Program Digest, 2019 IEEE International Ultrasonics Symposium (IUS)
Glasgow, Scotland, October 6-9, 2019

Novel Nanocomposite Materials for Improving Passive Layers in Air-coupled Ultrasonic Transducer Applications

Lorena Amoroso
International Institute for Nanocomposites Manufacturing, University of Warwick,
Coventry, UK
L.Amoroso.1@warwick.ac.uk

Sivaram Nishal Ramadas
Honeywell
Redditch, UK
nishal.ramadas@honeywell.com

Christoph Klieber
Honeywell
Mainz-Kastel, Germany
christoph.klieber@honeywell.com

Tomas E. Gomez Alvarez-Arenas
Instituto de Acustica CSIC
Madrid, Spain
tomasgaa@gmail.com

Tony McNally
International Institute for Nanocomposites Manufacturing, University of Warwick,
Coventry, UK
T.McNally@warwick.ac.uk

Abstract*—Recent research has focused on developing air-coupled transducers for use in industrial flow measurement applications. Optimal performance of ultrasonic transducers is only achieved with maximum energy transfer. Unfortunately, the significant acoustic impedance mismatch between the active layer and the load medium (i.e. air) in sensors reduces considerably the effective ultrasonic energy transmission and reception, with most of the energy reflected at the interface. Improved matching layers with an appropriate acoustic impedance and attenuation coefficient as low as possible can significantly improve the power efficiency and sensitivity of devices, decreasing energy loss by scattering. The aim of this research is to evaluate novel acoustic materials for use in a new ultrasonic transducer assembly process involving cost effective advanced manufacturing methods. More efficient and consistent signal shapes could be achieved by substituting current matching layers (e.g. syntactic foams) with new materials. Nanocomposite foams can be obtained via cost effective extrusion/moulding processes where microbubbles are formed inside the polymer when heated above a certain temperature. The reduction in density affects acoustic impedence, ultimately creating light passive layers for ultrasonic applications manufacturable in high volumes.

***Keywords*— nanocomposites, chemical foaming agent, extrusion, foaming, injection moulding, air-coupled transducers, acoustic impedance, attenuation at resonance frequency**

I. Introduction

Ultrasonic transducers are key components for distance, flow and level measurement as well as in power, biomedical and other applications of ultrasound [1]. Research has focused on developing non-contact air-coupled transducers, efficient and reliable for use in practical industrial applications for flow detection [2]. Currently, air-coupled ultrasonic transducers are utilized for many purposes in industry, including in measurement applications [3].

Passive materials have an important role in the performance of transducers, in addition to the active material, for enhancing energy transfer and preventing unwanted resonances in the transducer [4]. A suitable matching layer inserted in front of the transducer can lead to increased bandwidth and enable effective energy transfer, meeting the expectations of most applications requiring a transducer with a broad bandwidth and low loss [5]. The matching layer is therefore a critical component for the performance of high sensitivity transducers [6]. More efficient and consistent signal shapes could be achieved by substituting the materials currently used (e.g. syntactic foams) while obtaining a wider operating frequency range for such sensors.
In material selection for transducer design, in addition to cost and several other material properties to take into consideration (e.g. elastic constants, machinability), acoustic impedance and attenuation are the most important material parameters for the passive materials [5].

The aim of this work is to produce novel passive materials for ultrasonic applications that are superior in performance as well as cost effective to manufacture.

The design of a new air-coupled ultrasonic transducer assembly process, based on polymer manufacturing methods for the passive layers, can lead to cost effective, sustainable and reliable manufacture of ultrasonic devices, expected in industrial applications such as fiscal gas flow measurement.
Most thermoplastic nanocomposite foams to date are synthesized via a two-step process [7], namely mixing and a moulding steps. The pores are formed during the moulding process [8]. The mostly common method used for large-scale production of foams is the direct utilization of foaming (or blowing) agents to form the gaseous phase during the foaming

process [9]. A chemical blowing agent (CBA) is a reactive species that liberates a blowing gas (e.g. CO_2, H_2O, NH_3) in the foaming process under thermal decomposition [10]. The release of the gas causes the expansion of the polymer and reduces the density, as the volume of voids formed replaces the original material. Consequently, reductions in density are proportional to the concentration of the chemical blowing agent.

In this preliminary study, raw materials in powder form (high density polyethylene, different loadings of multi-walled carbon nanotubes acting as reinforcing material and a chemical foaming agent) were dry blended and melt mixed using a 16mm co-rotating parallel twin-screw extruder followed by injection moulding into disk shaped test specimens (25mm diameter x 1.65mm thickness). Ultrasonic air-coupled measurements through transmission were performed using an experimental setup to determine both the velocity and attenuation coefficient of ultrasound in the foamed materials by frequency-domain analysis. Selection of suitable materials for matching layers to insert into the sensor constructs can be possible whether eligible acoustic impedance values are obtained.

I. EXPERIMENTAL SECTION

A. Materials and Samples Preparation

High-density polyethylene resin (HDPE), grade HMA 025, with a melting point of 135 °C, density of 0.964 g cm^{-3} and a melt flow index (MFI) of 8 g/10 min at 190 °C/2.16 kg was purchased from ExxonMobil in pellet form. Non-functionalized commercially available thin multi-walled carbon nanotubes (MWCNTs) produced by catalytic carbon vapor deposition (CCVD), with an average diameter of 9.5 nm and average length of 1.5 μm (grade NC7000, purity: > 90%) were purchased from Nanocyl S.A., Belgium and used as received. The density of the MWCNTs was reported as 1.75 g/cm^3 [11], with a surface area of between 250 and 300 m^2/g [12]. Hydrocerol Compound (*OXABRG20930*), with density of 1.7 g/cm^3, activation temperature of 160˚C and thermal gas yield of ca. 140 cm^3/g gas), was purchased from Clariant in powder form.

HDPE pellets were first ground to a fine powder (μm diameter particles), using a SPEX® SamplePrep Freezer Mill 6870 (Stanmore, UK) and dried in a vacuum oven prior to processing to improve dry mixing between the polymer matrix and the filler. Composites materials were prepared by dry blending the raw materials (HDPE, different loadings of MWCNTs and the CBA) in powder form. The reinforcing material (MWCNTs) was loaded into the HDPE matrix according to the following percentages: 0.01 wt% (~0.01 vol%), 0.1 wt% (~0.06 vol%), 0.3 wt% (~0.17 vol%), 0.5 wt% (~0.28 vol%), 1 wt% (~0.55 vol%), 3 wt% (~1.68 vol%), and 5 wt% (~2.82 vol%). Loadings of 1 wt% and 4 wt% of the chemical foaming agent were admixed to composites and to pure HDPE as a control. Melt mixing of the materials was realized in a 16mm co-rotating parallel twin-screw extruder (PRISM ThermoFischer Scientific), with a temperature profile along the barrel from 160 (at feeding zone) to 175 °C (die zone) and a screw speed of 80rpm. Screw speed, which controls the pressure, and profile temperature are the operating variables in the extruder.
The molten extruded strands of composites with foaming agent added exiting the extruder die in the form of filaments were immediately cooled in a water bath and pelletized through a laboratory pelletizer.
After being dried, these pellets were injection moulded using a piston injection moulding system Thermo-Scientific Haake™ MiniJet Proto to produce circular disks of 25 mm diameter and 1.65 mm thickness. Specimens were used for Scanning Electron Microscopy (SEM) imaging of foam microstructure and further acoustic measurements. During the injection process, machine parameters were adjusted, repeatedly, for optimization of the foaming conditions. Therefore, different working conditions were investigated. Final moulding settings were developed with mould holder temperatures between 60˚ C and 80˚ C, temperatures in the harvesting cylinder between 160˚C and 170˚C, injection pressures between 450 bar and 600 bar, time of applied pressures between 6 and 10 seconds, post injection pressures between 200 bar and 250 bar and time of post pressures between 5 and 10 seconds. Injection pressures between 200 bar and 250 bar and time of post pressures between 5 and 10 seconds.

B. Morphological and Acoustic Characterization

The porous microstructure of cross sections of foamed specimens were examined using a Zeiss sigma field emission SEM fitted with a Gemini column. For measurements using the InLens detector, a working distance of 2.5 mm was used and an acceleration voltage of 3 kV. Prior to imaging, the sample disks were cryo-fractured using a hammer, by placing them in a liquid nitrogen bath for about~ 5 hours. The fractured surface was mounted on an aluminium SEM stub and sputter coated (~ 10 nm) using an Au/Pt metal target (Cressington 108 auto) under a weak argon atmosphere.

Ultrasonic air-coupled measurements through transmission were performed using an experimental setup to determine both the velocity and attenuation coefficient of ultrasound in the foamed materials by frequency-domain analysis. The experimental setup is showed in Fig.1.

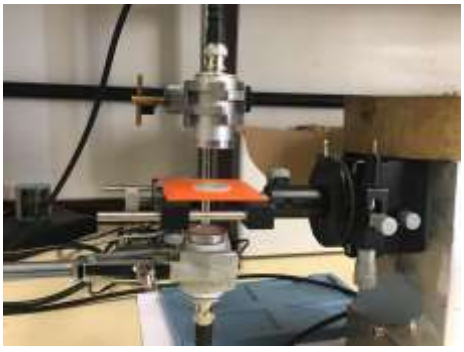

Fig. 1. Experimental setup employed for the ultrasonic air-coupled measurements (located in the “Instituto de Acustica CSIC”, Madrid, Spain).

A pair of specifically designed air-coupled piezoelectric transducers (center frequency of 673 KHz) was employed in the set-up for efficient transmission and/or reception from the air to the disk sample and vice versa. An airborne ultrasonic pulse was set to impinge normally on the sample surface and the through-transmitted signal is received and analyzed. The normal incidence ensured the maximum amplitude of the signal, while allowing for plane wave in order to neglect the diffraction effects of the sound beam. An optimal distance (ca. 2 cm) was fixed between transducers and sample for a clear signal and a good signal-to-noise ratio (SNR). The frequency domain investigated in the measurements [0.4MHz - 1.1MHz] enabled the observation of the resonance peak, as the air-coupled ultrasonic technique, described in detail in [13-15], relies on the first resonance peak of the sample plate. The analysis of the amplitude and phase of the ultrasonic transmission coefficient in the vicinity of the first thickness resonance allowed for the determination, simultaneously, of velocity and attenuation coefficient of the ultrasound in the material and thickness of the solid plate. Ultimately, a theoretical model (one-dimensional model) of the transmission of ultrasonic waves was applied for a best fitting of the experimental measurements with theoretical calculations, which required specific characteristics of the samples for the outcome of the measurement (i.e. isotropic and homogeneous materials with plane and parallel surfaces and uniform thickness).

II. Results and Discussion

Cryo-fractured surfaces of the specimens were observed via SEM scans under high magnification to determine the quality of the foams. Micrographs of the cross section surfaces of the foamed HDPE and foamed composites at different MWCNT contents, obtained under different foaming conditions, were analyzed. Comparisons between the materials upon additions of 1 wt% CBA and 4 wt% CBA were made.
Four examples of cell morphologies obtained are presented below in Fig. 2.

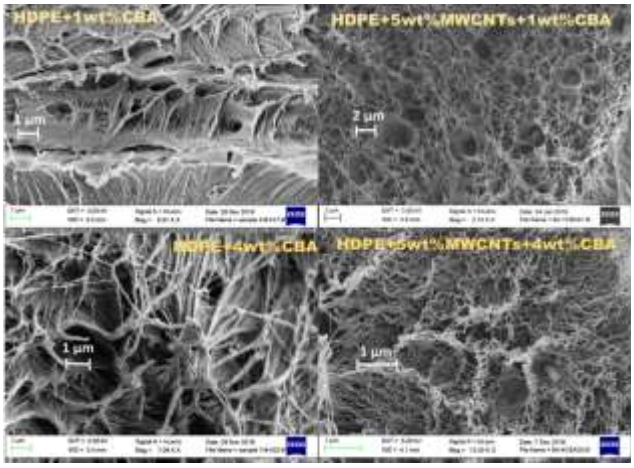

Fig. 2. SEM cross section of disk samples with porous microstructure obtained after the addition of CBA (loadings of 1 wt% and 4 wt%) in the foaming process. For brevity, only samples of HDPE and HDPE filled with the highest content of MWCNTs investigated (5 wt%) are reported.

Despite obtaining a foamed structure for the samples, detectable from the presence of cellular voids within the materials, these pores are not regular, suggesting a poor level of porosity upon addition of 1 wt% and 4 wt% of CBA and, consequently, poor quality of the extruded foam. There are several possible explanations for structure obtained. Firstly, the yield of gas may not be sufficient to produce a uniform distribution of pores. This is also complicated as foaming is a diffusion controlled process and the viscosity of HDPE in the molten state is higher than most polymers. The solubility of the gas produced for the polymer must also be considered. Finally, great care must taken to ensure there is no foaming during the extrusion step, critically foaming should all take place during the moulding step.

The velocity and attenuation coefficient of ultrasound in the samples produced were obtained by frequency-domain analysis through ultrasonic air-coupled measurements in transmission. Results are summarised in table 1.

TABLE I. Acoustic properties of various plastic foamed samples obtained under different processing conditions and, MWCNT and chemical blowing agent loadings. Samples disks of conventional materials commercially in use (a syntactic foam and a commercial matching layer) were also analysed and used as benchmarks

Sample	Density (kg/m3)	Velocity (m/s)	Acoustic Impedence (MRayl)	Attenuation at Resonant Frequency (Np/m)
Unfoamed HDPE	951	2339.19	2.22	12.41
*HDPE-1CBA_2	951	2329.22	2.22	10.24
HDPE-1CBA_3	952	2415.12	2.30	11.42
HDPE-1CBA_8	954	2391.70	2.28	9.26
2A-1CBA_1	952	2400.18	2.28	13.51
2A-1CBA_3	951	2418.67	2.30	12.15
2A-1CBA_4	953	2451.07	2.34	10.75
3A-1CBA_4	952	2406.21	2.29	10.33
3A-1CBA_9	953	2393.48	2.28	10.56
4A-1CBA_1	959	2418.15	2.32	10.47
4A-1CBA_4	959	2412.94	2.31	10.91
5A-1CBA_4	961	2370.69	2.28	9.50
5A-4CBA_1	962	2430.75	2.34	10.98
6A-1CBA_4	966	2402.92	2.32	12.19
6A-4CBA_1	967	2377.30	2.30	14.11
7A-4CBA_4	973	2497.42	2.43	13.41
7A-4CBA_1	983	2473.97	2.43	14.10
8A-1CBA_9	991	2472.76	2.45	13.81
8A-4CBA_4	990	2471.42	2.45	16.93
SYNTACTIC FOAM	704	2486.65	1.75	41.30
COMMERCIAL ML	441	2188.60	0.97	21.99

As can be seen form Table 1, the acoustic impedances in this preliminary investigation are still too high ($\geq$ 2.2 MRayl) if compared with the benchmark samples (syntactic foam and commercial matching layer) and need to be lower. A reduction in density was not obtained, confirming the poorly controlled level of porosity obtained during the foaming process using the processing parameters given above. However, resistant polymer materials with very low attenuation coefficients ($\leq$ 16 Np/m) were obtained, which is a positive finding in allowing more freedom to increase the pores size. Further optimization of the foaming processing is required to increase the pore (cell) density and control the level of pore uniformity.

III. Closing Remarks

In this preliminary investigation novel nanocomposite foamed materials with potential for improved passive layers in

air-coupled ultrasonic transducer applications were produced using scaleable, high-volume manufacturing techniques. Resistant polymer materials with low attenuation coefficients ($\leq$ 16 Np/m) were obtained. However, acoustic impedances of these materials were higher ($\geq$ 2.2 MRayl) than that required and need to be lowered. A reduction in density was not obtained suggesting a poorly controlled level of porosity, i.e. the foaming process.

The processing conditions employed for the foaming processing control the foam properties obtained, including foam density, porosity and cell morphology (i.e. cell size and cell size distribution), and therefore, the acoustic and mechanical behavior of the final materials.

Further work is on-going to determine the optimum processing conditions to produce the foam structure(s) required as well as concentrations of CBA so as to control the level of porosity. The melt viscosity of the material within the extruder may need to be modified to achieve the foam structure required.

ACKNOWLEDGMENT

L. A. thanks the EPSRC (EP/L016389/1) and Elster-Honeywell for funding her studentship.

REFERENCES

[1] K. Nakamura, Ultrasonic Transducers: Materials and Design for Sensors, Actuators and Medical Applications, 1st ed., Woodhead publishing, 2012, pp.1-703.

[2] V. K. R. Kommareddy, Air-Coupled Ultrasonic Measurements in composites, Master of Science thesis, Iowa State University, 2003.

[3] "Ultrasonic Sensor", catalog No. S15E-5, Murata Manufacturing Co., Tokyo, 2008, pp.1-13.

[4] G. Kossoff, The Effects of Backing and Matching on the Performance of Piezoelectric Ceramic Transducers, IEEE Transactions on Sonics and Ultrasonics, vol 13, 1966, pp.20-30.

[5] Q. Zhou, S. Lau, D. Wu, and K. Kirk Shung, Piezoelectric film for high frequency ultrasonic transducers in biomedical applications, Progress in Materials Science, vol 56, 2011, pp.139-174.

[6] J. Zhu, Optimization of matching layers design for medical ultrasonic transducer, Doctor in Phylosophy Dissertation, The Pennsylvania State University, August 2008.

[7] D. Klempner, K. C. Frisch, Handbook of Polymeric Foams and Foam Technology, Hanser Publishers, 1991, pp.1-408.

[8] P. S. Liu, G. F. Chen, Producing Polymer Foams, chap.7 in Porous Materials Processing and Applications, Elsevier, 2014, pp.345-381.

[9] L. J. Lee, C. Zeng, X. Cao, X. Han, J. Shen, G. Xu, Polymer nanocomposite foams, Composites Science and Technology, vol. 65, 2005, pp.2344-2363.

[10] J. A. R. Ruiz, M. Vincent, J-F. Agassant, T. Sadik, C. Pillon, C. Carrot, Polymer foaming with Chemical Blowing Agents: Experiment and modeling, Polymer Engineering and Science, vol. 55, 2015, pp.2018-2029.

[11] M. S. P. Shaffer, A. H. Windle, Fabrication and Characterization of Carbon Nanotube/Poly(vinyl alcohol) Composites, Advanced Materials, vol. 11, 1999, pp.937-941.

[12] R. Cardinaud, T. McNally. Localization of MWCNTs in PET/LDPE blends, European Polymer Journal, vol.49, 2013, pp.1287-1297.

[13] T. E. G. Alvarez-Arenas, A Nondestructive Integrity Test for Membrane Filters Based on Air-Coupled Ultrasonic Spectroscopy, IEEE Transactions on Utrasonics, Ferroelectrics, and Frequency Control, vol. 50, 2003, pp.676-685.

[14] T. E. G. Alvarez-Arenas, Air-coupled ultrasonic spectroscopy for the study of membrane filters, Journal of Membrane Science, vol. 213, 2003, pp.195-2017.

[15] T. E. G. Alvarez-Arenas, Simultaneous determination of the ultrasound velocity and the thickness of solid plates from the analysis of thickness resonances using air-coupled ultrasound, Ultrasonics, vol. 50, 2010, pp.104-109.