# EXPERIMENTAL VERIFICATION OF INNOVATIVE MULTI-PHASE MATERIALS COMBINING HIGH VISCOELASTIC LOSS AND HIGH STIFFNESS

A.P.Unwin[1], P.J.Hine[1], I.M.Ward[1], M.Fujita[2], E.Tanaka[2] and A.A.Gusev[3]
1- Soft Matter Group, School of Physics and Astronomy, University of Leeds, Leeds, LS2 9JT, UK
2 - The Kaiteki Institute, Mitsubishi Chemical Holdings,
1-1 Marunouchi 1-chome, Chiyoda-ku, Tokyo, Japan
3 - Institute of Polymers, Department of Materials, ETH Zürich, 8093 Zürich, Switzerland

**Keywords:** viscoelastic loss, strain magnification, particle composites

**Abstract**
In this work we present experimental data for a range of composite materials where the aim was to achieve high viscoelastic loss without significantly sacrificing composite stiffness. The material comprised rigid spheres coated with a thin viscoelastic polymer, and then incorporated into a polystyrene matrix. The dynamic torsion results for the coated particle system, at a range of particle fractions, showed a significant amplification of the viscoelastic loss at a temperature 25°C higher than the Tg of the coating. Importantly, this high loss was achieved without significantly sacrificing composite stiffness, with the composite stiffness around twice that of the pure polystyrene matrix. It was shown that the experimentally measured effects for all the systems were in excellent agreement with 'n-layered' micromechanical, or composite sphere model, analytically solved by Herve and Zaoui and so can be considered to be due only to micromechanical geometrical effects..

## 1. Introduction

There is still considerable interest into research to discover new materials that are able to quickly damp structural vibrations as this can be a major source of undesirable environmental noise. Moreover, a key goal is to have materials that have both a high stiffness (and hence can be used in structural applications) together with a high viscoelastic loss to enhance damping. This combination is highly desirable but it is a scientific challenge to develop such materials that simultaneously possesses these two requirements, namely high stiffness and high dynamic loss, as they are normally mutually exclusive.

A well-established method for achieving a combination of good stiffness and loss is to use laminates composed of a viscoelastic lossy layer sandwiched between stiffer layers (and non lossy) layers. [1-3]. Often enhanced structural damping can be achieved by attaching a visco-elastic layer to the structure and then capping this with a stiffer outer (metal) layer. This technique of enhanced energy is often referred to as loss amplification.

In a number of recent publications, using a combination of finite element studies and numerical micromechanical modelling, Gusev has investigated a number of different multi-phase composite system that could offer such a combination of high stiffness and visco elastic loss, but where the constrained layer is achieved throughout a sample, and on the sub-micron level. [4-7]. The most promising system that was proposed by Gusev, comprised stiff spherical particles in a glassy polymeric matrix, where the particles were first coated with a thin (sub-micron) viscoelastic polymeric layer.

A key parameter to emerge from these theoretical and numerical studies was the thickness of the visco-elastic layer. In particular, reference 7 predicted that the optimum amplification of the loss modulus, E'', occurred at a ratio between the coating thickness Δ to particle radius R of $\Delta/R \sim 0.01$. At this same ratio of $\Delta/R$, the value of the storage modulus E', was predicted to be significantly higher than for the pure, unreinforced, polymer. In our recent studies, which are described here (and for example) we have concentrated on experimental validation of these numerical predictions, using a variety of model systems based on a polystyrene matrix incorporating coated rigid particles.

## 2. Experimental details

### 2.1 Materials

#### 2.1.1 – Coated glass beads in a polystyrene matrix

The chosen composite matrix was polystyrene (grade BASF PS2). The viscoelastic coating was a water soluble polyurethane (Hydran AP40F). It was chosen to have glass transition temperature (Tg ~ 50°C) above room temperature but below that of the polystyrene matrix. To achieve the desired ratio of coating thickness to particle radius ($\Delta/R$), we chose a relatively large particle as the reinforcement. These were barium titanate beads (grade UB-02M average diameter 42μm). The beads were coated using a POWREX spray coater (MP MultiPlex). The target coating thickness was of the order of 200nm, which required a 0.22% suspension of the polyurethane. Spraying was carried out at 30°C followed by drying at 80°C. Figure 1 shows an SEM picture of a coated bead inside a manufactured sample, indicating that the coating survived the various manufacturing processes and was of the order of the set target value of ~200nm in the final composite blend.

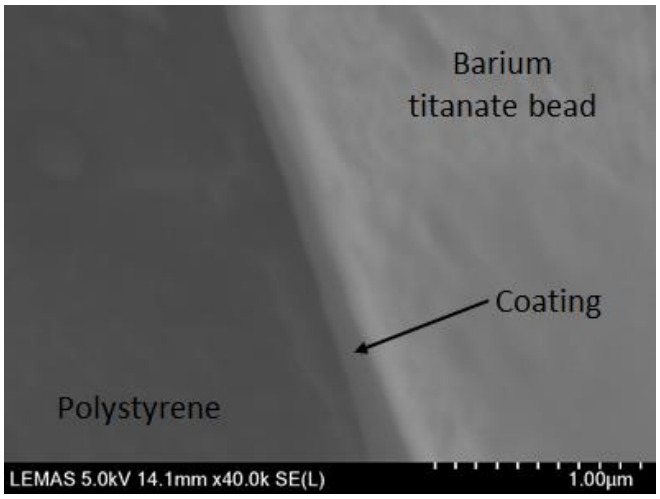


**Figure 1**: Image of a coated bead from a manufactured composite

### 2.2 Sample manufacture

Blends of the various particles and their corresponding matrices were manufactured using a Europrism twin screw extruder at a range of particle fractions. The twin screw extruder was also used to blend the PS and the triblock rubber for the uncoated particle systems (in a weight ratio of PS/rubber of 90/10). The resulting pellets were then compression moulded into samples for dynamic testing. A range of particle volume fractions was manufactured between 21 and 35%.

### 2.3 Viscoelastic testing

Viscoelastic tests were carried out in rectangular torsion using a Rheometrics Dynamic Spectrometer RDS II. Samples were tested over a range of temperatures (between +30 and +110°C) at a frequency of 1Hz and an oscillatory strain of 0.05%.

## 3 Experimental results

### 3.1 The properties of the composite components

Figure 3 shows dynamic torsion results for both the polystyrene matrix and a sample of the pure coating material. The results show that the coating has a loss peak (glass transition temperature) close to 50°C and lower than the polystyrene matrix (which is around 108°C).

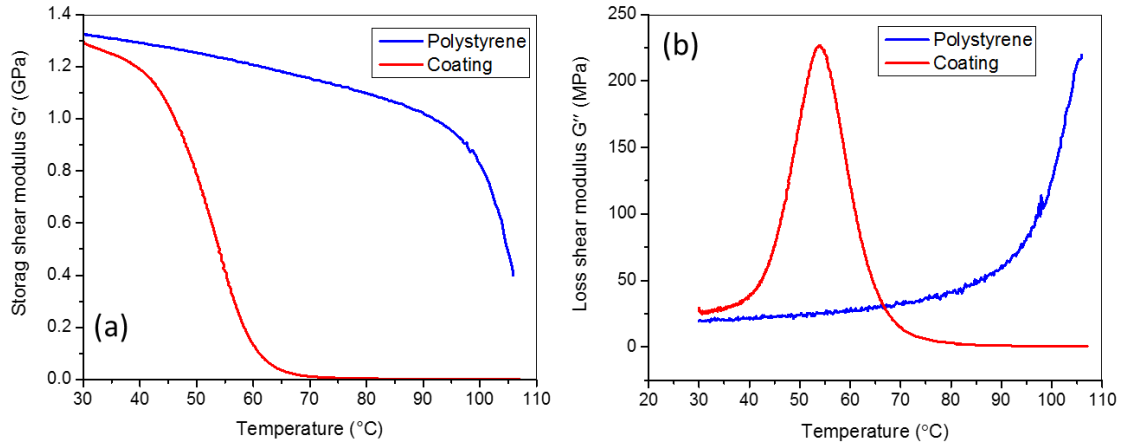


**Figure 3**: Dynamic torsion results comparing pure polystyrene and a sample of the pure coating material (a) storage shear modulus G' (b) loss shear modulus G''

### 3.1 The effect of particle volume fraction

Figure 4 shows a series of dynamic torsion results for a range of composite systems with coated particle volume fractions up to 35%. Figure 4a shows the storage shear modulus, G', and Figure 4b the loss shear modulus, G''. For G' it is seen that below the glass transition temperature of the coating, the composite modulus increases with increasing particle fraction, up a factor of close to 2. On the other hand, for the loss shear modulus, G'', there is the appearance of a large loss peak which we associate with the thin coating layer. Interestingly, it is seen to occur at a significantly higher temperature than for the pure coating sample (Figure 3b), around 25°C higher in fact. Also, the results show that the height of the loss peak increases as the particle volume fraction (and hence the overall fraction of the viscoelastic coating) is increased. Most importantly, at the temperature where the viscoelastic loss is at a maximum (~75°C) the storage shear modulus is still higher than the pure polystyrene matrix (nearly a factor of 2 again).

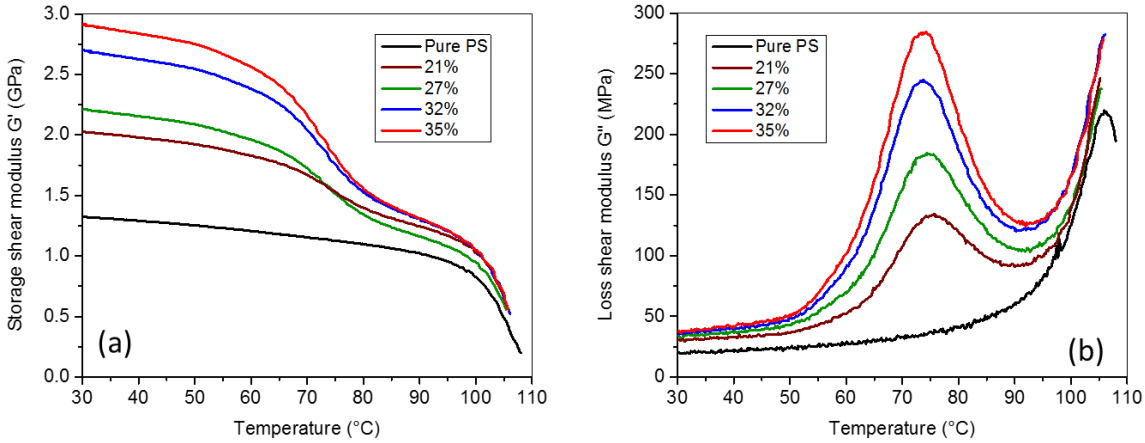


**Figure 4**: Dynamic torsion results comparing pure polystyrene and composite blends with a range of particle volume fractions from 21 to 35%. (a) storage shear modulus G' (b) loss shear modulus G''

### 3.3 A comparison with numerical modelling

As the motivation for this work came from previous numerical modelling studies, it was obviously of interest to compare the experimental results in Figure 4 with numerical predictions based on the n-layer model solved by Herve and Zaoui [8]. The numerical estimates were determined based only on the geometry and the properties of the three materials in the bulk (pure polystyrene, barium titanate beads and the viscoelastic coating). The most important variable is the thickness of the coating layer $\Delta$, and its ratio with the particle diameter R, $\Delta/R$. Here we used a value for $\Delta$, of 200nm, mainly from the evidence from the SEM pictures (Figure 1).

Figure 5 shows a comparison of experimental measurements and numerical predictions for the highest particle fraction (35%). The results compare a pure polystyrene sample (black line), experimental measurements for a composite blend with a coated particle volume fraction of 35% (red line) and numerical esrtimates (blue dotted line) for the same composite. Figure 5a shows the storage shear modulus G' and Figure 5b shows the loss shear modulus G''. The Figure shows that the agreement between the experimental measurements and the theoretical predictions is striking, both in terms of the amplitude and the position of the loss peak. Interestingly, the micromechanical model predicts the same upwards shift in the Tg of the composite system (of 25°C) as measured experimentally, based only on the bulk mechanical properties and the geometry. The agreement shown in Figure 5 suggests that the properties of the thin coating layer is not markedly different to the bulk, and that also the coating thickness must be fairly consistent, and that the loss amplification effect is purely determined by the micromechanical geometry for this coated particle system.

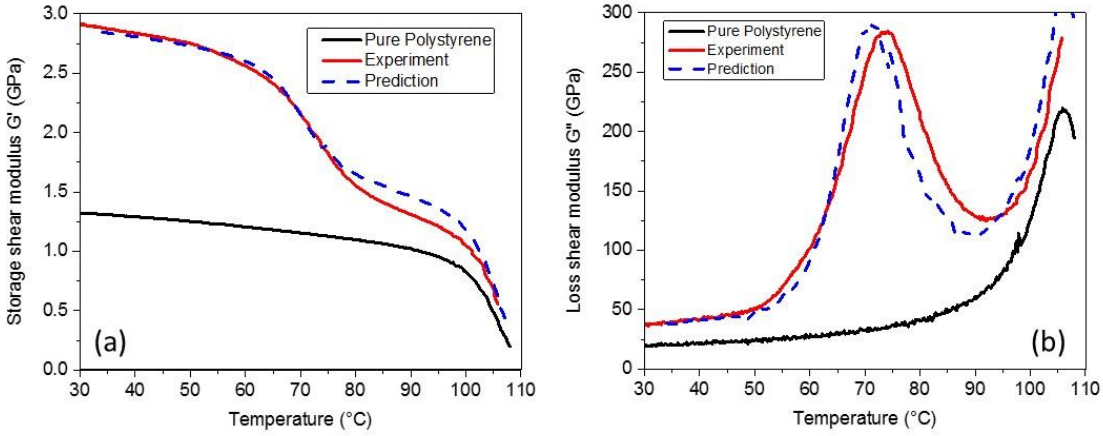


**Figure 5**: Dynamic torsion results comparing pure polystyrene and a composite blend with 35% coated barium titanate beads. (a) experimental and numerical predictions for the storage shear modulus G' (b) experimental and numerical predictions for the loss shear modulus G''

In subsequent research we have shown that a similar effect can be achieved by incorporating **uncoated** particles (both spherical and cylindrical) into a matrix composed of the same polystyrene but blended with a polystyrene/polyisoprene/polystyrene (SIS) triblock co-polymer that phase separated on processing. This builds on previous work on this blended material [9] and these results will also be presented at the conference.

## 4 Conclusions

In this study we have investigated the viscoelastic behaviour of a range of multiphase composite materials, which incorporate rigid coated particles into a polystyrene matrix [10]. DMTA torsion measurements showed that these composite materials displayed a novel combination of high shear stiffness and high viscoelastic loss. In particular, a second, highly amplified, loss peak was seen. For the composite system we attributed this unexpected behavior to the viscoelastic coating layer. The use of a numerical micromechanical model showed that the experimental measurements (both stiffness and loss) could be very accurately predicted based only on the bulk properties of the three components and the geometry. The numerical model was able to accurately predict both the amplitude of this novel effect, and the shift upwards of this peak, by a temperature of 25°C compared to the bulk coating material.

## Acknowledgments

The initial impetus for this work came from the discussions with Prof. G.H. Fredrickson of UCSB (Santa Barbara, U.S.A.) and this work was sponsored by The Kaiteki Institute, Mitsubishi Chemical Holdings, Japan.

## References

1. Ungar, E.E., *Noise and vibration control enginnering: Principles and Applications.* Noise, ed. L.L. Beranek, and Ver, I.L.,. 1992, Chichester: Wiley.
2. van Vuure, A.W., I. Verpoest, and F.K. Ko, *Sandwich-fabric panels as spacers in a constrained layer structural damping application.* Composites Part B-Engineering. 32: p. 11-19 2001.

3. Alvelid, M. and M. Enelund, *Modelling of constrained thin rubber layer with emphasis on damping.* Journal of Sound and Vibration. 300: p. 662-675 2007.
4. Gusev, A.A., *Micromechanical mechanism of reinforcement and losses in filled rubbers.* Macromolecules. 39: p. 5960-5962 2006.
5. Gusev, A.A., *Time domain finite element estimates of dynamic stiffness of viscoelastic composites with rigid spherical inclusions.* International Journal of Solids and Structures. 88-89: p. 79-97 2016.
6. Gusev, A.A., *Controlled accuracy finite element estimates for the effective stiffness of composites with spherical inclusions.* International Journal of Solids and Structures. 80: p. 227-236 2016.
7. Gusev, A.A., *Optimum microstructural design of coated sphere filled viscoelastic composites for structural noise and vibration damping applications.* International Journal of Solids and Structures. 128: p. 1-10 2017.
8. Herve, E. and A. Zaoui, *N-layered inclusion-based micromechanical modelling.* International Journal of Engineering Science. 31: p. 1-10 1993.
9. Unwin, A.P., P.J. Hine, I.M. Ward, O.A. Guseva, T. Schweizer, M. Fujita, E. Tanaka, and A.A. Gusev, *Predicting the visco-elastic properties of polystyrene/SIS composite blends using simple analytical micromechanics models.* Composites Science and Technology. 142: p. 302-310 2017.
10. Unwin, A.P., P.J. Hine, I.M. Ward, M. Fujita, E. Tanaka, and A.A. Gusev, *Escaping the Ashby limit for mechanical damping/stiffness trade-off using a constrained high internal friction interfacial layer.* Scientific Reports. 8: p. 2454 2018.