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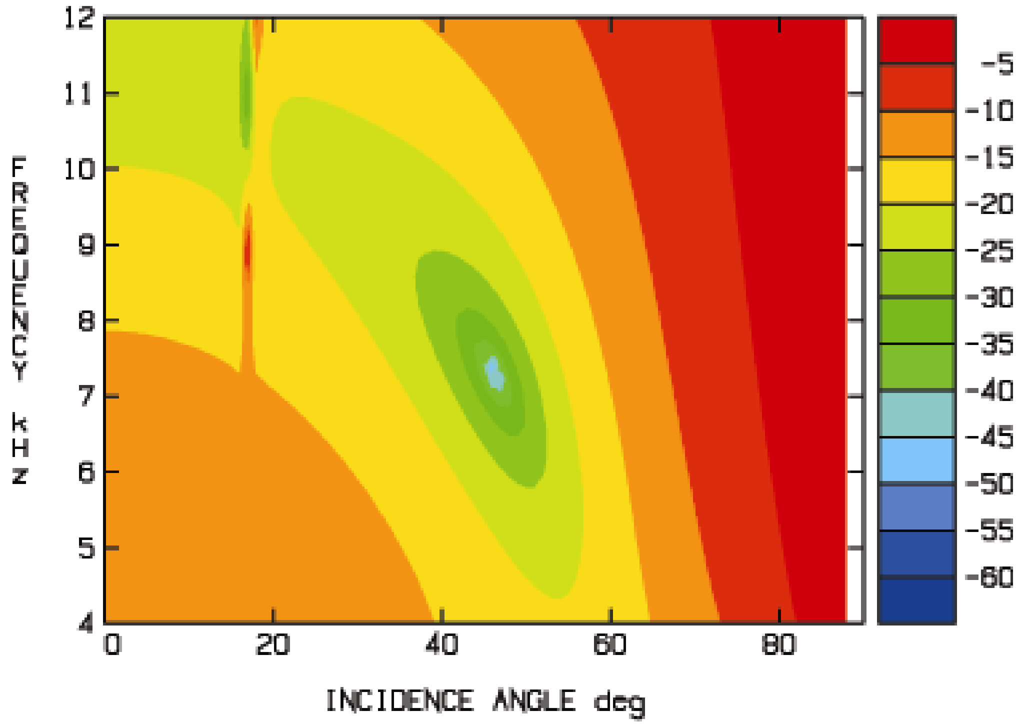


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**Abstract (not more than 200 words)**

This report concerns the early stages in the development of a new technology for underwater signature management. The aim of the work presented is on an anechoic coating with a tailored sonic velocity and absorption profile. Both a computational model to optimise the coating performance and the development of coating material are reported. In this initial stage of the development the coating is based upon homogeneous discreet layers rather then a gradient material. The individual layers are made up of polymer composite, where the matrix material is a styrene butadiene rubber (SBR) with nano- and micro-sized reinforcements.

**Keywords**

underwater signatures, underwater acoustics, anechoic coating, nanotechnology

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Ny teknik för hydroakustisk signaturanpassning


**Sammanfattning (högst 200 ord)**

Denna rapport sammanfattar utvecklingsarbetet av en ny teknik för hydroakustisksignaturanpassning. Målet med det presenterade arbetet är en ljuddämpande beläggning med en skräddarsydd ljudhastighets- och absorptionsprofil. Både en beräkningsmodell för optimering av beläggningens prestanda samt utveckling av själva materialet rapporteras. I det här tidiga skede av utvecklingsarbetet består beläggningen av ett skiktat material i stället för ett gradient material. De individuella skikten är gjorda a polymerkompositer där matrismaterialet är styren butaden gummi (SBR) med nano- och mikrometer stora partiklar.



**Nyckelord**

undervattenssignaturer, hydroakustik, R-beläggning, nanoteknik

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# Contents

# 1 Introduction

The motivation for this work is threefold. Firstly, the current anechoic systems developed in Sweden during the mid 20$^{th}$ century for submarines have up till now been considered to have acceptable performance. However, in recent times it has become apparent that improvements are needed for the reasons that:

1. The development of sonar technology has meant that protection is required from a wider range of wavelengths at the same time as the sensitivity of the sonars has become increasingly better.
2. Swedish submarines are increasingly deployed in other marine environments than current anechoic system was designed for due to increased international operations. Hence, a decrease in performance has been observed in those locations.

Additionally, advances in modelling of anechoic coatings make it possible to optimise performance if the wave velocity and absorption profiles in the material are tailored [1]. Recent developments in materials technology means that structures on the nanometre scale can be created. In the literature this technology has been termed as ‘nanotechnology’ and has shown that new and enabling property combinations can be realised [2][3]. Hence, one of the goals was to explore the potential of this technology in anechoic materials and to verify the results from the recent mathematical models. Finally, the production process of the current anechoic system is old-fashioned and could probably be modernised with technology that has less negative environmental impact both for the worker and for the environment at large.

This report is written with the intent to consolidate the knowledge collected during the course of this project. The objective is to have a text that can be part of the platform for further work in this research field.

# 2 Theory

A thorough review of the well-established theory of wave propagation and absorption in layered elastic structures is beyond the scope of this work, however good accounts may be found in several textbooks, e.g. Aki and Richards [4], Brekhovskikh and Godin [5], Miklowitz [6]. We remark that significant advancement of numerical methods and computer technology in the past decades enables using this theory for quantitative studies of coatings/steel plate structures more fully today than in the development work of the currently used coatings during the 1950s as presented in a report by Söderqvist [7].

In a macroscopic sense an incident wave can experience four different phenomena:

1. Transmission.
2. Absorption (the wave energy is converted into another energy form e.g. heat)
3. Specular reflection
4. Scattering in other directions

To avoid detection a submarine would like to minimise its specular reflections. A coating that absorbs the incident acoustic waves would be ideal but often enough scattering also has to be utilised to minimize the reflections.

Absorption can be accomplished in at least three different ways:

1. Internal friction e.g. in an elastomer
2. Enhancement of shear wave excitation by inhomogenities, e.g. cavities, in the coating
3. A viscous fluid vibrating in a porous matrix

Scattering can be promoted by inserting cavities in the coating, possibly with dimensions tuned to induce resonance oscillations at frequencies of interest.

# 3 Research Approach

Elastomers (e.g. styrene butadiene rubber, SBR), containing resonant cavities are often used for underwater acoustic damping. This is known as an Alberich type absorber. The pattern of cavities is designed to scatter incoming acoustic energy and the shape of each cavity to transform the acoustic wave from a longitudinal mode to a shear mode. The energy of the latter is much more easily damped in elastomers. Damping of the reflected wave by destructive interference may also occur. The predominant mechanism for sound absorption in elastomers is via friction losses between the elastomers chains, and is therefore dependent on the internal structure of the elastomer. Below the glass transition temperature ($T_g$), where the elastomers are in the glassy state, damping is relatively low, increasing to a maximum around $T_g$. In this work we are concerned with studies of the intrinsic material damping, not the dimensions, shape, spacing or other geometrical properties of any possible cavities.

The initial research proposal put forward two interesting approaches, which had received little or no research attention for this application. These two areas of research were:

**Acoustic properties of nano- and micro-porous material structures.** Porous materials have good acoustic damping properties over a wide spectral region. With nano- and/or micro-porosity the pore at the material to hull interface can be regarded as micro roughness. Hence, it is expected to enhance the adhesion of the damping material to the hull. A challenge with a porous structure of air, water and solid material is the impedance tuning which has to be addressed so that acoustic energy in the incident wave is absorbed and damped by the porous material.

**Damping properties of structures of memory metals.** Memory metals are known to have especially good capability to transform shear wave energy to heat. How this can be utilised in an anechoic system ought to be explored. The two main alternatives identified at the outset was a metal foam or three dimensional structure of membranes or fibres that could absorb the acoustic energy through shear loads. Even in this case the difficulty is how to get the energy into the material at the material to liquid interface with minimal reflection as result.

However, at the start up of this innovation project it was realised that the scope to consider both of these avenues was too broad. It was also recommended by the selection committee that only one of these material classes should be studied. Hence, it was decided to concentrate the efforts on the nano- and micro-structured material.

## 3.1 Optimizing coatings

As was mentioned in the Introduction on page 5, one of the driving forces for this project was advances in modelling of underwater acoustic absorbers. Therefore, it was appropriate that the starting point for this work would be an attempt to model an “ideal” acoustic absorber on a steel plate using the new modelling tools. This would then give material parameters to aim for in the material development stage.

In this section we consider coatings composed of several homogeneous layers with equal thicknesses but different rubber materials. Our purpose is to investigate the efficiency - in terms of echo reduction as function of frequency and incidence angle - achievable with this type of coating applied on a water-immersed steel plate with known thickness and elastic parameters. Assuming that the thickness of the coating and the number of rubber layers are given, we want to determine elastic parameters (density, bulk and shear modulus and loss factors) for each layer, that minimize the sound energy reflected by the coated plate in a given range of frequencies and incidence angles.

In the following, we give a brief description of a numerical technique for designing optimal coatings of the above mentioned type, and illustrate the technique by designing a coating composed of six 1 mm thick rubber layers on a 10 mm thick steel plate.

### 3.1.1 Computational model

The coated plate is modeled as a transversally homogeneous medium of coupled solid layers surrounded on both sides by half spaces of homogeneous water, see Figure 1.

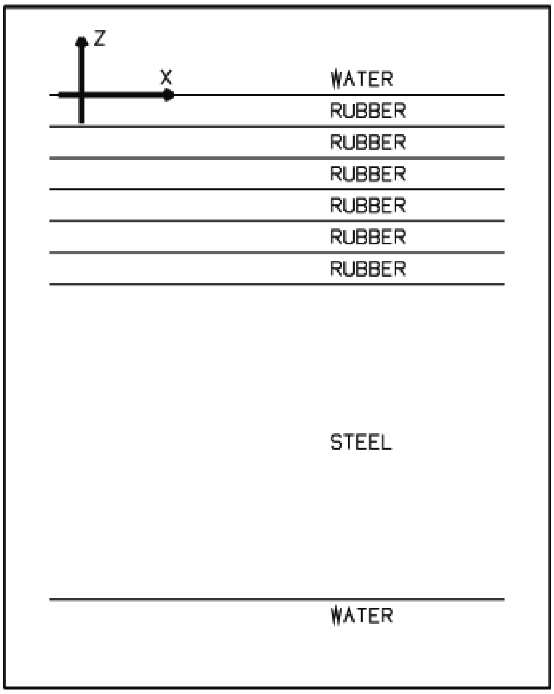


**Figure 1.** Computational model of coated steel plate

The problem of computing the elastodynamic wavefield from a given source in this type of media has attracted much interest in the past two decades. The range-independent geometry admits using variable separation leading, for a monofrequency field in the horizontal wavenumber domain, to a boundary-value problem for a system of ordinary differential equations (ODEs). The wavefield in the physical domain is then obtained as the inverse Hankel transform of the solution of the ODE system. The computations reported here were done with the NFEM code [8,9], which uses finite elements for solving the ODE system and adaptive high-order numerical integration with error control for the inverse Hankel transform.

### 3.1.2 Parameter optimization method

A Cartesian co-ordinate system with origin at the coating/water interface and the $z$-axis orthogonal to the plate is introduced as shown in Figure 1. Thus the coating-steel and the steel-water interfaces are $z = -d_c$ and $z = -d_c - d_s$ where $d_c$ and $d_s$ are the given thicknesses of the coating and the steel, respectively. Then the main steps of the method for solving the inverse problem of finding elastic parameters of the coating that minimize the energy of sound reflected by the coated plate are:

**1.** Consider the case in Figure 1, but with the multi-layered coating replaced by a single layer with thickness $d_c$, and with material parameters in the coating of the form

$$F_m(z) = F_{m0} + \sum_{j=1}^{J} \gamma_{jm}\phi_j(z) \qquad -d_c < z < 0 \quad m = 1,...M \tag{1}$$

where $\phi_j(z), j = 1,...,J$ are pre-defined basis functions. $F_1(z),...,F_M(z)$ denote a subset of $M \le 4$ of the four elastic parameters $\Re(\lambda + 2\mu)$, $\Im(\lambda + 2\mu)$, $\Re(\mu)$, $\Im(\mu)$, where $\lambda = \lambda(z)$ and $\mu = \mu(z)$ are the complex Lamé parameters. The basis functions are smooth - a few times continuously differentiable - at the water-coating interface $z = 0$, to suppress reflections from that interface. In the example case shown below the basis functions were integrals of B-splines, other possible choices are monomials, $\phi_j(z) = z^{1+j}, j = 1,...,J$ .

**2.** The FEM discretization of the equations for the wavefield excited by an incident single-frequency plane wave with wavenumber vector $k = (k,0,0)$ is

$$A(k)x = b(k) \tag{2}$$

The global stiffness matrix $A$(k) is a function of the horizontal wavenumber $k = k(\alpha) = \omega/c \sin\alpha$ where $\omega$, $c$ and $\alpha$ are the angular frequency, the speed of sound in the water and the angle of incidence of the plane wave, respectively. The right hand side $b(k)$ represents the plane-wave source, and the components of $x$ are values of the sought field variables (scaled complex pressure in fluids, complex displacements in solids) at the nodes of the FEM discretization.

When the system is assembled using conventional finite elements, $A(k)$ is a linear function of density $\rho$ and the complex Lamé parameters $\lambda$ and $\mu$ . Thus, when the material parameters are given by (1), the system (2) is of the form

$$\{A_0(k) + \sum_{m=1}^{M}\sum_{j=1}^{J} \gamma_{jm} A_{jm}(k)\}x = b(k) \tag{3}$$

where each matrix term $A_{jm}(k)$ corresponds to terms in the ODE system proportional to a specific material parameter.

**3.** The solution $\hat{x}$ of equation (3) is

$$\hat{x} = \hat{x}(\alpha, \gamma)$$

where

$$\gamma = (\gamma_{11},...,\gamma_{J1},...,\gamma_{1M},...,\gamma_{JM})^T \tag{4}$$

is the $JM$ -dimensional vector of the coefficients $\gamma_{jm}$ . Let $p_{tot} = p_{tot}(\alpha, \gamma)$ be the subvector of $\omega\hat{x}$ corresponding to nodes of the FEM grid in the water above the coating in Figure 1. The components of $p_{tot}$ are values of the complex pressure of the wavefield at such nodes. The corresponding vector of values of the <u>reflected</u> complex pressures is

$$p_{ref} = p_{ref}(\alpha, \gamma) = p_{tot}(\alpha, \gamma) - p_{inc} \tag{5}$$

where $p_{inc}$ is the vector of the incident complex pressure, i.e. of the plane wave field in a homogeneous water space.

The problem of finding parameters for the one-layer coating, that minimize the reflected acoustic energy in a given range of incidence angles is then

$$\text{Minimize} f(\gamma) = \sum_{k=1}^{K} \left\| p_{ref}(\alpha_k, \gamma) \right\|_2^2 \tag{6}$$

where $\alpha_1, ..., \alpha_K$ is a grid covering the specified incidence angle range, and $\| \ \|_2$ denotes the Euclidean norm, i.e. $\|x\|_2^2 = \sum_i^n |x_i|^2$.

By assembling all the terms $A_{jm}(k)$ in the expansion of the stiffness matrix $A(k)$, both the solution $\hat{x}(\alpha, \gamma)$ of equation (3) and its first and second derivatives as function of $\gamma$ can be computed in a straightforward way. Thus rapidly converging numerical methods are available for solving the nonlinear least squares problem (6). In this study a trust region method [10] was used that makes use of the first and second derivatives of the objective function $f(\gamma)$.

Using the expansions (1), the solution $\hat{\gamma}$ of (6) defines the optimal material parameters for the one-layer coating as smooth functions of $z$. The parameters of the sought coating composed of thinner layers of homogeneous rubber are then obtained by interpolating the smooth profiles with piece-wise constant functions.

### 3.1.3 Conditions for physical realizability

A necessary condition for a coating to be physically realizable is imposed by the requirement that the strain energy function must be positive definite everywhere [11, Sec 12.6]. This condition is equivalent to requiring that the complex bulk and shear module must be in the 4th quadrant of the complex plane. Stated in the Lamé parameters $\lambda$ and $\mu$ used in eqn (1) the conditions for physical realizability are;

$$\Re(\lambda + 2\mu/3) > 0 \tag{7}$$

$$\Im(\lambda + 2\mu/3) \leq 0 \tag{8}$$

$$\Re(\mu) > 0 \tag{9}$$

$$\Im(\mu) \leq 0 \tag{10}$$

In the optimisation example presented above, a simple a *posteriori* check was carried out to ensure that these conditions for physical realizability are satisfied by the optimal $\lambda = \lambda(z)$ and $\mu = \mu(z)$ for all $z$.

We remark that the conditions (7)-(10) that must be satisfied by *any* physically realizable solid material will in general allow for parameter combinations that are unattainable with materials of a given type. Thus, for the elastomers available for the experimental study additional restrictive conditions imposed by correlations between the longitudinal and the shear wave parameters were found. The optimisation method described above could be modified to incorporate such additional conditions in a straightforward way, however such studies could not be fitted into the time-frame available for this study.

## 3.2 Material Development

Although the optimal material parameters resulting from the modelling satisfy the general conditions for physical realizability, the parameters were found to be unattainable with the material types available for this study. Therefore, the strategy adopted was to use a standard Styrene Butadiene Rubber (SBR) as a matrix material for synthesizing nano- or micro-composites with different particles as fillers and to study to which extent the material properties could be altered. This means that no attempts were taken to match any of the modelled parameters and no attempt to optimise the matrix material was made during the material development. This part of the project was carried out in a MSc project [12]

### 3.2.1 Background

Pure rubber is an excellent sound absorber, but has poor resistance to abrasion, and rapidly degrades when exposed to ultraviolet light. To produce a material with acceptable mechanical and environmental resistance for a submarine application the rubber must be reinforced, normally with a filler of carbon-black (very small particles of soot). Other materials are currently being developed, including nanoparticles of silicon dioxide (silica, or quartz). New forms of carbon-black – nanostructured carbon-black have also recently become available. These materials have been developed to improve the wear resistance of rubber tyres and similar products. While improving the mechanical and environmental resistance of the rubber, these reinforcements have a negative effect on the damping or sound absorption of the rubber. It is therefore an advantage to be able to use as little reinforcement as possible, concomitant with acceptable mechanical properties and UV resistance.

#### 3.2.1.1 Porous media

Porous media have well-recognised good sound damping properties. In fact they are commonly used for sound damping applications in buildings and vehicles of all kinds. However, in order to minimise the reflection at the water/solid interface and enable the acoustic energy to enter the material the acoustic impedance has to be matched with that of water. The acoustic impedance is a product of the sonic velocity and the density of the media ($u\rho$). For a rubber material the density and the speed of sound lie close to that of water. If we introduce gas into the material both of these two parameters will be lowered and consequently the acoustic impedance decreases. This would result in an increased reflection at the water/coating interface. Also, a porous elastomer would be hydrostatic pressure dependent, which would lead to different effectiveness of the coating depending on the depth.

Hard porous polymers are commercially available as hydroacoustic damping materials. These utilise the fact that increased sonic velocity in the hard polymer offsets the lowered density due to the porosity. However, due to their hardness they also tend to become brittle. At the quay a brittle submarine coating may be crushed and the hydrostatic pressure resistance of such a coating may be limited. Thus, replacing the current anechoic system with such a material may cause more problems than it solves. Another factor governing material selection was that within the time frame of this project we did not have access to any suitable method of producing porous elastomers.

Due to the factors above, porous materials were discarded as an avenue in this project.

#### 3.2.1.2 Polymer based nanocomposites

Recently it has been proven that inorganic particles and fibres with dimensions in the nanometre regime are very effective as reinforcement in polymers, but without the negative embrittling effect larger particles of inorganic fillers normally have. Polymer-based nanocomposites are therefore currently attracting research and development interest due to their greatly improved property combinations. Evidence for similar improvements in elastomers is much more limited, although the little work that has been published indicates that similar effects and improvements have been obtained.

The carbon-black commonly used in many rubber products consists of agglomerates of nanometre-size particles of carbon (soot). Normally, these agglomerates are not dispersed during production of the rubber. The newer forms of *nanostructured* carbon-black now available are easier to disperse as individual particles. These have higher surface areas per unit weight, and are claimed to be more effective at reinforcing than conventional carbon black. We can therefore hypothesize that the amount of carbon black needed to obtain adequate abrasion and UV resistance can be reduced, which may result in improved (increased) acoustic damping.

Our hypothesis is that nanoparticle fillers can be used to improve the damping in rubber. In this work we elaborate somewhat on this hypothesis. In addition, we have studied the influence of nanoparticles with much higher density (iron); particles of similar density but very different composition (silica) and particles of similar density but different form (flake-like clay). We have also studied one addition of very high density and large particle size (wolfram). As reference material, a sample of a conventional carbon-black reinforced rubber was used.

The material property data generated were intended for use in the modelling and simulation activities.

### 3.2.2 Parameter constraints for polymer materials

The combinations of elastic parameters attainable with polymer materials are more restricted than those permitted for general solid materials satisfying the theoretical conditions for physical realizability. In polymers the two velocities, for example, are interlinked in a complex way, depending on the level of polymer-chain interaction (e.g. cross-linkage, entanglement, etc….). Despite the ability to change the ratio between $u_p$ and $u_s$ to some degree, literature lists $u_p/u_s \approx 2 \pm 0.5$ (see e.g. Table 14.3 in [13]). This was confirmed during the course of the project as well; see Table 3.7 in Appendix A. Further, a very strong correlation exists between the absorption coefficients.

Some conclusions can be drawn from the literature regarding sonic absorption [13]:

1. $\alpha$ has its maximum around $T_g$.
2. Rubbers with low cross-link density show very high sound absorption.
3. The ratio between shear and longitudinal absorption is nearly constant, viz. $\alpha_s/\alpha_p \approx 5$.
4. In the temperature regions wherein no transitions are observed, the following experimental rule can be observed;

$$\alpha_p\left(\text{dB/cm}\right) \approx 40\left(\nu - 0.30\right) \tag{11}$$

where $\nu$ is Poisson ratio.

### 3.2.3 Experimental details.

A range of samples containing the reinforcement particles listed in the table below, at levels corresponding to 0; 20; 40; 60; 80; 104; 200; and 320 phr (per hundred rubber weight) were prepared by mechanical mixing in the conventional way. Initial experiments were made using natural rubber (NR) as the matrix, until it was decided that SBR allowed better comparison with the reference material. The following table also shows the total composition of the samples, including vulcanising agents, accelerators and plasticizers.

**Table 1.** The reinforcing particles used, their average particle sizes and densities, and surface area.

| Type | Particle size [nm] | Surface area [$m^2/g$] | Density [$kg/dm^3$] |
|---|---|---|---|
| Carbon Black N550 | 40 – 48 | 94 | 1.8 |
| Carbon Black N339 | 26 – 30 | 42 | 1.8 |
| Printex XE 2B | ~35 | 1000 | 1.8 |
| Carbon Black S160 | ~20 | 150 | 1.8 |
| Carbon Black FW18 | ~15 | 200 | 1.8 |
| Iron powder | ~45000 | - | 7.8 |
| Carboniron CM | ~22000 | - | 7.8 |
| Carbon iron HS | ~3500 | - | 7.8 |
| Wolfram | ~40000 | - | 19.2 |
| Silica R202 | | 100 | ~1 |
| Nanoclay | Sheets | - | - |

**Table 2.** The composition of the samples prepared.

| Ingredients | Quantity (phr) NR | Quantity (phr) SBR |
|---|---|---|
| Rubber | 100 | 100 |
| Zinc oxide | 6 | 5 |
| Stearic acid | 0.5 | 2 |
| Sulphur | 3.5 | 2.5 |
| MBT* | 0.5 | |
| CBS** | | 1.25 |
| Softener | | 0, 7 |
| Filler | 0, 20, 40, 60, 80 | 0, 20, 40, 60, 80, 104, 200,320 |

* Accelerator for NR

** Accelerator for SBR

These compositions were chosen so as to be similar to conventional acoustic absorbers.

After production and pressing into thin (2 millimetre) sheets, rectangular samples were prepared and measured using Dynamic Mechanical Thermal Analysis (DMTA), a form of mechanical spectroscopy, to determine the acoustic damping (loss tangent, tan δ) of the materials. In this technique, the samples are made to vibrate at different frequencies and temperatures, and the damping measured. The glass transition temperature, $T_g$ can also be obtained from these measurements. Measurements were made at frequencies of 0,1; 1; 10; and 100 Hz while scanning from temperatures of -65 °C to +50 °C. From each measurement the elastic modulus and loss tangent was calculated. From these measurements, it was possible to calculate a master curve (see Appendix A for a detailed discussion on master curves), at a reference temperature and frequency. The reference temperature selected was 10 °C and a frequency of 20 kHz. In principle any other temperature and frequency could be chosen and data evaluated from the master curve. A typical master curve for SBR containing 104 phr carbon black type N550 is shown in Figure 2 below. An addition level of 104 phr was chosen as this corresponds to the addition level in the reference material. Note that this is chosen for comparison purposes only, and should not be considered an optimum value.

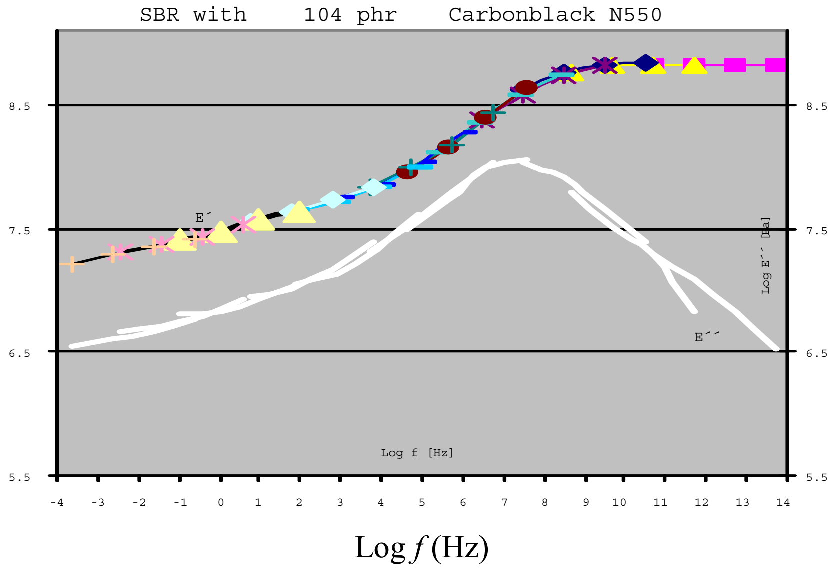


**Figure 2.** Master curve E' – E'' for SBR with 104 phr carbon black type N550, reference temperature 10 °C.

# 4 Results and Discussion

## 4.1 Example of an optimal coating

As an example, we consider a coating of six 1 mm thick rubber layers to be applied on a 10 mm thick steel plate with density 7850 kg/m$^3$, P-wave velocity 6001 m/s, S-wave velocity 3208 m/s and zero absorption. The coating is to be optimized for frequencies centered at 8000 Hz and incidence angles from $0^\circ$ to $60^\circ$, where $0^\circ$ is normal incidence.

The basis functions in (1) were chosen to integrals of B-splines, with $J = 2$. Only $\Re(\lambda + 2\mu)$ and $\Im(\lambda + 2\mu)$ (i.e. the P-wave speed and absorption) were sought, while the density was constant at 1000 kg/m$^3$. The shear wave absorption profile was preset to nominally increasing, while the shear speed was kept constant at 500 m/s during the optimization, and adjusted after convergence to make the complex bulk modulus $\lambda + 2\mu/3$ lie in the 4'th quadrant of the complex plane, as required for physically realizable elastic materials.

The resulting smooth material parameter profiles for the one-layer coating are shown in Figure 3. Note that depth in the figures corresponds to $-z$ in Figure 1. As expected a characteristic of the profiles is that the wavespeeds decrease and the absorption increases with depth.

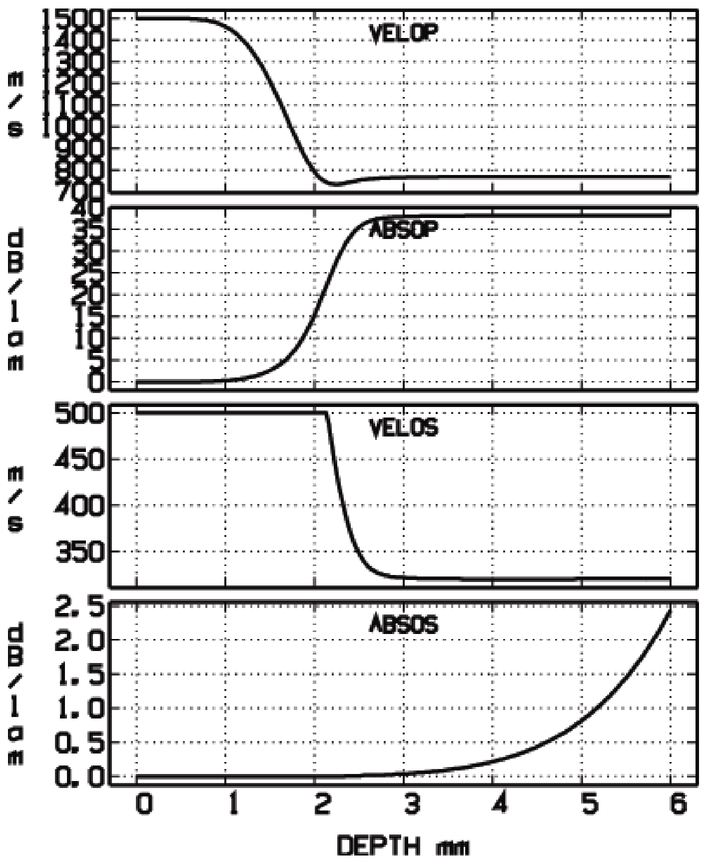


**Figure 3.** Optimal material parameters for one layer coating.

The material parameters for the six-layer coating, obtained by staircase interpolation of those in Figure 3, are shown in Figure 4.

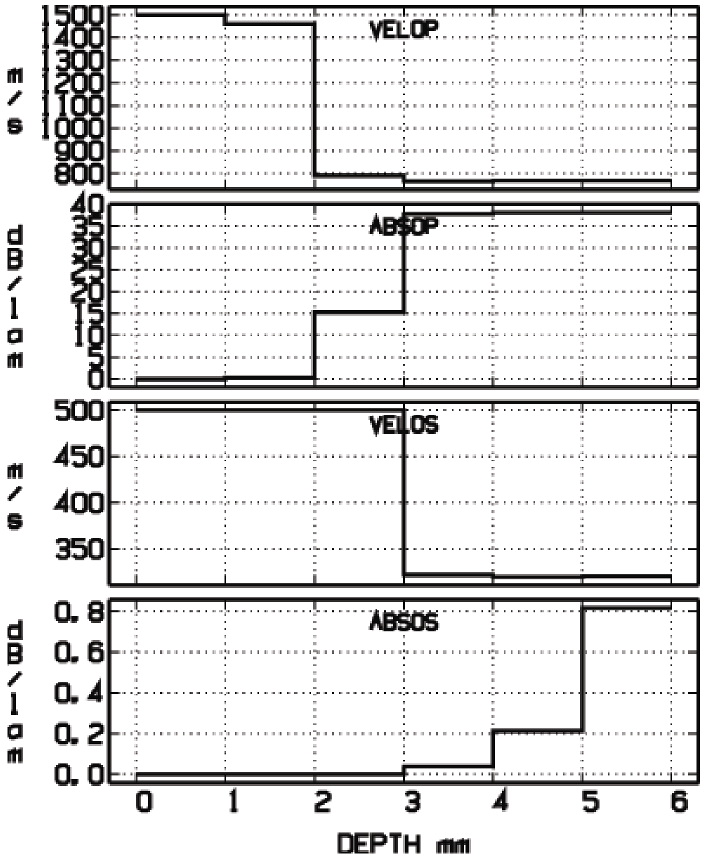


**Figure 4.** Optimal material parameters for six-layer coating.

The performance of the six-layer coating is displayed in Figure 5 and Figure 6, showing the reflection coefficient as function of incidence angle at the centre frequency 8 kHz, and as a function of incidence angle and frequency for frequencies from 4 to 12 kHz, respectively.

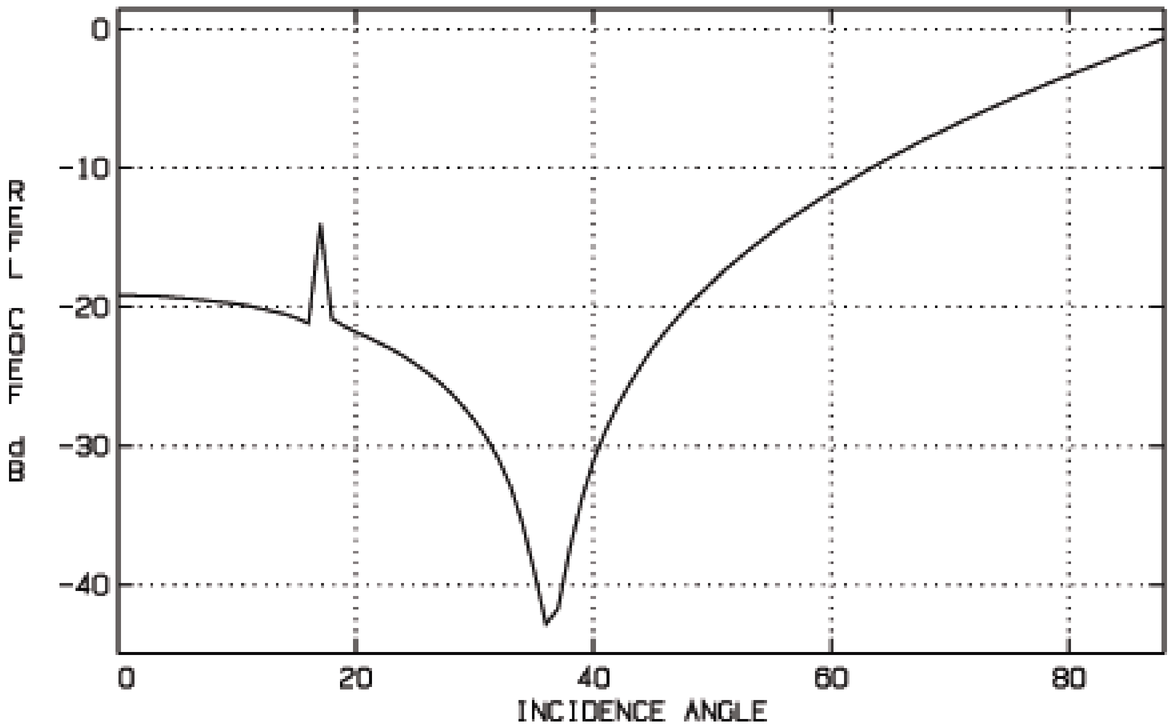


**Figure 5.** Reflection coefficient at 8 kHz as function of incidence angle. Optimal six-layer coating.

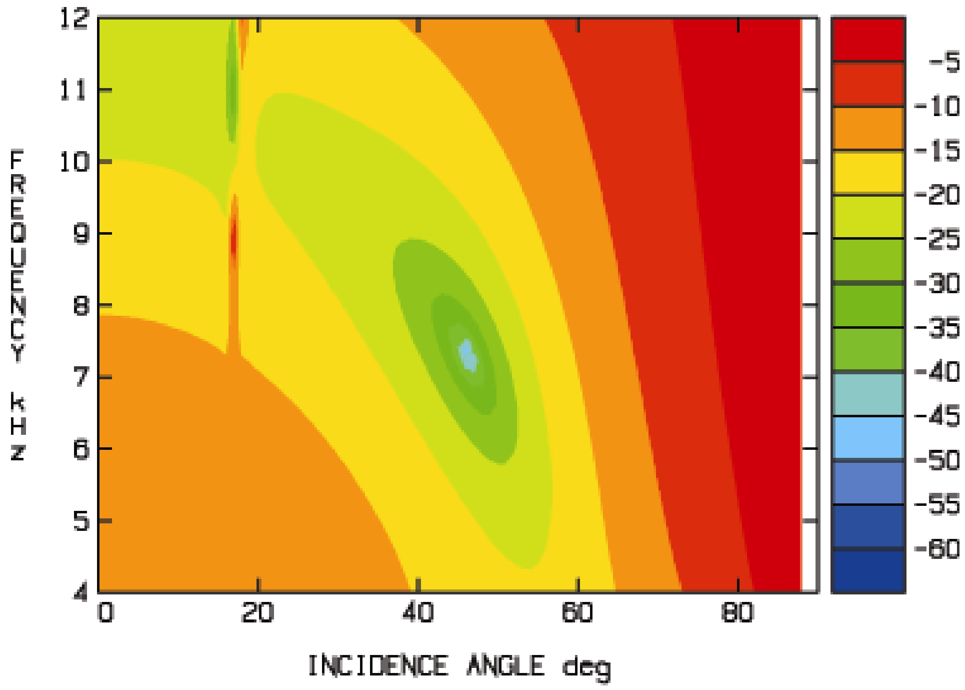


**Figure 6.** Reflection coefficient as function of frequency and incidence angle. Optimal six-layer coating.

## 4.2 Material Development

Figure 7 shows the results obtained for SBR containing 104 phr of all ten additions investigated, the reference material and pure SBR.

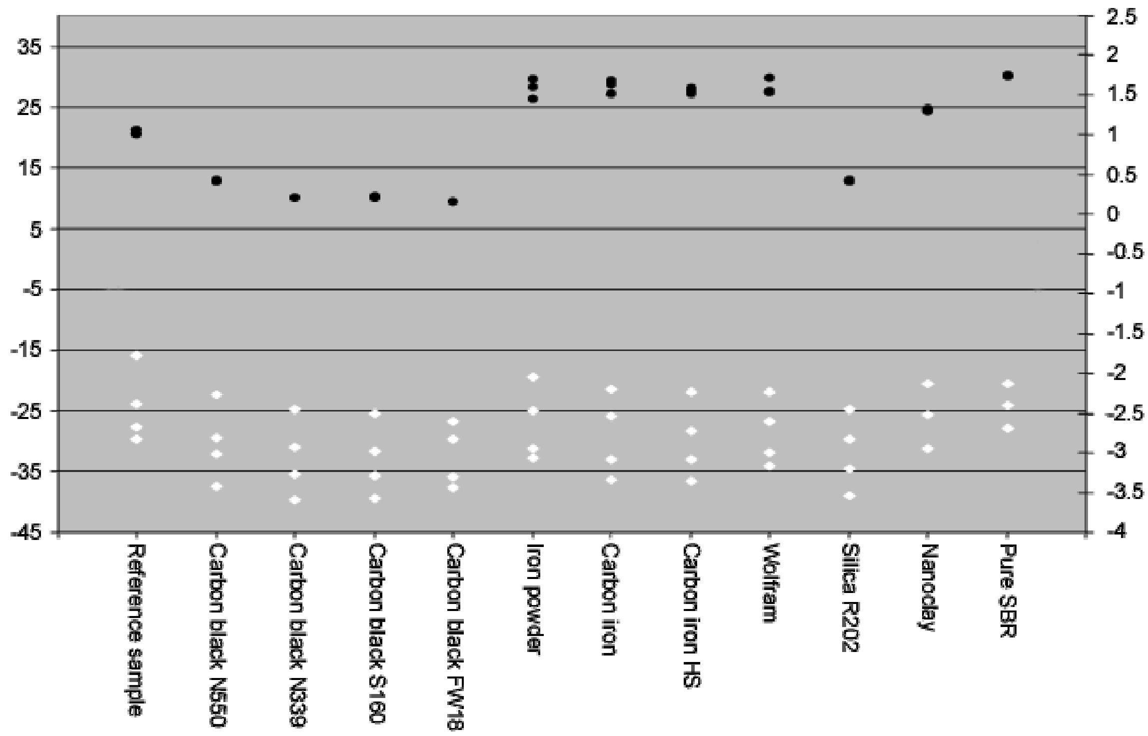


**Figure 7.** Tg (diamonds) and tan δ (filled dots) for the reference material, 104 phr samples and pure SBR at three frequencies.

The variation in Tg for a particular frequency was modest, all the materials falling within a 10 degree band. For the carbon-black samples, Tg decreased slightly with decreasing particle size, but the variation is not significant. This is consistent with previous work [14], which reported no dependence of Tg on carbon-black particle size, using a less accurate measurement technique. What is more relevant is that the loss tangent also decreased with decreasing particle size. This observation is consistent with the reference material, in which the effective carbon-black particle size is assumed to be larger than those investigated here. Again, this is consistent with earlier work [14].

Pure SBR shows the highest loss tangent, followed by the samples containing carbonyl iron of various particle sizes and wolfram. Tg is independent of the particle reinforcement type. Silica addition resulted in a decrease in the loss tangent. The nanoclay addition resulted in a slightly higher loss tangent than the reference material, and a similar or slightly lower Tg.

These results can be said to be generally consistent with previous work, although the latter was done using carbon-black and graphite particles sizes generally larger than those investigated here. Clearly, pure SBR offers the best damping (i.e. highest loss tangent) of the materials studied, followed closely by the carbonyl iron and wolfram containing materials. However, pure SBR has undoubtedly inadequate mechanical properties and UV stability to be useful in marine applications. The same may be assumed of the carbonyl iron and wolfram containing materials. Compositions containing iron additions will undoubtedly degrade quickly in a marine environment due to diffusion of water into the material, followed by corrosion, but iron was chosen for convenience, and for its density. Wolfram is unlikely to corrode.

In conventional rubber compositions, carbon-black is added in considerable quantities (up to about 100 phr) to provide adequate mechanical properties and UV stability for marine use. However as shown, carbon-black additions reduce the loss tangent. What is needed is to achieve a compromise between additions of carbon-black (or other effective reinforcement) to obtain acceptable mechanical and environmental properties. There are many reports which show that additions of clay nanoparticles to polymers result in very significant mechanical property improvements at quite low levels (a few weight percent). There is less information available on similar effects on elastomers, but it is reasonable to suppose that similar improvements can be achieved, if the nanoparticles can be successfully dispersed in the elastomers. Modification of the surface properties of the nanoclay particles to match the matrix (polymer or elastomers) is an essential factor to obtain optimum dispersion, but due to time and economic restraints, this was not done in this work.

# 5 Conclusion and future work

The optimal material parameters for a coating of general elastic solid materials were found to be unattainable with the isotropic elastomer materials available for experimental study. In an elastomer the shear wave (S-wave) velocity, $u_s$ is linked to the longitudinal wave (P-wave) velocity, $u_p$, and the absorption coefficients of shear and compression waves are also correlated to one another.

This study confirms the adverse effect on sonic damping of carbon-black additives, which are needed to preserve the mechanical and UV integrity of the material. It also concludes that smaller sized particles have a greater undesirable effect. However, it is likely that the amount of carbon-black, which needs to be added to achieve the required mechanical properties and UV stability can be reduced if newer forms of nanostructured carbon black are used. The levels used in this work (104 phr) were chosen to enable comparison with existing materials. It has been shown in several studies that around the particle a glassy region is formed. Hence, a greater volume percent of the polymer is in a glassy state. However, the size of this glassy region around each particle has not been established. The fact that the reinforcement type with the largest surface area (1000 $m^2$/kg), Printex XE 2B, produced at 40 phr a material too hard for further evaluation of its performance in the DMTA indicate that surface area plays an important role. Hence, the most likely reason for the behaviour observed in this study, is that every particle influences the surrounding elastomer to behave in a more glassy manner. Since the filler weight was constant smaller particles means more particles and a higher percentage of the elastomer in a glassy state. Further, the larger surface area of the smaller particles has a greater interaction with the polymer, resulting in an even higher degree of glassiness. This in turn will lower the acoustic absorption.

Recent work by Ivansson modelling rubber material with spherical air cavities has shown that the scattering from the periodic patterns of cavities enhances the echo reduction in an anechoic coating. Also, noted in the same work was that shear losses are important for the overall performance of the coating. The latter is supported by observations from earlier development work of the original anechoic system. An interesting hypothesis put forward by Ivansson is that filling the cavities with a harder material would enhance the scattering effect of these sites. One of the observations from current work is that a few large high-density particles does not decrease the sonic damping of the material as much as many smaller particles of lower density. Adding high-density particles means that the density of the composite material increases. One way around this effect would be to introduce cenospheres, i.e. ceramic gas filled spherical particles, which could act as rigid scattering sites while balancing the overall density increase of the heavier particles.

**Recommendations for further work**

- Acoustic damping measurements should be made under realistic conditions (larger samples in water or a shock tube) on selected samples from this work. Measurements should be made on Alberich-type samples containing cavities, for direct comparison with existing acoustic absorbers.
- Acoustic damping measurements and mechanical property and UV resistance measurements should be made on rubber matrices containing lower levels of nanostructured carbon-black.
- Models on Alberich-type absorbers should be used for comparison to the homogeneous material models.
- Realistic material parameters should be used in the model presented in this report (higher constraints on $u$ and $\alpha$ but lower on $\rho$).

- Optimisation with respect to the mechanical and UV stability versus sonic damping effectiveness of the amount nano-sized carbon-black.
- High-density fillers and cenospheres should be considered for tailoring the density (acoustic impedance).
- A FEM simulation of existing materials containing periodic arrays of cylindrical cavities should be made to identify how the cavities deform during isostatic pressure changes.

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