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# Novel phase separated multi-phase materials combining high viscoelastic loss and high stiffness

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ABSTRACT

In a previous study we showed that a unique combination of high stiffness and high viscoelastic loss could be achieved by filling a polystyrene matrix with rigid inorganic spheres coated with a thin (~200 nm) layer of a viscoelastic material. The sandwiching of this 'lossy' layer between the two rigid components was found to give a significant amplification of the tanδ loss peak associated with this material, without significantly compromising the sample stiffness. This was an experimental validation of the effect originally proposed by Gusev using finite element numerical studies. Following on from this, in the current study we have developed this concept further and shown that a similar amplification of viscoelastic loss can be achieved by incorporating rigid, but *uncoated*, particles into a phase separated matrix blend of polystyrene (PS) and a polystyrene/polyisoprene/polystyrene triblock co-polymer (SIS). The inspiration for this choice of the PS/SIS blend as the matrix came from some previous work where we studied, and modelled, the viscoelastic properties of these materials. In this work we show that in the filled PS/SIS blends, the loss amplification effect can been seen for different PS/SIS ratios, for different SIS polymers with different glass transition temperatures and also for glass fibres as well as for spherical particles. The key to seeing this effect is the fact that the SIS rubber phase was found to form a thin coating on the surface of the embedded particles during processing, effectively producing a surface coating layer on the particles (as well as phase separating within the PS matrix). As with our previous studies, it is shown that the experimentally measured effects are closely predicted by numerical micromechanical modelling based on the measured bulk properties of the three discrete components.

## 1. Introduction

The research into new composite materials for reducing sound and vibration levels remains a dynamic area of scientific study due to ongoing concerns of environmental noise pollution. Thus, for example, when designing new buildings, or new vehicles (for instance cars or aircraft), the level of noise that is generated or the ability to absorb noise in service is an important consideration for the designer. Access to materials that are both structural (have a reasonable stiffness) and able to absorb or damp unwanted noise or vibration is highly desirable but it is a technological challenge to develop materials that simultaneously possess these two requirements, namely high stiffness and high dynamic loss.

One method to trade-off stiffness and damping, is to utilise a composite material where the reinforcing fibre has improved damping characteristics, such as the recent work of Rueppel [1]. An alternative strategy for achieving this balance between structural stiffness and loss properties is through the use of laminate systems, for example a sandwich composed of a viscoelastic 'lossy' layer between two stiff and elastic layers [2,3]. Van Vuure [4] describes how this approach can help to damp out structural vibrations by exciting additional shear deformation in the constrained layer. Alvelid [5] also describes how a laminate system can help reduce the number of vibrational modes in an automotive body, and how a high loss visco-elastic layer was attached to the base structure and then capped by a stiffer outer (metal) layer. Alvelid also proposed that when the base structure was subjected to bending, high shear deformations were developed in the visco-elastic layer leading to enhanced energy absorption. The phenomenon of enhanced energy loss in dynamic loading of composite structures has come to be referred to as loss amplification.

Kristensen [6], following on from earlier theoretical studies by, for example, Kerwin [7] and Wang [8] has explored the phenomenon of loss amplification using modelling. Using a combination of simple beam theory and a full 2D finite element model he was able to demonstrate loss amplification in composite beams and show how the addition of a stiff outer constraining layer led to enhanced damping of the structure by forcing large shear strain deformations into the constrained visco-elastic layer, thereby confirming the proposal of Alvelid. Other authors have used intricate finite element simulations to explore the phenomenon and shown that the damping properties of sandwich structures can

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be optimised using either continuous [9] or discrete visco-elastic layers added as patches onto a composite structure [10].

A key parameter to emerge from these theoretical studies is the thickness of the visco-elastic layer. In a further theoretical paper, Gusev [11] showed that for a laminate morphology composed of two alternating layers (a stiff, non lossy layer and a weak, lossy layer) the effective loss modulus of the combination passed through a peak at a volume fraction of the lossy layer of ~0.001. Intriguingly, the loss amplification was very large, with the loss modulus of the combination being around 300 times larger than the value for the individual viscoelastic layer.

While these loss amplification effects in laminate composites are very interesting and currently used commercially, there is a significant limitation as laminate structures can be inappropriate for manufacturing parts with non-simple shapes. Gusev [11,12] offered an alternative to the multi-layer laminate approach, based on the incorporation of coated spherical inclusions. A combination of finite element studies and analytical modelling approaches showed that significant amplification of the loss properties could be achieved by coating each particle with a thin, and lossy, visco-elastic layer. These results mirrored those for the laminate beams, but offered a material in which the amplified lossy behaviour was isotropic and which also could be processed into a complex final shape using, for example, injection moulding. In a recent study [13], we proved that such materials could be experimentally realised by embedding coated glass spheres into a polystyrene matrix, and that the loss amplification effects produced were in close agreement to those predicted micromechanically.

In this current work we have further developed this idea by utilising and combining a number of existing concepts from the polymer blend literature [14,15]. In a recent paper [16], we investigated the properties of a range of blends of polystyrene (PS) and a polystyrene/polyisoprene/polystyrene (SIS) triblock thermoplastic rubber copolymer using a combination of experimental and numerical approaches. The two components were found to phase separate during processing. But most importantly, as is found in this current work, on incorporation of a rigid particle (either spheres or fibres) a thin layer of the SIS copolymer is seen to form on the surface of the particles, see Fig. 1, effectively producing a coated particle as investigated and described in our previous work [13].

Four main systems were fabricated and studied in this work and were as follows: spherical Barium titanate beads in a 90/10 PS/SIS (glass transition temperature Tg 10 °C) matrix; spherical Barium titanate beads in an 80/20 PS/SIS (Tg 10 °C) matrix; spherical Barium titanate beads in a 90/10 PS/SIS (Tg −15 °C) matrix; glass fibres in a 90/10 PS/SIS (Tg 10 °C) matrix.

## 2. Experimental

### 2.1. Materials

All the composite samples investigated here have been produced using a combination of three components, namely a polystyrene, a triblock rubber and a rigid glass filler. The polystyrene was a commercially available, grade BASF PS2, with a weight-average molecular weight (Mw) of 274 000 g/mol and a polydispersity of 2.74. The triblock thermoplastic Hybrar rubbers had the chemical structure polystyrene/polyisoprene/polystyrene (SIS) and were obtained from Kuraray Co Ltd. The symmetric SIS triblocks had a total fraction of polystyrene in the end blocks of 20%.

Two Hybrar grades were chosen that had glass transition temperatures (Tg) significantly lower than that of the PS grade (108 °C), with which they would be blended. Our previous research [16] showed that this PS/SIS combination formed phase separated blends. The two grades were 5127 with a Tg of 10 °C and 7125 with a Tg of −15 °C: for the remainder of this paper these will be designated as high Tg and low Tg.

Two forms of rigid fillers were used in this study, in the form of glass spheres and glass fibres. The spherical glass spheres, grade UB-02M, were obtained from Unitika, Ltd. and were selected for the narrowness of its size distribution, but mainly to retain consistency with previous studies where they were used in a coated form [13]. The beads were made from a Barium titanate glass with a density of 4.2 $gcm^{-3}$ and had an average diameter, measured using a standard particle sizer, of 42 μm. The glass fibres (E glass) were supplied by Asahi Fiber Glass Co. Ltd and had a diameter of 10 μm and an average aspect ratio of 20.

### 2.2. Sample manufacture

#### 2.2.1. Production of the composite blends

Two stages were involved in the preparation of the composite samples, namely preparation of the matrix (PS/SIS blends) and subsequent incorporation of the fillers into these blends. Both of these stages were carried out using a Europrism twin screw extruder set to a temperature of 220 °C.

The matrix for all the composite samples considered here was a blend of the PS and the SIS triblock, so these materials needed to be blended as a prerequisite to composite production. A premix, at the desired PS/SIS ratio, was first produced by weighing pellets from the two components. These hand mixed pellets were then introduced at the start of the extruder using a controlled speed feeder. The blended extrudate was passed directly into a water bath and then immediately chopped into pellets. Two blend ratios of PS/SIS were prepared, namely 90/10 and 80/20 by volume. As described in a previous publication [16], these blends were phase separated comprising distinct zones of the SIS rubber within the PS matrix as also previously reported by Matsuo [17].

The second stage was to blend the particles into the chosen matrix. For this stage, the blended extrudate pellets of the matrix were reintroduced at the start of the extruder barrel while the particles were introduced between the second and third mixing zones using a controlled feed from a second hopper. The mass feed rates of the two hoppers were first calibrated, so a range of mass fractions of the final composite could be achieved. Particle volume fractions between 0 and 40% were prepared for the various blends. Final particle fractions were determined by measuring the sample densities and knowing the densities of the various phases. Table 1 shows the four different composite systems that were investigated.

#### 2.2.2. Preparation of samples for the viscoelastic testing

Pellets of the blended composites were placed between brass plates in a hot press set at a temperature of 180 °C and then pressed for four minutes before slow cooling to room temperature under pressure. Spacers were placed between the brass plates to achieve the required specimen thickness for the subsequent tests.

### 2.3. Dynamic mechanical thermal analysis (DMTA)

The viscoelastic tests were carried out in rectangular torsion using a Rheometrics Dynamic Spectrometer RDS II. Samples of the required dimensions (10 mm wide, 1.4 mm thick and 55 mm long) were cut from the compression moulded sheets. Samples were tested over a range of temperatures (between −40 and + 70 °C) at a frequency of 1 Hz and an oscillatory strain of 0.05%.

### 2.4. Morphology SEM and TEM

The morphology of the multi-phase blends was studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). For the SEM micrographs, the samples were prepared in two different ways. The chosen surfaces were first prepared using a cross section polisher (JEOL Ltd Model SM-09010), which irradiates the sample with an argon beam inside a vacuum chamber and produces a