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Predicting the visco-elastic properties of polystyrene/SIS composite blends using simple analytical micromechanics models

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Abstract

This paper is concerned with the prediction of the viscoelastic properties of rubber filled polymer blends. The question asked was as follows. Can the temperature dependent viscoelastic properties of phase separated polymer blends be adequately predicted using only a rational two phase micromechanics based analytical model with no empirical fitting parameters? In particular using only a knowledge of the individual bulk phase properties and the blend microstructure, but without any further detailed polymer physics knowledge such as the presence of an interphase region or any additional nanoscale structures within the separated rubber phase with the properties different from those of the two bulk phases?

Blends of a polystyrene matrix and phase separated rubber inclusions (a polystyrene-polyisoprene-polystyrene triblock polymer (SIS)) were manufactured in a range of blend fractions (up to 20 vol. % of the triblock co-polymer). Experimental measurements, for the storage modulus G' and the loss tangent tanδ, of both the individual phases and the blends, were made using dynamic mechanical tests over a range of temperatures from -50 to +70°C.

Numerical predictions, of the same parameters, were first obtained using the generalised self-consistent Christensen and Lo model which uses a simple representative volume element (RVE) of an isolated sphere of the minority rubber component in a surrounding sheath of polystyrene matrix embedded in a homogeneous effective medium. The agreement between the Christensen and Lo model and the experimental measurements, for G' and tanδ, was found to be excellent for rubber contents up to 10%. For a 20% rubber content, an improved prediction was obtained by altering the RVE to include the observed effect of having a polystyrene central core in a number of the dispersed rubber zones at this rubber fraction, using the Herve and Zaoui generalization of the Christensen and Lo model. Although conjoined (and therefore non-spherical) zones became more prevalent at the highest rubber content, use of the Tandon and Weng model showed that this shape anisotropy would not be expected to affect the viscoelastic properties.

1 Introduction

A well know strategy to optimise material behaviour is to mix together two components with disparate mechanical properties in order to produce a 'composite blend' which builds on the best aspects of both phases [1, 2]. Published work is extensive, from the early work studying the various morphologies produced in polystyrene or high impact polystyrene blends (for example [3-5]) to much more recent work where researchers have continued to search for new processing methods [6] to optimise performance. The final morphology of the multi-phase material, including the size and shape of the phase separated minority component [5], is an important aspect in controlling the balance of mechanical properties and depends on a number of factors including the fraction of the two components and their relative viscosity in the melt. A phase separated rubber structure, on the length scale of a micron, has been shown by many authors to help impact performance by inducing additional energy absorbing mechanisms such as craze initiation and shear yielding [7, 8].

The continuing development of new blend materials is significantly aided by the use of modelling, which allows a wide range of variables to be studied without the need to manufacture and test each particular material. One of the most cited early models was that proposed by Nielsen [9], for predicting the elastic shear modulus of a matrix containing spherical inclusions. However, and in common with a number of other early semi-empirical models on which it was based [10, 11], the model contains an unknown parameter, in this case the limiting packing fraction for the inclusions, which is often found by 'fitting' experimental data. Subsequently the modelling approaches have often added additional complexity, either by utilising finite element techniques [12] or adding an interphase region between the matrix and inclusions (e.g. Diamant et al [13]). Other authors (for example Wang et al [14] and most recently Alam et al [15]) have pursued the use of analytical models with no unknown parameters to predict both elastic and latterly viscoelastic properties. Wang et al developed a quasi-sphere model [14], while Alam et al [15] used the Herve and Zaoui model [16], termed the *n*-layered model, to predict the viscoelastic properties of Hot Mix Asphalt (HMA).

A validated analytical model, with no unknown or 'fitting' parameters, is preferable to an FE approach as it permits a fast solution to be obtained, allowing a wide range of parameters to be efficiently explored by the engineer or designer. Such an approach is available to all researchers, rather than just those who have a vast array of parallel processors so for this reason we have followed this philosophy in this work. Inspired by this, in a recent paper [17] Gusev used detailed finite element simulations to show that the Christensen and Lo model [18] gave very accurate predictions of composite elastic stiffness over a wide range of spherical particle fractions. In a follow up paper [19] Gusev also used time domain finite element simulations to show that the Christensen and Lo model could similarly be used for excellent predictions of viscoelastic properties of such spherical particle reinforced composites, utilising the viscoelastic correspondence principle.

In the spirit of these previously published works we have investigated the accuracy of a range of analytical models for predicting viscoelastic properties (the storage modulus G' and the loss tangent tanδ) starting first with the Christensen and Lo model and then comparing the predictions with experimental measurements. Additional insight into the link between composite microstructure and viscoelastic behaviour was accomplished using two other well known 'elastic' analytical micromechanical models (again containing no empirical fitting parameters) together with the correspondence principle. First, the Tandon and Weng model [20], which was used to assess the effect of having non-spherical inclusions at higher rubber fractions. Secondly, the *n*-layered model of Herve and Zaoui [16] (which is an extension of the Christensen and Lo model) was used to assess a refinement of the isolated spherical inclusion microstructure (observed in SEM pictures) where some of the rubber inclusions are themselves filled by a polystyrene core.

2 Modelling

In previous purely theoretical studies, [21-23], Gusev and co-workers investigated the viscoelastic properties of composite materials, comprised of glass spheres coated with a 'lossy' layer in a polymeric matrix. In those theoretical studies, a combination of finite element and micromechanical modelling methods were used to explore the behaviour of these materials. It was shown that the chosen micromechanical model, which was the 'n-layered', or composite sphere, model analytically solved by Herve and Zaoui [16], could provide almost identical results to a finite element approach but with a fraction of the numerical effort required [23]. The n-layered model contains no empirical parameters. As input it requires the volume fractions of the constituent phases and their respective bulk and shear moduli. As output, the model yields the effective bulk and shear moduli. The previous studies also made use of the elastic-viscoelastic correspondence principle [24, 25] where the phase elastic moduli are replaced by a complex form incorporating both elastic and loss components.

The success of this approach prompted us to ask the question whether this model could also predict the viscoelastic properties of a polymeric matrix filled with dispersed rubber particles. In the first instance a model with an even simpler RVE was assessed, namely the Christensen and Lo model, on which the n-layered model of Herve and Zaoui is based upon. The RVE of the Christensen and Lo model is shown in Figure 1a, where a central spherical inclusion, radius R_1, is surrounded by a matrix sheath of radius R_2, which is then surrounded by an effective medium: the fraction of the spherical inclusion is given by the ratio of $\left(\frac{R_1}{R_2}\right)^3$. For solving, the medium is subject to uniform strains at infinity and the displacement and stress continuity conditions at interfaces are solved self-consistently by requiring that the average strain energy density stored in the multi-layered inclusion be the same as that in the effective medium at infinity. In the current study the Christensen and Lo model was used to produce numerical predictions of the storage shear modulus (G') and the loss tangent (tanδ) of the chosen model system for a range of dispersed rubber particle fractions from 3 to 20%.

As with all modelling approaches, there are a number of assumptions that were made. The first is that the real material can be represented by this simple RVE composed of a single isolated rubber inclusion surrounded by a sheath of pure polystyrene as shown in Figure 1a. Secondly, as normal to most simulations, it is assumed that there is a perfect bond between the various phases. Thirdly, that there is no transition or diffuse boundary layer between the two phases. Early models for predicting the properties of phase separated blends used discrete separate components. However, as the field has progressed, more involved models have been developed that, for instance, involved the location of a diffuse boundary layer between the two phases as described by Diamant et al [13]. However the properties of this layer are often unknown and are used more as a fitting procedure to match to experimental results. In our opinion, a model without this complexity (and the added empiricism) would be preferable if the predictions can be proved to be adequate.

The fourth main assumption is that the properties of the two phases, that comprise the blend, are the same as those measured for the two individual ‘pure’ components. This is obviously a key point and has a number of important aspects. First, as shown by a typical TEM picture of the phase separated blend as seen in Figure 2c, there is a very fine (nanoscale) level of structure within each phase separated rubber zone. Although such nanostructures have been researched extensively and reported in the literature (e.g. Fredrickson and Bates [26]), in this work we decided to see first if the macroscopic viscoelastic properties could be predicted in the absence of this detailed structural knowledge.

The fifth assumption is that the model predictions are due only to micromechanical effects. It is well known that polymers under confinement, approaching molecular dimensions, can see changes in dynamics and properties such as the glass transition temperature (T_g) [27]. However, in this study the properties of the phase separated rubber zones, whose size can approach 100nm, is proposed to be identical to that measured experimentally for the macroscopic SIS rubber sample (which has centimetre dimensions).

The sixth, and final assumption, is that we have assumed that the bulk modulus, K, which is required for the predictions, is both elastic and temperature independent (although it is known that there is some change through Tg [28]). As part of a recent paper on modelling composites with spherical inclusions, Gusev [19] showed that there was no measurable difference in predicted viscoelastic properties when using either a temperature independent real bulk modulus, or a more realistic complex temperature dependent value. From this previous work, the value used here for the bulk modulus was 4GPa.

As will be seen from the results section, the agreement with the predictions from the Christensen and Lo model was good for rubber concentrations up to 10%, but showed some differences at a rubber concentration of 20%. For this reason, two additional analytical models were used to investigate further aspects of the effects of the blend morphology on predicted viscoelastic properties. The first was the Tandon and Weng model [20], which is well known to give excellent predictions for the elastic properties of short glass fibre reinforced composites (for instance from our own work [29]) although to our knowledge this model has not been used for the prediction of viscoelastic properties of polymer blends. The Tandon and Weng model was used here to assess whether consideration of particle shape anisotropy would change the numerical predictions for the 80/20 blend. Isotropic predictions, using anisotropic shaped rubber zones, were formed by rotation averaging the Tandon and Weng five independent stiffness constants, as we previously validated using experimental measurements [30] for elastic properties.

The final analytical modelling route that was used, was due to Herve and Zaoui [16], and is termed the *n*-layered model. This model is an extension of the Christensen and Lo model, but using multiple layers (Figure 1b) rather than just a single spherical inclusion. This was motivated by SEM pictures which suggested polystyrene cores in a number of the dispersed rubber zones (Figures 2a and 2b). This model requires the same inputs as the Christensen and Lo model and also produces the same outputs for G' and tanδ.

3 Experimental

3.1 Materials

The matrix used was a commercially available polystyrene, BASF PS2 with a weight-average molecular weight (Mw) of 274 000 g/mol and a polydispersity of 2.74. The dispersed phase was a triblock thermoplastic rubber and had the chemical structure polystyrene/hydrogenized polyisoprene/polystyrene (polystyrene/polyisoprene/polystyrene – termed SIS) and was obtained from Kurary Co Ltd. The particular grade used (5127) was chosen because it had a quoted glass transition temperature (Tg) of 20°C, close to room temperature and separated significantly from the Tg of the polystyrene (108°C), with which it would be blended. This symmetric SIS triblock has a total fraction of polystyrene in the end blocks of 20%.

3.2 Sample manufacture

3.2.1 Production of the composite blends

Manufacture of the blends was carried out using a Europrism twin screw extruder set to a temperature of 220°C. The extruder had an L/D screw ratio of 40:1 and was operated at a screw speed of 300rpm for all the blending experiments. The extruder screws were set up with three mixing zones and the extruder allowed material to be added at the entry side of any of these mixing zones.

A premix, at the desired polystyrene/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, so the material passed all three blending zones. The blended extrudate was passed directly into a water bath and then immediately chopped into pellets. Three blend ratios of polystyrene/SIS were prepared, namely 97/3, 90/10 and 80/20 by volume. It was observed that the blended materials were white in appearance, as opposed to the pure polystyrene which was transparent, suggesting phase separated structures within the blended material of the order of the wavelength of light, which was later confirmed by SEM and TEM morphology studies.

3.2.2 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. Samples of the pure polystyrene and pure SIS materials were produced in a similar fashion using temperatures of 180°C and 120°C respectively.

3.3 Dynamic mechanical testing (DMTA)

The majority of the viscoelastic tests were carried out in rectangular torsion using a Rheometrics Dynamic Spectrometer RDS II. Samples of the required dimensions (10mm wide, 1.4mm thick and 55mm long) were cut from the compression moulded sheets. Samples were tested over a range of temperatures (between -50 and +70°C) at a frequency of 1Hz and an oscillatory strain of 0.05%. This level of strain was chosen so as to achieve a balance between producing a high enough strain to give a measurable force, while remaining in the linear regime and keeping the normal force to a minimum.

To determine the properties of the thermoplastic rubber above its glass transition, additional tests were carried out using a parallel plate testing geometry (25mm diameter and 1.4mm thick) on a MCr502 rheometer. The details for the parallel plate tests were a temperature rate of 1 C/min, a frequency of 1 Hz, a constant shear stress amplitude of 300Pa and a normal force of 5N. Tests were carried out between room temperature and 70°C.

3.4 Morphology by SEM and TEM

The morphology of the multi-phase blends was studied using two different techniques at two length scales: scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in order of increasing magnification. For SEM study, surfaces for analysis were first prepared using a cross section polisher (JEOL Ltd Model SM-09010). This equipment irradiates the sample with an argon beam inside a vacuum chamber and is able to produce a flat surface for examination without the plastic deformation often seen in other preparation techniques (for example freeze fracture). Following the polishing, the samples were subjected to ion-beam milling. This technique preferentially etches away any softer components allowing for contrast and visualisation of the morphology of the composite materials. The TEM studies were carried out using a JEM1230 (JOEL Ltd). The prepared microtomed slices were stained with osmium tetroxide. The dispersed rubber phase was preferentially stained darker by this technique.

4 Results

4.1 Morphology

Before presenting the experimental and modelling results, it is worth examining the morphologies created in the model blends. Figure 2a (magnification x20,000) shows a typical SEM image for the 80/20 blend, taken after cross section polishing and ion milling, which preferentially etches the minority rubber component, seen as the darker phase here. The image shows detail of the phase separated rubber zones. The majority of the zones are roughly spherical in shape and in the range of half a micron and smaller, although there are some elongated zones, mostly below an aspect ratio of 3:1. There is seen to be no preferred orientation of the elongated zones. An interesting aspect seen at this magnification is the presence of some polystyrene rich regions within the phase separated rubber zones, which show as lighter in colour due to being more resistant to the preparation etching procedure.

Figure 2b shows a similar picture for the 90/10 blend at a slightly lower magnification of x8,000, although taken using TEM. The overall structure is very similar, with a range of rubber particle sizes from 1μm and lower. In this particular region, the elongated rubber regions show a preferential alignment, but analysis of a range of such regions showed no overall preferred orientation direction.

Figure 2c shows another TEM image containing a roughly spherical rubber region, but at a much higher magnification (x100,000). At this magnification it is seen that there is a further level of nano-structure located within the phase separated rubber zones. It is clear that the triblock nature of the rubber itself forms a structured nanostructure, where the darker regions are the isoprene fraction, which themselves form aligned structures within the phase separated rubber. The shape of these internal nano-structures are seen to template on the boundary of the separated rubber zones. The proposition of this work is that these nano-structures can be disregarded and that the properties of the rubber component are the same as those measured from a bulk sample.

4.2 Mechanical behaviour

4.2.1 Torsion tests on the pure SIS triblock rubber

Figure 3 shows the experimentally measured results for the pure triblock rubber using the two different test methods: rectangular torsion from -50°C to +18°C and parallel plate measurements from +18°C up to +70°C. For the storage modulus (G’) the data from the two different tests was found to match perfectly (Figure 3a), with just a small temperature shift of 3°C. It was decided to shift the parallel plate data up to match the rectangular torsion data as it is this latter measurement that will be used to characterise all the composite blends. For tanδ, there was a small gap where the data was not considered reliable from either test (between +18 and +23°C). For the rectangular torsion test, above 18°C, the material became too soft to get good loss measurements. Conversely, for the parallel plate tests, the tanδ results became very noisy below +23°C (as can be seen from the data), although the measurements did give a good indication of the maximum value of the peak in tanδ. It was decided to bridge this gap in the loss tangent measurements using a parabolic cap function as shown by the dark line in Figure 3b. As a check, the G’ and tanδ results were used to predict the values of the loss modulus G’’, in this missing temperature range. Figure 3c shows that this combination gave an excellent bridge for the loss modulus G’’ in this temperature gap. It was decided to use only G’ and tanδ for the remainder of this study. The results from Figure 3 form the inputs for the modelling predictions (along with similar measurements on pure polystyrene, see Figure 4), and comparison with experimental measurements on the composite blends, which will be reported in section 5.

4.2.2 Torsion tests on the composite blends

The two left hand graphs on Figure 4 show the rectangular torsion measurements for the pure polystyrene sample and the three polystyrene/SIS composite blends. For the pure polystyrene sample, it is seen that the values of G’ and tanδ do not change significantly over the measured temperature range of -50°C to +70°C. There is a small decrease in the storage modulus (G’) as the temperature heads towards the glass transition temperature of polystyrene (108°C) accompanied by a gentle rise in tanδ over the same measured temperature range.

The top left picture shows the storage modulus (G’) results for pure polystyrene and for polystyrene/SIS blends of 3%, 10% and 20% of rubber. As would be expected, the storage modulus in the blends shows a transition at a temperature around the glass temperature of the triblock rubber. As the fraction of the rubber was increased, the modulus fell at all temperatures, with a much larger drop above the glass transition of the rubber.

The bottom left picture shows the measured loss tangent (tanδ) for the four materials. The blends all showed a peak in tanδ associated with the phase separated rubber. This is a distinct transition, well away from the peak of the pure polystyrene phase. This distinct peak would, itself, be a strong signal of a separated phase, even without the evidence from the micrographs shown in Figure 2. The height of the peak increases significantly with the increasing fraction of the triblock rubber, with an associated small increase in the peak position with respect to temperature.

5 A comparison between experimental measurements and modelling predictions

5.1 Christensen and Lo model – composite sphere model with all rubber core

Figure 4 also shows the predictions from the Christensen and Lo model (right hand two graphs) for the storage modulus and the loss tangent. It is clear that there is good qualitative agreement between the experimental measurements and modelling predictions. Above the glass transition temperature of the rubber, the predicted plateau shear modulus of the blend is shown to fall as the percentage of rubber is increased, in agreement with experimental measurements. The peak in tanδ is predicted to increase in magnitude as the percentage of rubber increases, as seen experimentally. The predicted amplitude of the tanδ peak is also at the appropriate magnitude.

To get a better comparison of the experimental and model predictions for the 80/20 blend (where the discrepancy between experiments and model predictions is largest), the results are replotted in Figure 5. For the storage modulus, G', the agreement is excellent below Tg, but above Tg the experimentally measured plateau modulus is lower than predicted by the Christensen and Lo model. For the loss tangent (tanδ), the peak height is well predicted by the numerical model. The experimental results are, however, broader towards the higher temperature side of the transition.

In summary, the simple RVE of the Christensen and Lo model predicts the viscoelastic properties of the polystyrene/SIS composite blends well up to a volume fraction of 10% but shows some small differences at a rubber percentage of 20%. In this case, a more complicated microstructural RVE was assessed for its predictive capabilities, based on the observed morphology. The SEM pictures shown in Figure 2 suggest at least two aspects where the RVE could be altered to better reflect the micron level structure of the 80/20 blend.

1) Coalescence of dispersed spherical regions to form elongated zones, with aspects ratios between 2 and 3 (so two or three joined spherical zones). The pictures suggest no preferred orientation of these conjoined zones
2) A number of the larger rubber zones show the presence of a lighter material in the core, which we suggest could be polystyrene.

These two microstructural aspects are now assessed in the following two sections using two further analytical models.

5.2 Anisotropic particle shape and orientation – the Tandon and Weng model

The Christensen and Lo model is not able to predict the effect of particle shape anisotropy so another micromechanical model was required. In previous studies, we have shown that the model of Tandon and Weng [20], based on the ideas of Eshelby [31], gives excellent predictions for the effect of aspect ratio of rigid fibre inclusions. Eshelby considered an elasticity problem of a single ellipsoidal inclusion in an infinite matrix of a different material subjected to a uniform strain at infinity. One of his key theoretical results was to prove that the resulting strain in the inclusion was uniform and hence, there exists a tensor relating the two strains. However, for composites this Eshelby result is only strictly applicable to the dilute regime. Mori and Tanaka introduced a concept of the average strain in the matrix [32], which was then used to modify the Eshelby dilute approximation approach to yield the famous Mori-Tanaka model [33]. Tandon and Weng [20] simplified the expressions of the Mori-Tanaka model and presented a set of convenient equations, which are nowadays frequently termed the Tandon and Weng model. Many authors (for example Tucker and Liang [34]) consider the Tandon and Wemg model the best micromechanical model for predicting the elastic properties of the short fibre RVE. To our knowledge, this model has not been used to date for predicting viscoelastic properties of polymer blends. As with the Christensen and Lo model, this is complete analytical solution with no disposable parameters and so can be solved analytically. As input, the model requires the volume fractions of the phases, their elastic moduli and also the fibre aspect ratio. As output, the model gives five independent effective elastic constants of the aligned composite unit. Here we have once again used the correspondence principle to derive predictions for the five respective viscoelastic constants of the aligned composite unit. These five elastic constants were then rotationally averaged using the Voigt bound, which in a previous study [30] we showed was the most appropriate bound for determining the elastic properties of filled composites with an anisotropic particle shape. We first used an aspect ratio of 1, and compared the predictions to those of the Christensen and Lo model. The results for G' and tanδ were nearly identical for the two models and so are not shown here.

The Tandon and Weng model can now be used to assess the effect of anisotropic particle shape (but no preferred orientation of these shaped zones) on the two parameters (G' and tanδ). From the pictures shown in Figure 2, we have restricted ourselves to aspect ratios between 0.3 and 3 to span the likely range seen. Figure 6 shows these predictions, together with the experimental results for G' and tanδ. It is seen that an anisotropic particle shape, with aspect ratios comparable to those seen in the real materials, when rotationally averaged, does not change the predicted viscoelastic calculations.

5.3 Herve and Zaoui model – composite sphere with a polystyrene/rubber core

To address the second morphological aspect, namely the presence of a polystyrene core in the centre of some of the phase separated zones, we utilised the Herve and Zaoui [16] extension of the Christensen and Lo model, the *n*-layered model (Figure 1b). Here we have used a 3 layered representation, where the central sphere is polystyrene, surrounded by a sheath of the SIS triblock rubber, itself encased in a sheath of the polystyrene matrix. The radii in the model were varied to achieve the desired volume fraction of the two components. By inspection of the SEM pictures the fractions for the central polystyrene core were evaluated, between 20 and 40%.

Figure 7 shows the predictions from the Herve and Zaoui model (3 layered) in comparison with the experimental measurements for the 80/20 blend. It is seen that presence of the central polystyrene core at a level of 40% reduces the plateau modulus to that measured experimentally and also widens the tanδ peak, although not as much as measured experimentally. Using the Herve and Zaoui model, the presence of the polystyrene core showed a closer prediction of the experimentally measured storage modulus (G') and loss tangent (tanδ).

The excellent agreement between the experimental measurements and the numerical calculations shown in Figure 7 is a confirmation of the strategy of this paper, in that excellent predictions can be achieved using a simple analytical model and with the input phase properties based on bulk measured properties. However it is clear that if the size of the phase separated rubber particles were to be significantly smaller, and approach molecular dimensions of the order of tens of nanometres, then this simple strategy would likely not give such accurate predictions as the polymer dynamics would be affected. Additionally, such small nano-sized particles would also significantly increase the interfacial surface area between the matrix and particles, making this aspect much more important. In fact such nanocomposites have been extensively over the last ten years. In two very recent examples, Hattemer et al [35] used molecular dynamics simulations to highlight various synergistic effects that could occur at such small dimensions when polymer dynamics are affected. Similarly, Davris et al [36] studied filler size effects but for an inverted system to that studied here, with an elastomer filled with nano-sized rigid fillers. The results presented in this paper strongly suggest that provided the filler size remains of the order of fraction of a micron, then these effects can be discounted. It would be very instructive to create a range of samples with different particle sizes down to 10nm (but with the same separated rubber if feasible) in order to establish at which length scale the current modelling strategy would break down, and this will be the subject of future research.

7. Conclusions

In summary, this paper has explored the use of a rational two phase micromechanics based analytical model to predict the viscoelastic properties of a phase separated rubber filled polystyrene, with sub-micron sized particles. It has been shown, that the simplest model, of an all rubber spherical inclusion particle, can give excellent predictions of the storage modulus G' and the loss tangent tanδ for rubber fractions up to 10%, where this structure holds true. Above this rubber fraction, the predictions are good, although the experimentally measured plateau modulus is lower than predicted and the experimentally measured tanδ peak is broader. While at first sight this might be envisaged as being due to the rubber particles beginning to agglomerate at this higher rubber fraction, numerical modelling using a combination of the Tandon and Weng model and the Voigt orientation average showed that this would not explain the measured results. Instead, it was shown that the experimental results could be better predicted by the presence of a polystyrene core in some of the rubber particles, as seen from the morphological studies.

Overall the study showed the huge potential for a rational two phase micromechanics based analytical model to predict the viscoelastic properties of these blends, and also the capacity to very quickly assess how various morphologies might impact on measured properties, using the unaltered bulk properties of the two constituent phases. It is this latter aspect that makes these models so attractive to materials designers, offering the possibility to explore various combinations of phase properties and microstructures to search out novel combinations that might have unusual and unexpected viscoelastic performance. While it may be possible to get a 'perfect' match to experimental measurements if all aspects of the microstructure down to the nano-scale and all other issues are taken into account, the respectable accuracy of these simple models is already highly valuable in offering a way to quickly look for new materials with novel visco-elastic behaviour.

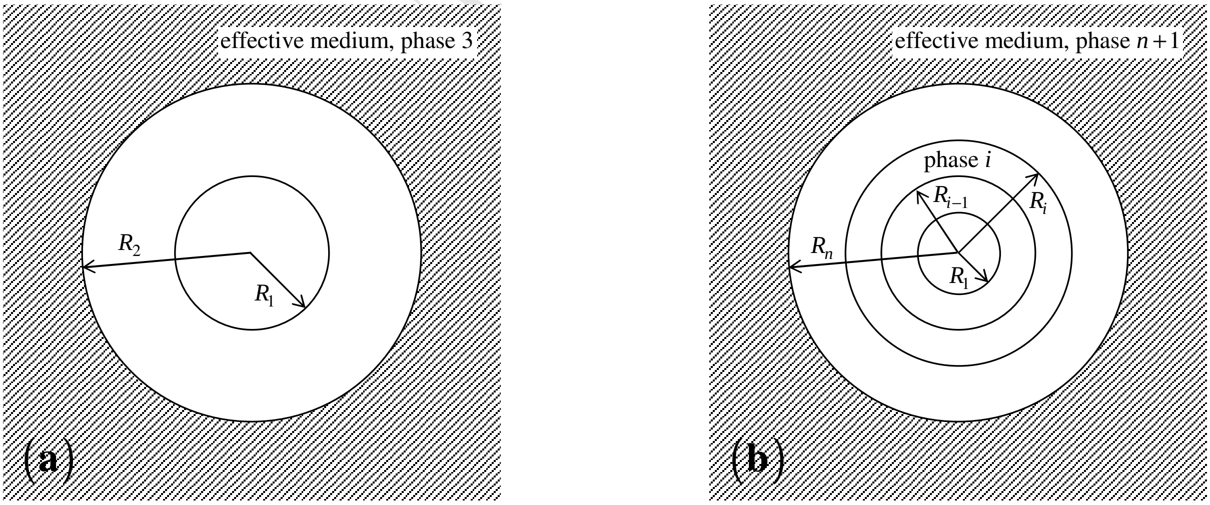

Figure 1: The representative volume elements used in the modelling

a) Christensen and Lo model b) Herve and Zaoui *n*-layered model.

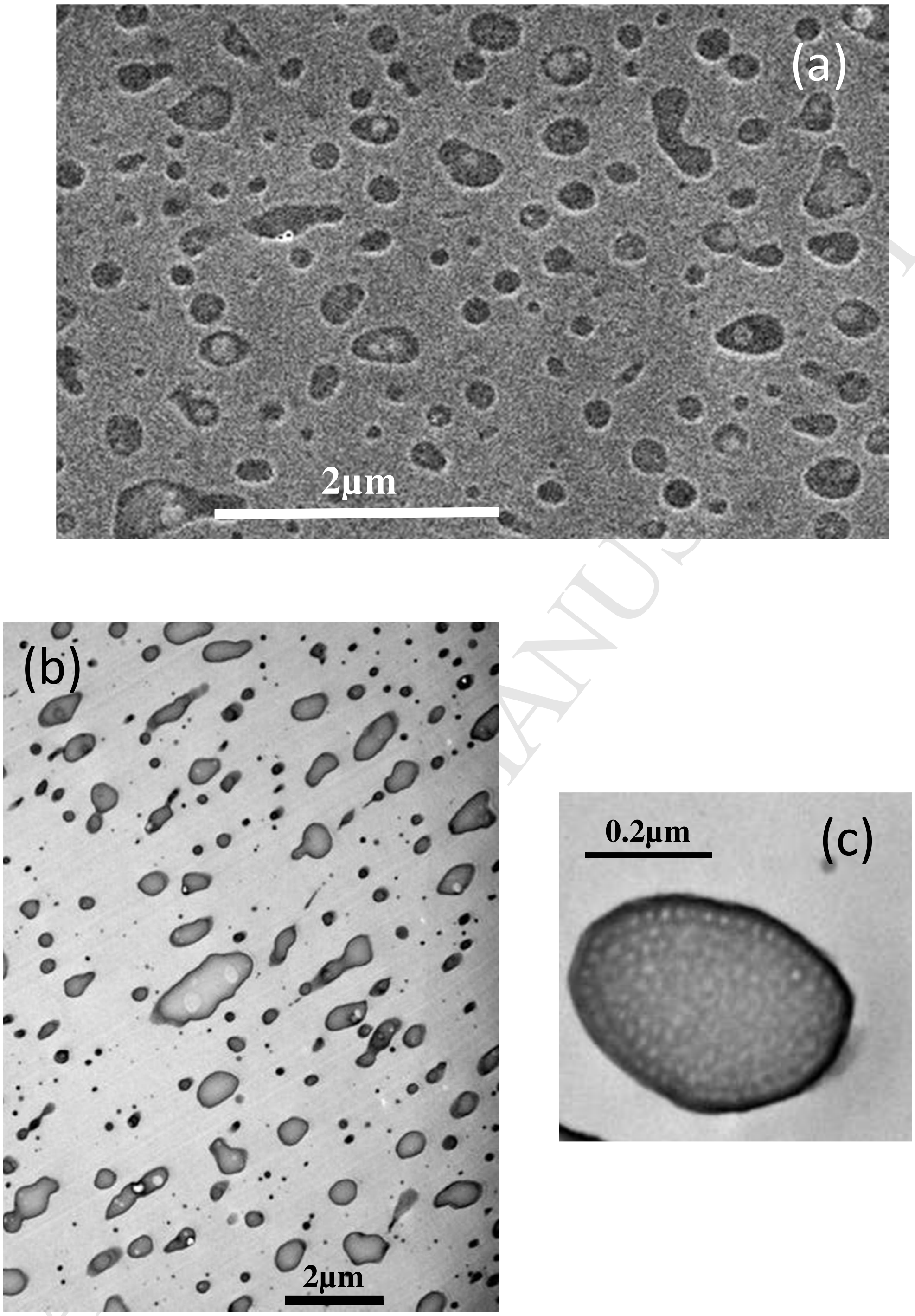

Figure 2: Aspects of the morphology of the phase separated blends

a) SEM picture of the 80/20 polystyrene /SIS blend

b) TEM picture of the 90/10 polystyrene/SIS blend

c) TEM picture of a phase separated rubber zone showing the internal microstructure.

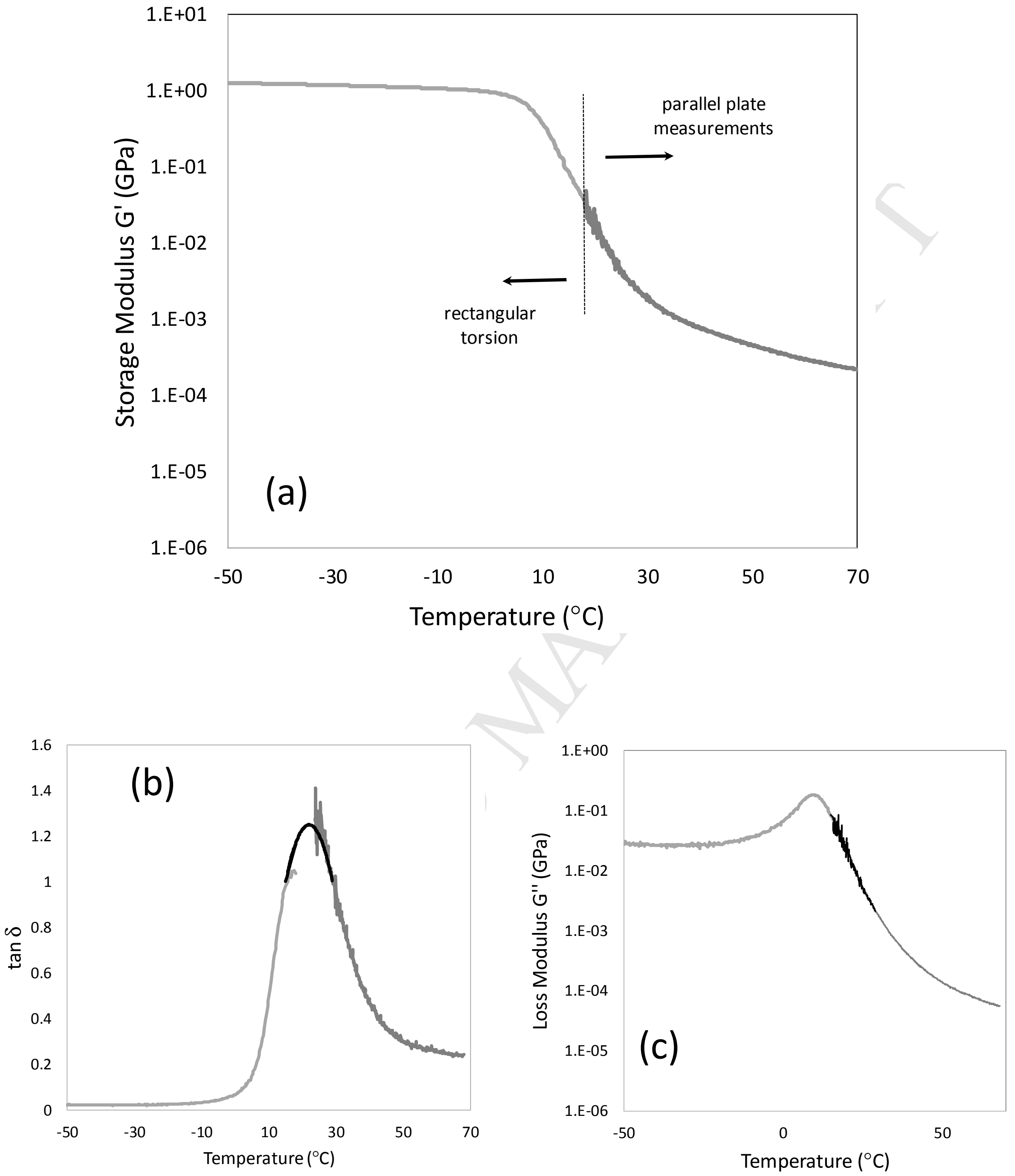

Figure 3: Storage modulus (G’), loss modulus (G’’) and loss tangent (tan δ) for the pure SIS triblock showing rectangular torsion measurements (below 18°C), parallel plate measurements (above 23°C) and the interpolated results (solid black line).

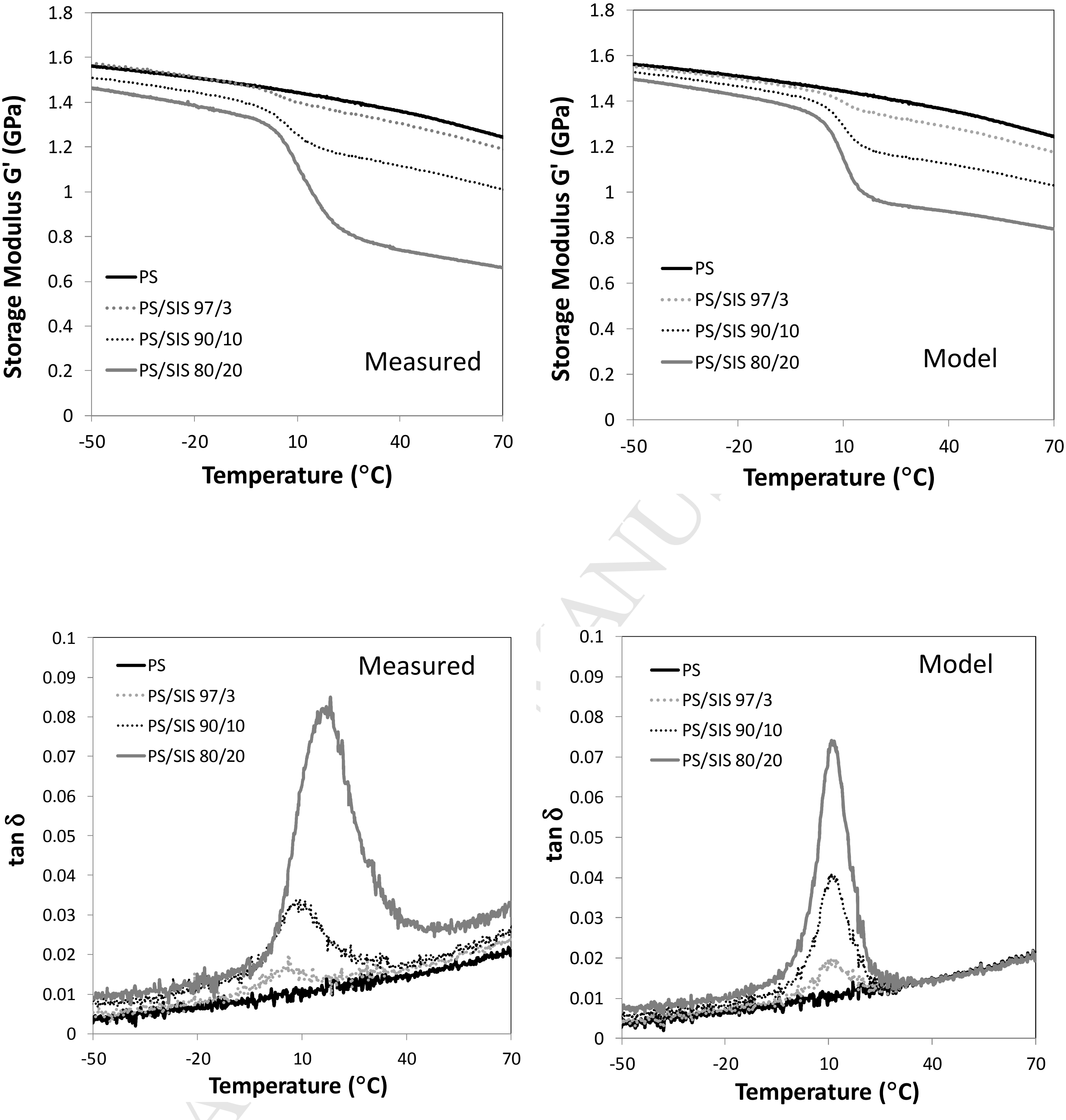

Figure 4: Storage modulus (G') and tanδ versus temperature for pure polystyrene (PS) and PS/SIS blends. The left hand graphs are the experimental measurements and the right hand graphs are the predictions from the Christensen and Lo model.

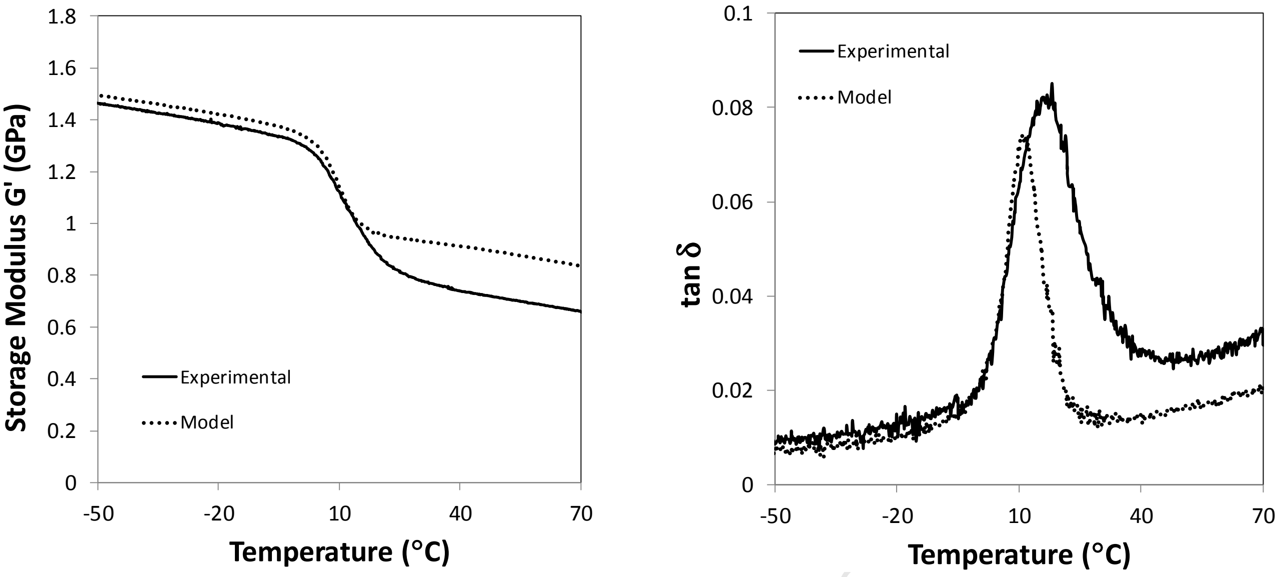

Figure 5: A comparison of the experimentally measured and Christensen and Lo model predictions of G’ and tan δ for the PS/SIS blend at a ratio of 80/20

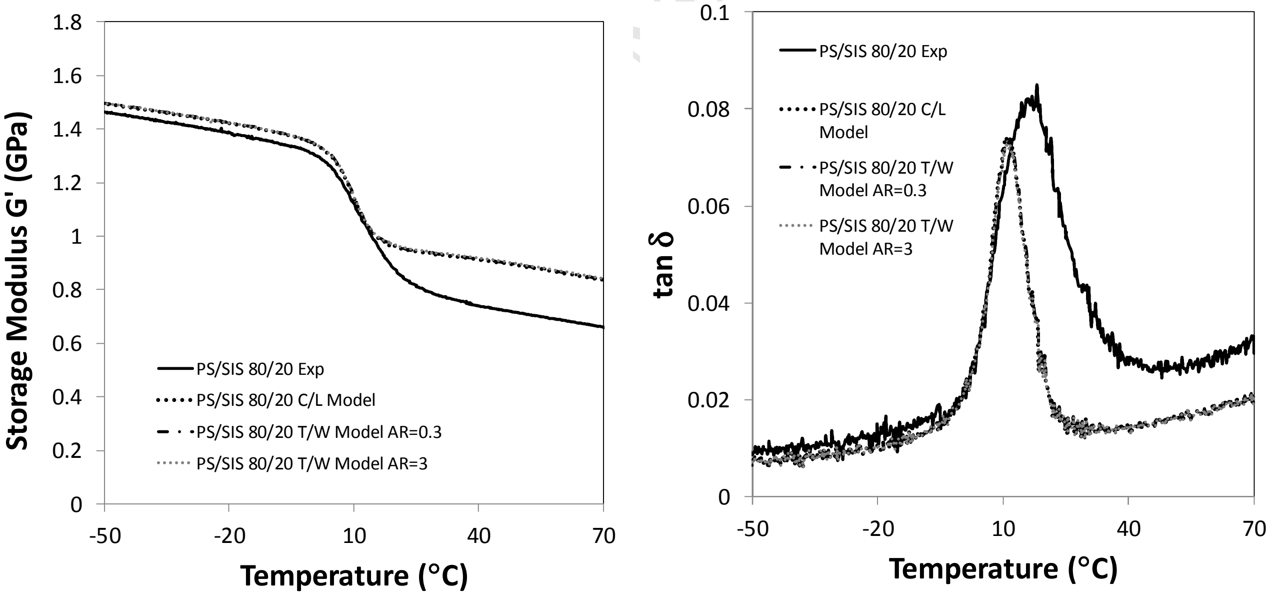

Figure 6: A comparison of the experimentally measured viscoelastic properties (G’ and tanδ) with the Christensen and Lo model (C/L) and a combination of the Tandon and Weng model (T/W, aspect ratios AR = 0.3 and 3) and the Voigt orientation average for the PS/SIS blend at a ratio of 80/20: All three models give almost identical predictions.

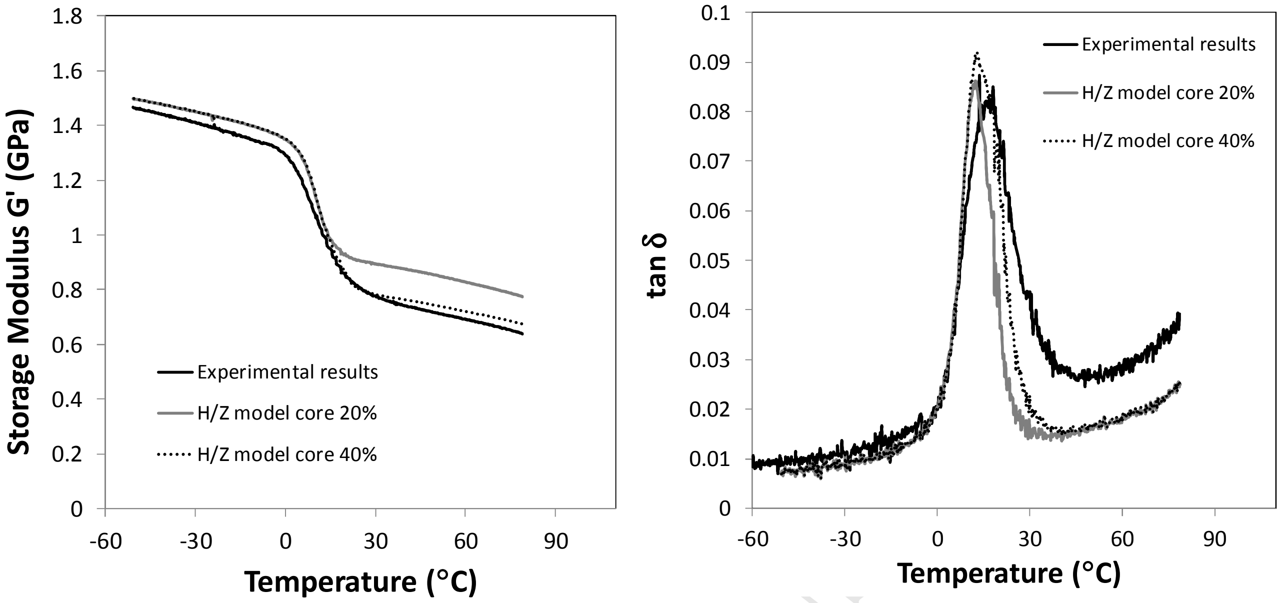

Figure 7: A comparison of the experimentally measured and Herve-Zaoui model (H/Z) predictions of G' and tan δ for the PS/SIS composite blend at a ratio of 80/20 with a polystyrene core for the dispersed rubber zones:

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