ, ACOUSTIC ATTENUATION COEFFICIENT α, AND OPTICAL ABSORPTION COEFFICIENT μ_a FOR VARIOUS PVCP FORMULATIONS FROM THE LITERATURE

Formulation	Ref.	c (10^3 m·s^{-1})	ρ (10^3 kg·m^{-3})	α (dB·cm^{-1})	μ_a (cm^{-1})
Triple hardness PVCP	[14]	1.395	-	1.05 @ 4.5 MHz	-
PVCP (M-F Manufacturing)	[8]	1.40 @ 1 MHz	0.98 - 1.01	0.57 @ 1 MHz	0 - 3.7 @ 1064 nm
PVCP with 25% softener	[9]	1.58	0.98	-	-
PVCP with 50% softener	[9]	1.44	0.91	-	-
PVCP with 75% softener	[9]	1.42	0.93	-	-
PVCP with 90% softener	[9]	1.36	0.74	-	-
PVCP cured at 130 °C	[10]	1.43	0.97	0.66 @ 1 MHz	-
PVCP cured at 170 °C	[10]	1.43	0.97	0.92 @ 1 MHz	-
PVCP Protocol S1	[11]	-	-	-	0 - 1.07 @ 600 - 1000 nm
Dual-plasticizer formulation	[18]	1.35 - 1.54	-	1 - 30 @ 4.0 MHz	0.07 - 10 @ 500 - 1100 nm
PVCP with 5-20% softener	[19]	1.40 @ 5 MHz	1.01	6.45 - 8.12 @ 5 MHz	0 - 3 @ 400 - 2000 nm
PVCP at investigated curing conditions	Current study	1.40 @ 5 MHz	0.95 - 1.07	7.26 - 8.24 @ 5 MHz	0.45 - 16 @ 500 - 2200 nm

samples are presented in Section III, and their stability over time is reported.

II. MATERIALS AND METHODS

A. Phantom Fabrication

Considering the reviewed fabrication methods, the PVCP samples were initially made following protocol S1 [11] and using Lure Flex Firm provided by Lure Factors. The following observations were made. First, the movement of the magnetic stirrer bar was soon disabled, as the surrounding suspension solidifies more quickly. Second, it is considered that the temperature/time recommendations from the protocol [11] may have been inaccurately reported. The suspension temperature was monitored using a suspended thermometer and exhibited a slow temperature rise, reaching 130 °C after 30 min, as opposed to the reported 180 °C, which could not be achieved within a reasonable amount of time (a maximum of 6 h was tested). It was noticed that if the thermometer was touching the bottom of the flask, a higher temperature occurred within the amount of time reported, but this meant that the actual readings were taken of the Duran glass and not the suspension. The saturation temperature of the suspension using the oil bath setup was 150 °C. This temperature depended very little on the concentration of softener used. Nonetheless, the protocol proved to give optically inconsistent phantoms (the acoustic properties were not investigated at this point). Preventing bubble formation or premature solidifying during pouring into the mold was also a significant challenge. These difficulties encountered while following the fabrication protocol S1 may be related to the composition of the PVC-plasticizer suspension used, as the effect of the particle size and distribution on PVCP viscoelasticity is a well-reported phenomenon [23].

The fabrication method suggested by the provider of the PVCP suspension utilizes a microwave oven. However, following this method caused the PVCP to carbonize even at the lowest microwave power level. It was thus concluded that making PVCP should involve a gradual heating process.

Finally, a method was adopted following the main guidelines from [10] with additional steps to prevent bubble formation. The fabrication process was as follows.

1) The PVCP suspension was mechanically mixed (by shaking for approximately 5 min) with any softener/hardener agent or pigment dispersion additives.
2) The mixture was then sonicated using an ultrasonic bath (T9, L&R Manufacturing Co., Kearny, NJ, USA) with the heater set to 40 °C for 10 min in order to improve component mixing.
3) The mixture was poured into the Anumbra resistance glass Petri dishes (Ø50 mm) used as molds and degassed for 10 min in a vacuum chamber at 0.4 mbar to eliminate the bubbles created during mixing. The sample thicknesses were around 5 and 10 mm.
4) The dishes were placed in an oven (ED 23, Binder, Tuttlingen, Germany) preheated to 40 °C, and the temperature gradually elevated to the desired set temperature (average heat up time of the oven from 40 °C to the set temperature was 20 min) after which the mixtures were left to cure over the chosen amount of time.
5) Upon curing, the disk-shaped samples were left to cool at room temperature before demolding and stored in the glass containers at 2 °C.

In order to investigate the effect of curing temperature and time on the PVCP properties, first, the minimum and maximum curing temperatures were established. The maximum time of 2 h was chosen in order to keep the fabrication process convenient. The curing timing was started at the point when the oven reached the set temperature. Gradual heating of the PVCP suspension is desirable, as placing the samples at high temperatures causes layered solidification and results in the nonuniform samples. The minimum temperature required for the solidification of PVCP was 120 °C, while the samples started to burn at 220 °C. Thus, 14 samples were made at temperatures ranging from 120 °C to 200 °C in steps of 20 °C and curing times of 15, 30, 60, and 120 min. For temperatures below 180 °C, the minimum time required for solidification was 30 min, while the samples at 200 °C were only cured for 15 min, as longer times were not achievable because the fabrication conditions constituted a fire hazard due to oven limitations and laboratory safety conditions.

Several phantoms were also made using pigment dispersions as additives. Various colors were used in different concentrations (0.01%, 0.1%, and 1%) obtained by the serial dilution of pigment with PVCP suspension. All pigments were supplied

by the same manufacturer as for the PVCP suspension. The colored samples were cured at 160 °C for 120 min. Cylindrical phantoms with volumes up to ≈200 mL have also been made using the same fabrication protocol, although there should be no inherent limit on the size of the phantom.

B. Optical Characterization

The PVCP optical properties were characterized using a dual-beam spectrophotometer (Lambda 750, Perkin Elmer, Waltham, MA, USA). The PVCP disks were placed on sample mounts, and the collimated-transmission absorbance measurements were made at four different locations on each sample (two per side) over the wavelength range from 500 to 2200 nm. The total optical attenuation arises from the combined effects of absorption and scattering. In the absence of scattering, the optical absorption coefficient could be calculated from these measurements using the sample thickness values taken from the acoustic measurements described in the following. A qualitative assessment of the optical transparency of PVCP (the degree of scattering) was also made by placing the samples over a mesh pattern and observing their clarity.

C. Acoustic Characterization

The density of the phantoms was determined using the buoyancy method in accordance with BS EN 1183-1:2019. The precision balance used for these measurements was ML203T/00 (Mettler Toledo, Columbus, OH, USA). The density was further used to calculate the acoustic impedance by multiplying the density and the speed of sound of the phantom.

The acoustic properties of the samples were characterized using a broadband through-transmission setup [24] available in the NPL Materials Measurement Facility (National Physical Laboratory, Teddington, U.K.). The speed of sound and the transmission loss were measured using a substitution technique with reference to water [25]. A broadband transducer with a center frequency of 10 MHz and an active diameter of 10 mm (Force Technology, Brøndby, Denmark) was used as the emitter, and a 30-mm active element diameter broadband bilaminar hydrophone manufactured by Marconi, Essex, U.K., was used as a receiver. Thickness was also simultaneously evaluated using the reflected signals from the front and rear surfaces of the samples. Attenuation was obtained from the transmission loss data using the samples of two different thicknesses [26] of around 5 and 10 mm. The temperature during the measurements was 20 °C ± 0.5 °C, measured using a calibrated spirit-in-glass thermometer (IP 39C, G. H. Zeal, London, U.K.).

The measurement uncertainty was evaluated following the guide to the expression of uncertainty and confidence in measurement [27]. The expanded measurement uncertainty quoted in Section III was determined using both Type A (random) and Type B (systematic) uncertainty evaluations and is given as the standard uncertainty multiplied by a coverage factor, $k = 2$, providing a coverage probability of approximately 95% ($p = 0.95$), according to the method recommended in [27] and [28]. Systematic uncertainties arise from several sources, which were independently evaluated at different frequencies. Some of these include the temperature variations, diffraction errors, oscilloscope resolution, and the linearity of the amplifier and the receiver [26], [28].

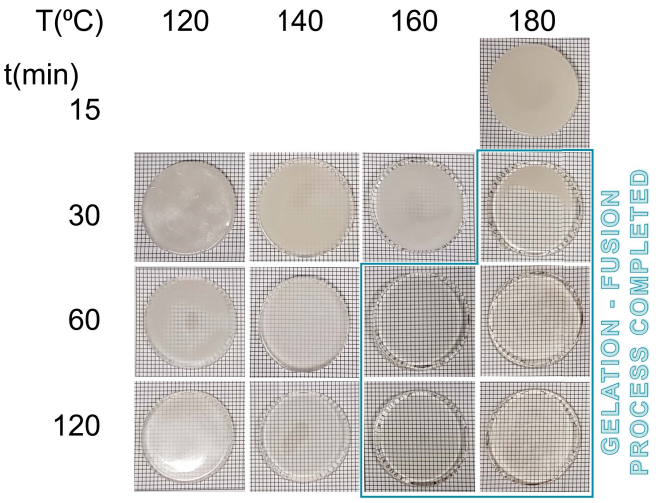

Fig. 1. Color and transparency of PVCP assessed by placing the samples over a mesh pattern.

D. Stability Characterization

In order to evaluate the phantoms' stability over time, the percent mass and the density loss, as well as the acoustic and optical properties, were measured 16 weeks after fabrication. Initial characterization measurements were done within 72 h of fabrication. Density was included as a parameter, as this made the intersample comparison more clear.

III. Results and Discussion

A. Optical Properties

Fig. 1 shows a comparison of the color and opacity of the PVCP samples fabricated with different curing temperatures and times. The partially cured samples (incomplete gelation–fusion) appear white and are opaque and inhomogeneous, while the fully cured samples (complete gelation–fusion) are optically clear. This is a good method of testing whether the fabrication process was successfully completed. It is concluded that the optimal fabrication temperature lies above 160 °C and the required curing time decreases with an increasing temperature. As the fabrication method does not include mixing during heating, a shorter curing time is desirable in order to reduce the settling of particles when scatterers are added. Consequently, the recommended curing conditions are a temperature of 180 °C and a curing time of 30 min. The samples heated to 200 °C with a curing time of 15 min exhibited a yellow appearance, thus indicating thermal degradation [13]. In industry, the coloration of PVC formulations is commonly used as an indication of the grade of the thermal degradation of the samples [29]. It is a consequence of the polymer dehydrochlorination and leads to the changes in cross-linking, poor mechanical properties, and potential stability issues [30]. Thus, these samples were exempted from further investigation.

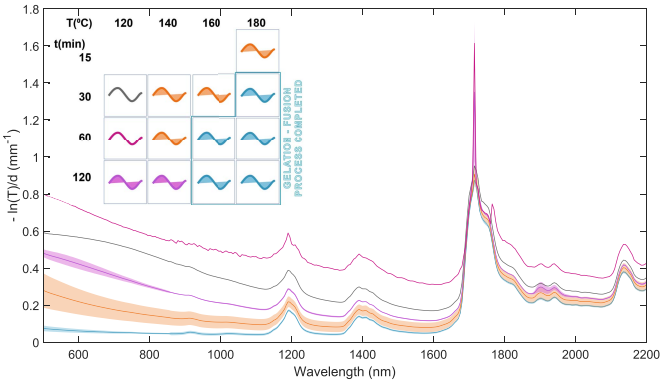

Fig. 2. Optical attenuation spectra of PVCP samples made with different curing temperatures and times. The spectra are plotted as the natural log of the proportion of the energy transmitted T normalized by the sample thickness d over the wavelength range from 500 to 2200 nm. In the absence of optical scattering, such as can be seen in the samples with complete gelation–fusion, this will equal the optical absorption coefficient.

The grade of the completeness of the gelation–fusion process is also indicated by the characteristic optical attenuation spectra of PVCP samples, arising from the combined effects of absorption and scattering. In order to simplify the intersample comparison, these are presented as the natural log of the proportion of the energy transmitted T normalized by the sample thickness d. In the absence of optical scattering, this will equal the optical absorption coefficient. Fig. 2 shows the spectra that are grouped by their similarity. The intrinsic absorption peaks of PVCP can be observed at 910, 1190, 1400, 1720, 1940, and 2140 nm (the last two peaks are not commonly reported, possibly due to the available wavelength measurement range). For fully cured samples, the spectra are dominated by the optical absorption and do not depend on the curing temperature or time. For partially cured samples, it tends to be higher, which is due to a reduced transmittance caused by the clustering of PVC particles and thus increased effect of scattering, especially prominent at shorter wavelengths. The total optical attenuation spectra of partially cured samples approach the values for fully cured samples with an increasing curing temperature and time, as the optical scattering coefficient decreases to zero when PVCP has reached complete gelation–fusion.

With the addition of pigment dispersions, the intrinsic absorption peaks are less prominent as the spectrum is dominated by the color but are, nevertheless, still present. Fig. 3 shows the optical absorption spectra of PVCP samples with 0.1% v/v BPC, 0.1% v/v green pigment, and a representative spectrum of fully cured PVCP with no additives, all cured at 160 °C for 120 min. The values of the total optical absorption coefficient increase as a linear function of pigment concentration [19]. For BPC, the spectra are qualitatively identical, while for other pigments, the spectrum contains additional absorption peaks characteristic of the added color, thus indicating that a suitable pigment dispersion can be chosen for the wavelength of interest. It can also be observed that the addition of BPC increases the μ_t values more than the same concentration of the green pigment dispersion used as an exemplary color spectrum.

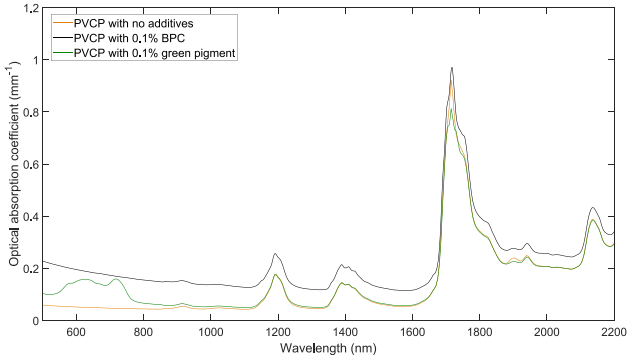

Fig. 3. Optical absorption spectra of PVCP samples with pigment dispersions in comparison with the PVCP formulation with no additives.

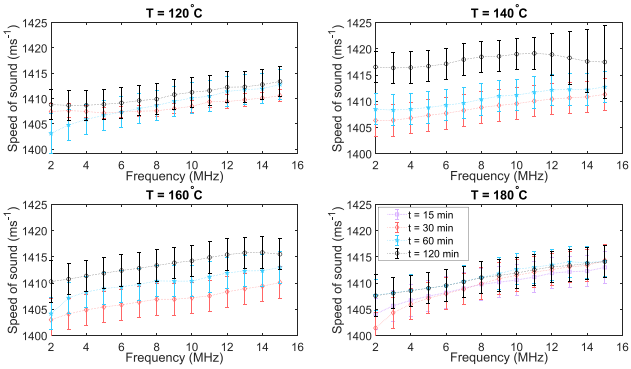

Fig. 4. Effect of curing temperature and time on PVCP speed of sound at 20 °C over the frequency range from 2 to 15 MHz. Error bars represent the expanded uncertainty ($p = 0.95$), which equals 3 m · s^{-1} for all the measurements.

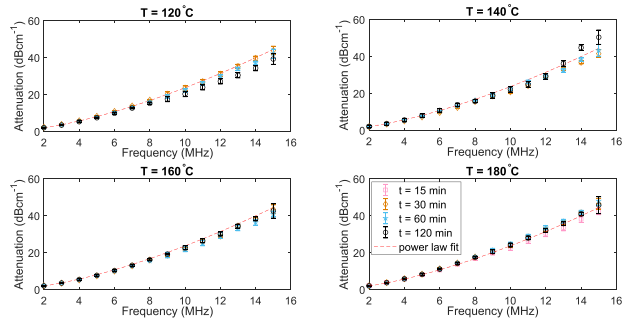

Fig. 5. Effect of curing temperature and time on PVCP acoustic attenuation coefficient at 20 °C. Error bars represent the expanded uncertainty ($p = 0.95$) over the frequency range from 2 to 15 MHz. The power-law fit was obtained using the mean of the data for fully cured samples.

B. Acoustic Properties

The effect of curing temperature and time on the acoustic properties of the PVCP samples is shown in Figs. 4 and 5. The uncertainty in the speed of sound is 3 m · s^{-1} in the whole frequency range (mostly due to temperature variations). The speed of sound (see Fig. 4) increased with curing time for a given curing temperature, but not significantly, whereas the acoustic attenuation (see Fig. 5) remained unchanged. The values for the speed of sound are at the lower end of the range for human fatty tissue [31]. The measured frequency-dependent

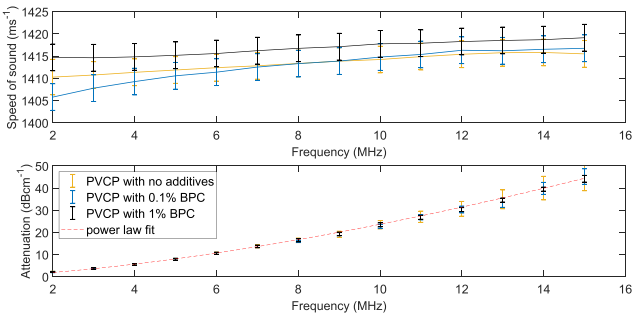

Fig. 6. Comparison of the speed of sound and acoustic attenuation of PVCP with no additives and samples with 0.1% and 1% BPC at 20.0 °C. Error bars represent the expanded uncertainty ($p = 0.95$) over the frequency range from 2 to 15 MHz. The power-law fit was obtained using the mean of the data for fully cured samples.

acoustic attenuation coefficient was fit with a power law of the form $\alpha = \alpha_0\ f^y$ over the frequency range from 2 to 15 MHz, where $\alpha_0 = 0.6643$ dB/cm/MHz^y and $y = 1.552$ ($R^2 = 0.95$). The power-law fit was obtained using the mean of the data for fully cured samples. These are similar to the values for normal human breast tissue [31]. Expanded uncertainty was evaluated as in [26] to be 12% in the range 2–3 MHz, 10% in the range 4–7 MHz, 7% in the range 8–12 MHz, and 5% in the range 12–15 MHz. The density of all samples was 1000 ± 0.03 kg $\cdot$ m^{-3}, while the acoustic impedance values for fully cured samples ranged from 1.39 to 1.51 $\times$ 10^6 kg/(m^2 $\cdot$ s) at a frequency of 5 MHz, which is similar to the values for fatty tissue and water at 20 °C [31].

The addition of pigment dispersions of up to 1% had a very small effect on the speed of sound (up to 5-m $\cdot$ s^{-1} increase) and no effect on the acoustic attenuation of samples. Fig. 6 shows a comparison of the acoustic properties of the PVCP samples with no additives, 0.1% BPC and 1% BPC, all cured at 160 °C for 120 min.

C. Stability

The samples were stored in the glass containers and kept at 2 °C. The statistical analysis was performed as described in [26] and [32], and the normalized error was calculated over the measurement frequency range. This analysis was used to establish the significance of the observed difference between the two sets of measurement data. For the values of normalized error lower than and equal to 1, the compared samples were considered statistically equivalent with respect to the parameter under consideration. The observed mass and the density losses over 16 weeks were less than 2% for all samples, and no significant change was observed in the measured acoustic properties. The speed of sound changed by $\pm$ 5 m $\cdot$ s^{-1}, and however, this was evaluated to be statistically insignificant. No change was measured for the acoustic absorption. Optical attenuation showed an increase of less than 2% for all samples.

IV. Conclusion

The effect of curing temperature and time on the PVCP properties is presented. The samples were fabricated using an optimized process in which the suspension is poured into a mold prior to curing at the high temperatures required for the completion of the gelation–fusion process in order to avoid premature solidification and bubble formation. A simple visual method of determining the optimum temperature and the time of curing was utilized by studying the color and opacity of the cured samples that become transparent when fully cured. The density, the speed of sound, the acoustic attenuation, and the optical attenuation of the PVCP samples were measured. The stability of these properties was also assessed 16 weeks after fabrication. The results show that the acoustic properties of PVCP are robust to changes in the fabrication method, and its optical properties are stable, provided that the material has reached complete gelation–fusion. The values of the speed of sound, the acoustic attenuation, and the acoustic impedance correspond to the typical values for human fatty tissue, while the optical properties can be tuned with the addition of pigment dispersions and/or scatterers. The new fabrication method is scalable to larger volumes essential for full-size imaging phantoms used for evaluating deep-imaging photoacoustic devices.

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