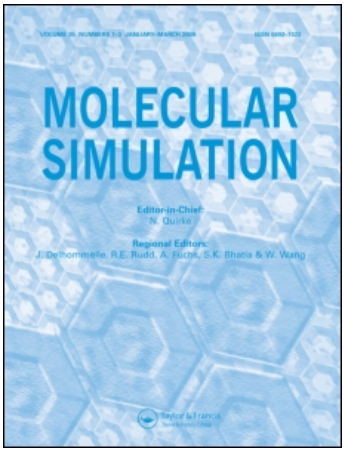

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Validating software and force fields for predicting the mechanical and physical properties of poly(bisbenzoxazine)s

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Validating software and force fields for predicting the mechanical and physical properties of poly(bisbenzoxazine)s

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Molecular models for two polymers, (**1**) based on the monomer 6,6′-bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)isopropane and (**2**) based on the monomer 6,6′-bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)sulphone, are imported from Cerius$^{2®}$ into Materials Studio®. Molecular dynamics (MD) and molecular mechanical analysis are performed on both models with the aim of validating the results produced by Materials Studio against previously recorded results from Cerius^2 and empirical data. MD results are obtained, which are in reasonable agreement with empirical data. For instance, Materials Studio predicts a T_g range of 188–196°C for polymer (**1**), which is within 11 K of the empirical value of 177°C, whereas for polymer (**2**), a T_g of 133°C is predicted, which is within 16 K of the empirical value of 117°C. Similarly, molecular mechanics simulations produce some encouraging results, predicting a Young's modulus of 5.9 GPa for (**1**), compared with the empirically measured value of 4.3 GPa.

Keywords: bisbenzoxazines; thermoset; molecular modelling; Materials Studio

1. Introduction

Poly(bisbenzoxazine)s (sometimes simply referred to as benzoxazines) are a family of thermosetting polymers that are made by step-growth ring-opening polyaddition from bisbenzoxazine monomers, which are themselves the products of the Mannich reaction between a bisphenol, formaldehyde and a primary amine [1].

Unlike many other thermosetting resins, which evolve condensation products such as water or ammonia, benzoxazine monomers react very cleanly to form a polymer without any reaction by-products [2]. The reaction used to make bisbenzoxazine monomers can also yield a proportion of dimers and oligomers, which can affect the properties of the resin before and during cure. The polarity of the solvent used in the reaction has a significant influence on the formation of dimers and oligomers; thus solvents of greater polarity assist bond formation between unreacted phenols and the heterocyclic benzoxazine ring, resulting in a greater yield of dimers and oligomers [1]. The monomer–oligomer ratio in the yield can also be influenced by using an excess of formaldehyde and amine during the synthesis. This alteration of stoichiometry causes the products to form via a different mechanism, resulting in a greater excess of monomer over dimers and higher oligomers [3]. Polymerisation of the monomer does not require the utilisation of strong catalysts, a characteristic with many advantages, i.e. not only is the material cost of the catalyst itself saved, but also the manipulation of possibly highly corrosive media is avoided and possible damage to processing equipment is not an issue. Furthermore, the environmental impact from producing benzoxazines is considerably less than a polymer that would require a strong catalyst [3].

This paper will be concerned with the modelling of two poly(bisbenzoxazines): the polymer made from 6,6′-bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)isopropane (Figure 1(a)), which shall hereafter be referred to as (**1**) and the polymer made from 6,6′-bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)sulphone (Figure 1(b)), which shall be referred to as (**2**). These two models were previously created in Cerius$^{2®}$ by Hamerton et al. [3] during an earlier piece of work to predict glass transition temperatures (T_g) and other mechanical properties including Young's modulus. The simulations carried out in Cerius^2 were carried out using the Dreiding force field. These modelling experiments have been repeated in Materials Studio® using the universal force field (UFF) and the polymer consistent force field (PCFF), so that comparisons can be made between the two modelling packages and the force fields.

The Dreiding force field and UFF are older ones than PCFF and are classified as class I force fields. To calculate energies, they use general force constants and geometry parameters based on simple hybridisation rules parameterised from experimental observations of vibration spectroscopy, gas-phase molecular structures, thermodynamic properties and crystal structures. However, class II force fields (including PCFF) use tailored rules based on quantum mechanics for specific atom interactions [4–6]. The Dreiding force field is best suited towards molecules

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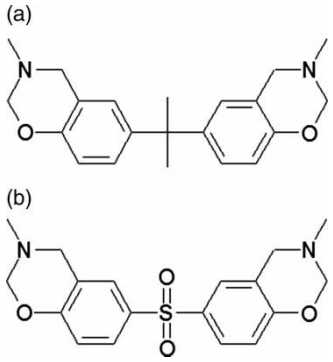

Figure 1. (a) 6,6′-bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)isopropane monomer and (b) 6,6′-bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)sulphone monomer.

containing carbon, nitrogen, oxygen and hydrogen atoms, with only limited application within geometries, conformational energies, intermolecular binding energies and crystal packing. The Dreiding force field has recently fallen into disuse since the introduction of the more universally applicable class II force fields [4–6].

The UFF is also a class I force field [6]; it has been parameterised on element, hybridisation and connectivity to cover the whole periodic table and has been validated for main group compounds, organic molecules and metal complexes. The downside of the UFF is that, with the aim of being able to simulate any system, it is not as accurate as a force field designed specifically for one class of molecule or compound [6,7].

Polymer consistent force field is an evolution of its predecessor, CFF91. It was designed to work well with polymers and organic materials such as polycarbonates, melamine resins, polysaccharides, lipids and nucleic acids with much validation work already carried out [6]. Advancing from the older class I force fields, it can produce good results for cohesive energies, mechanical properties, compressibilities, heat capacities and elastic constants. It is worth mentioning that, although not used in the study, the condensed-phase optimised molecular potentials for atomistic simulation studies force field (COMPASS FF, a newer version of PCFF) is now considered a superior tool for working with polymer models [6].

1.1 Modelling of thermoset polymers

When thermosetting (i.e. network forming) polymers are considered for molecular modelling, there are various constraints and approximations which need to be applied to make the task achievable. The most striking difference between network polymers and many of the other substances, which are modelled, is their sheer size. Unlike a drug, protein or linear polymer, it is impossible to consider the system as a discrete molecule as there is only one enormous molecule in a sample of network polymer. By far, the most common method for modelling network polymers is to create a unit cell that could be considered representative of the polymer bulk. Then periodic boundary conditions are applied, so the cell is modelled like a large sample and not a nanoparticle [3,8–10].

Like many other network polymers, benzoxazines are amorphous, meaning they show no inclination towards crystallinity in the solid state, consequently representing their structure within a periodic cell could lead to inaccurate calculations. It can be considered though, that if the repeated unit cell is sufficiently large, then the periodic crystallinity will be over such a large range as to be negligible. It can be very time consuming and difficult to create a cell of such size from scratch because there can be many hundreds of atoms that need individual placement and connection. One approach to simplify this task is to create a less complex cell containing a smaller number of monomer units. This cell is constructed in such a manner that multiple copies can be positioned adjacent to the first and bonds connected to make a single ‘supercell’.

Although in the first instance this is creating crystallinity, a high-temperature molecular dynamics (MD) simulation will allow the model to take on a more amorphous character because the individual cells within the supercell are allowed to behave differently and become random in their conformation and the effect of this can be seen in Figure 2(a) and (b). The number and arrangement of unit cells used to make the supercell is obviously a careful consideration point. The size of the supercell is a simple trade-off between computational resources and required accuracy. Clearly, using a small number of unit cells will be less processor intensive, but will possibly return unusable results [3]. On the contrary, too many unit cells can produce excellent results, but on a timescale that is impractical. With regard to the shape of the supercell, it is thought that a supercell with sides of equal length would be optimum, as this will maximise the distance in any direction before the cell is repeated.

Molecular modelling can be used to determine several properties about polymers by simulation and calculation. Of these, perhaps the most important are the T_g and Young’s modulus, since these relate to the potential technological application of the material [8]. The importance of T_g lies in its importance in determining the temperature range in which the polymer can be processed and utilised [8]. Thus, being able to determine the T_g of a novel polymer by computational methods would be a great benefit when screening candidate structures for further investigation. Instead of calculating the glass transition temperature from parameters, the MD method can be utilised with a molecular model to estimate T_g [3] without such extensive knowledge of the polymer chemistry. MD will simulate the location and velocity vector for each atom within the model over time under specified conditions. This method can be used to calculate T_g by running

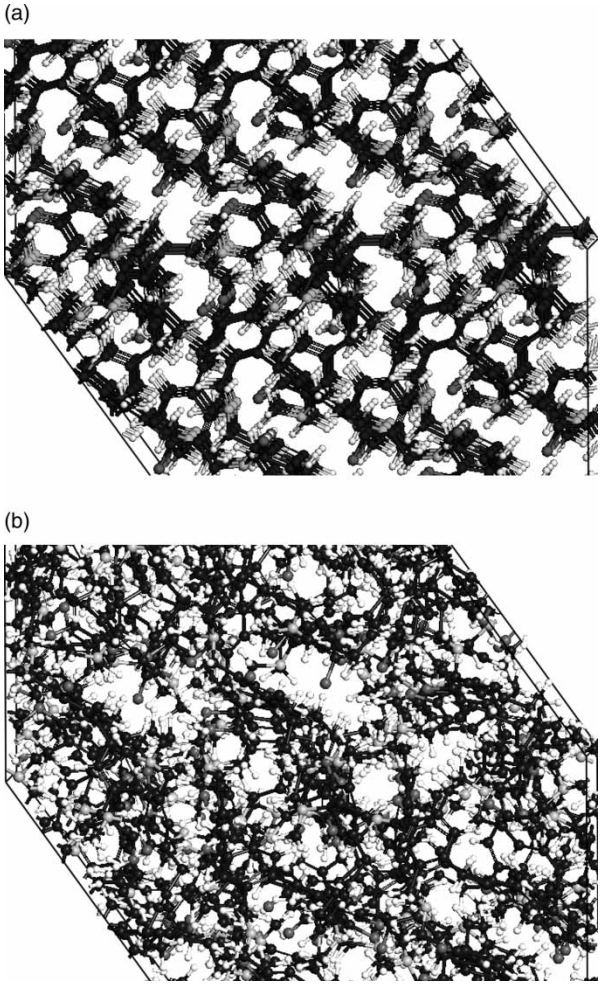

Figure 2. Molecular model of (**1**) (a) before and (b) after high-temperature molecular dynamics.

simulations at various temperatures and taking readings for volume. These data can then be used to plot a graph and T_g can be estimated as the point of intersection between the thermal expansion gradients for above and below the glass transition temperature [9]. To find the two thermal expansion gradients, the datasets will need to be subdivided into two groups, for above and below T_g, but naturally at this stage the T_g is unknown. This requires a number of possible graphs to be drawn up, each splitting the data at a different temperature. This set of graphs can then be compared visually and by correlation coefficients to determine which should be used to define the range of T_g.

From these graphs, the volume thermal expansion coefficient (α) can be calculated from the gradient using Equation (1)

$$\alpha = \frac{1}{V}\left(\frac{\delta v}{\delta T}\right)_P, \quad (1)$$

where V is the volume, T is the absolute temperature and the system is barostatic at pressure P. The volume thermal expansion coefficient is useful in molecular modelling because it can be compared with literature or experimental data for the material as a means of validation [9,11]. It should be noted, however, that MD simulations can be very computationally intensive, and accurate results can sometime take weeks or months to produce [3].

Young's modulus is a measure of the stiffness of a material and is an important property to consider when choosing a material for a specific application. The modulus of a material can be calculated from the molecular structure using the Discover module in Materials Studio. The objective of these small-scale simulations is to reproduce the observed mechanical properties; by these means the process can then be made truly predictive. The ultimate aim of simulation is to ensure that there are no motions in the bulk sample, which are not reproduced in the model.

2. Computational methodology

Two computers were used for this work: a client PC running Materials Studio (Accelrys Software Inc., San Diego, CA, USA) under a Windows environment and a server for processing the calculations. The server was using a dual-core, Intel Pentium D CPU 3.40 GHz processor running at 2289 MHz with 2016 Mb RAM and a Linux operating system.

The molecule files used in this study were previously created in Cerius[2] using the Dreiding force field. Initially, a two-dimensional model of each monomer was constructed using the 'Crystal Builder' module in Cerius[2] (using the three-dimensional (3D) builder module) on an atom-to-atom basis to form a bisbenzoxazine dimer with explicit hydrogen atoms and with each benzoxazine ring left as a non-bonded group. Energy minimisation was performed on this molecule using the second derivative method until it achieved convergence to an RMS force of 0.01 kcal/mol. Three further monomers were added to form a pentamer and this structure (termed a single 'unit cell') was minimised until convergence, again to an RMS force of 0.01 kcal/mol. In order to apply periodic boundary conditions, periodic cells were constructed in which the oligomeric chains contained within the cells were 'manually' linked together by breaking and forming the appropriate bonds, thus forming a 'cross-linked', 3D network. Thus, two cells were visualised in the x-axis by moving necessary bonds close to one another and removing cell boundaries, and the 3D lattice was then built up by connecting the nitrogen atoms on non-bonded benzoxazine rings and non-bonded carbon atoms in the benzoxazine dimer, across the x-, y- and z-directions of the structure. At each stage, the growing group of unit cells were subjected to energy minimisation, so the energetically optimised conformation of the polymer was obtained. Additional unit cells were added to make a 3D model (i.e. a super unit cell comprising 27 individual units)

[3]. These molecule files were in the format used by Cerius[2] and needed to be imported into Materials Studio; this was done using Materials Visualizer, a constituent of Materials Studio.

The geometry was then optimised using Materials Studio's Forcite module with the following settings:

- UFF with default settings;
- Ewald summation for van der Waals forces;
- dynamic cell dimensions and angles;
- smart algorithm, which is a cascade of the steepest descent, adopted basis Newton–Raphson, and quasi-Newton methods;
- maximum iterations unlimited and
- 'ultra-fine' convergence tolerance;
  - $< 2 \times 10^{-5}$ kcal/mol energy variance;
  - < 0.001 kcal/mol/Å force variance and
  - $< 1 \times 10^{-5}$ Å displacement variance.

Once the cell geometry had been optimised, MD simulations were carried out for the prediction of glass transition temperatures using the Forcite module running the 'UFF' on medium quality. Van der Waals forces were controlled by Ewald summation. The simulation was run as an NPT ensemble, keeping the number of atoms, pressure and temperature constant. Although the volume of the cell could change, the cell angles and hence the shape were fixed, unlike an NVT ensemble where the volume and shape of the cell are kept constant. An external pressure of zero was barostatically maintained. The simulation was run for 25 ps with a 1 fs time step, temperature was controlled by the Nosé thermostat (Q ratio $= 1.0$) and pressure was controlled by the Berendsen barostat (decay constant $= 0.1$ ps).

To predict T_g, MD simulations were run at the following temperatures in the order shown: (temperatures measured in degrees celsius)

(**1**) 427, 327, 277, 252, 227, 202, 177, 152, 127, 102, 77, 27

(**2**) 427, 327, 277, 227, 202, 177, 152, 127, 102, 77, 52, 27, − 23, −73.

The simulation was continuous, with the final state of the previous simulation trajectory used as the start state for the next.

Young's modulus and other elastic properties were calculated using the static elastic properties analysis within the Discover module using the PCFF at medium quality. This analysis is performed on a single conformation of the model at 0°C, and the program will return values for the elastic properties without a need for further calculation.

3. Results and discussion

The results from the simulations are displayed in Figures 3(a) and 4(a) with SD error bars and best-fit thermal expansion gradients for above and below T_g. It is noteworthy that the results from the 427°C simulation were left out from the thermal expansion gradient calculation because at this temperature the polymer may well be involved in a transition separate from the glassy–rubbery transition. This step was still important from the perspective of the whole simulation though because it helped to give the model more amorphous character. The low-temperature points were also excluded from the results because it was desired to base the best-fit line on the results we had confidence in belonging to the linear part of the volume–temperature curve.

3.1 Analysis of polymer cured from 6,6′-bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)isopropane (1)

To determine T_g from the data, two best-fit lines must be drawn, one representing the thermal expansion below T_g, and one representing thermal expansion above T_g. Soldera et al. [12] have published a method which uses the top and lowest five points in the VT curve to plot the lines and get the intersection point, T_g. The point at which to make this cut-off is typically not known, and so several different possible cut-off points were tried. This set of graphs is analysed visually, and the R^2 correlation coefficients were used to accurately find the point of gradient change. From these trials, the intersection points of the best graphs were taken to give two possible T_g values, 188 and 196°C, with greater confidence in the prediction of 188°C from R^2 correlation coefficients (Table 1). This can be considered as a T_g point of 188°C or, more correctly, a T_g range of 188–196°C.

The cut-offs that gave rise to a predicted T_g of 188°C displayed a higher R^2 correlation coefficient product, which means higher confidence in the data; hence, it was chosen for comparison with previous work conducted by Hamerton et al. [3] (Figure 3(a) and (b)). The comparison of these two graphs shows a very close similarity in T_g values, with the intersection for the new data at 188°C compared with a temperature of *ca.* 180°C from the older work.

It can be seen from the graphs that quite different temperature regimes were investigated. The earlier experiments were taken over a broader temperature range of 600 K with points generally 50 K or more apart, whereas the recent work focused attention over a range of 300 K with points generally 25 K or more apart. This new approach was considered an improvement as more data were obtained closer to T_g where they are more relevant. Furthermore, when the temperature deviates greatly from T_g, the polymer will be involved in other transitions that will disrupt the linear thermal expansion, which is required to obtain an accurate intersection point.

Although the R^2 correlation coefficients and SDs were not calculated for the previous work, a visual inspection of Figure 3(a) and (b) clearly shows how Materials Studio

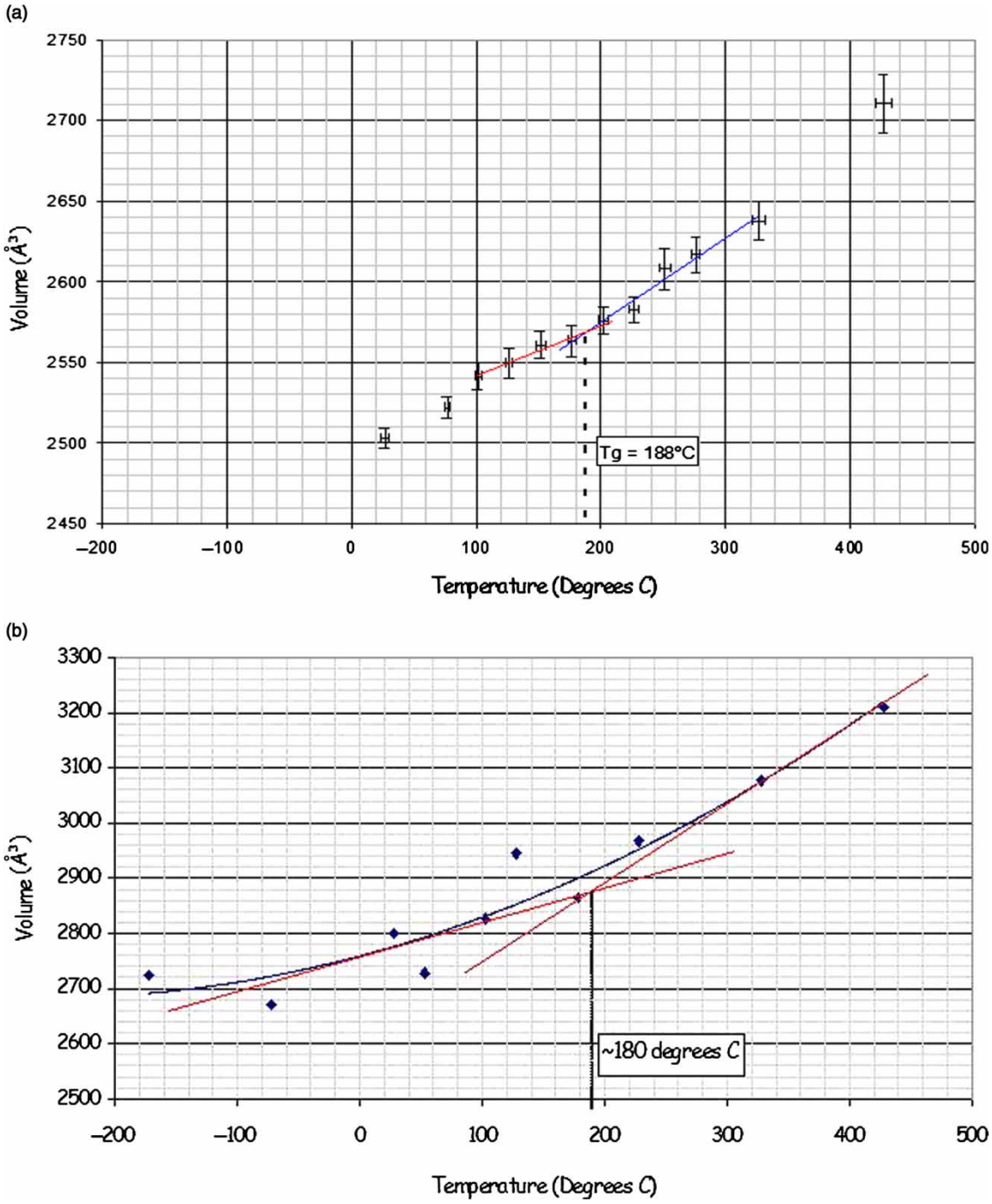

Figure 3. Change in cell volume with temperature from (a) recent work with (**1**), showing SD with error bars, and from (b) previous work with (**1**) [3].

yields results that are more self-consistent than those calculated by Cerius[2].

The simulation data for (**1**) can be compared with the empirical differential scanning calorimetry (DSC) data obtained in previous work [3]. The T_g of 188°C determined in the simulation is quite comparable with the DSC T_g range of 163–177°C (10 K/min heating rate, 5 min isothermal hold at 250 K, cooling at −10 K/min). A common feature of simulations in the recent and previous work is that the predicted T_g is higher than the empirical value for T_g. It is thought that the defect-filled amorphous structure of the cured plastic containing solvent molecules and unreacted groups will have a lower T_g than the defect-free, slightly crystalline structure (an artificial construct), which

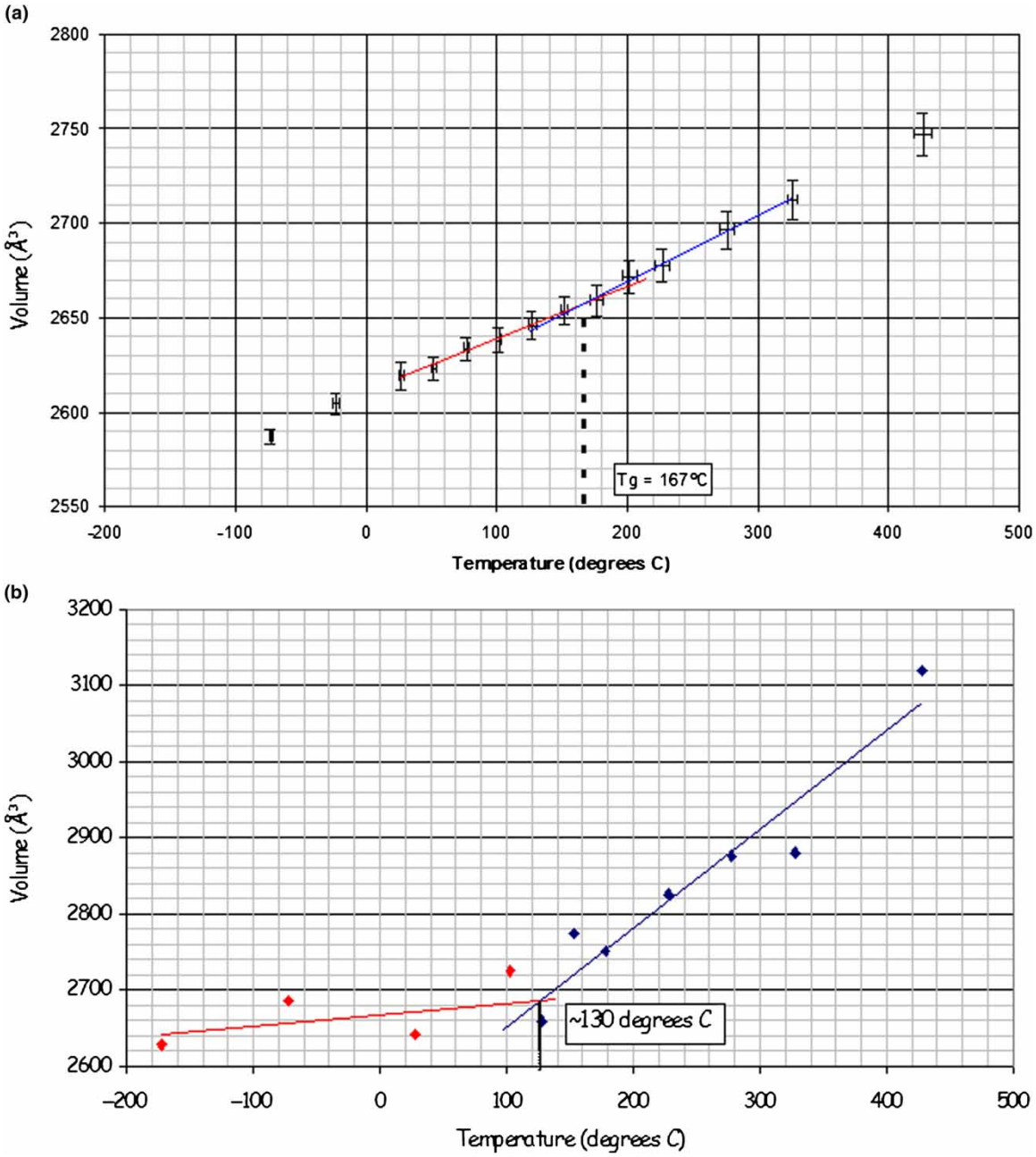

Figure 4. Change in cell volume with temperature from (a) recent work with (**2**), showing SD with error bars, and from (b) from previous work with (**2**) [3].

is actually being modelled. This discrepancy between the physical material and the molecular model is something that will need to be addressed if the accuracy of the results is to be improved.

The densities of the models at 0°C as predicted by Materials Studio (1.03 g/cm^3) and Cerius^2 are both lower than the empirically measured value of 1.12 g/cm^3 [11] (Table 2). The reason for this lower-than-expected density could be explained by the fully cured and slightly crystalline model, allowing cavities to be held open by the structure, whereas a true sample would have a little more freedom, allowing it to pack more tightly. It could also be true that impurities such as solvent molecules and moisture (which are not represented in the models) could pack in the cavities, increasing the mass without significantly affecting the volume.

Materials Studio also has the ability to calculate effective isotropic elastic constants from a molecular model and these are displayed with the constants that were calculated by Cerius^2 and empirical data from Ishida et al.

Table 1. Summary of data.

Parameter	Materials Studio®		Cerius^2 [3]		Empirical data [3,11]	
	(**1**)	(**2**)	(**1**)	(**2**)	(**1**)	(**2**)
T_g range (°C)	188–196	133–167	–	120–150	–	–
T_g point (°C)	188	167	180	130	177	117
Density (g/cm^3)	1.03	1.14	0.93	1.15	1.12	–
Bulk modulus (GPa)	4.12	3.37	36.3	17.6	–	–
Poisson's ratio	0.29	0.31	0.29	0.23	–	–
Lamé constant λ (GPa)	2.75	2.40	24.5	15.7	–	–
Lamé constant μ (GPa)	2.06	1.46	23.6	11.0	–	–
Young's modulus (GPa)	5.92	3.82	48.0	30.0	4.3	–

in Table 2. Although the data are in the right vicinity, with both programs producing parameters in the GPa range, the correlation is not sufficiently close to make effective use of these data, with the obvious exception of Poisson's ratio. Unfortunately, there is not a large amount of empirical data available for these materials, which could be used to verify which modelling software attained the more accurate results. There was, however, an empirical value for Young's modulus of (**1**) and, although it would be preferable to compare a number of other cell parameters as well, it would suggest that Materials Studio is producing notably more accurate results. The slightly higher result for Young's modulus over the empirically measured value is to be expected for the same reason that the T_g values were high, the defect-free system will always be stronger than the actual material that cannot cure to a 'perfect', fully cross-linked structure.

3.2 Analysis of polymer cured from 6,6′-bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazinyl)sulphone (2)

The methods for analysing and processing the data for (**2**) were the same as those used with (**1**). The data can be considered to represent a T_g range of 133–167°C with the point of gradient change more likely at 167°C. The comparison of the best fit for the recent work with the previous work (Figure 4(a) and (b)) can be considered in two different ways. The initial impression is that the two graphs do not show an overwhelmingly good correlation, and this may be so, with the old T_g prediction of 130°C being a significant 37 K lower than the recently predicted T_g of 167°C. However, if the two sub-ambient temperature results are omitted from Figure 4(b), for the reasons mentioned previously, the two graphs would have similar distributions of data.

Comparison of DSC thermogram results show a T_g of 117°C [3] with simulation data predicting a T_g of 167°C (Figure 4(a)) for (**2**), this is not as encouraging as the same comparison as with (**1**). It would perhaps be useful at this stage to consider that the simulation data could also be used to show a prediction of 133°C (if different cut-off points are used to separate data into $< T_g$ thermal expansion and $> T_g$ thermal expansion). Although this interpretation was not chosen as the best analysis of the data, it still has a high R^2 correlation coefficient, indicating a close fit. It is thought that the analysis of (**2**) will require better resolution between 50 and 250°C to help narrow down the predicted T_g range.

Although there is no empirically measured value for density, it is interesting to note the similarity between the density predicted by Materials Studio and Cerius^2. Unfortunately, the density results for (**1**) do not show such close correlation, and so we cannot conclude that the two programs will always equilibrate the same model to the same density.

The effective isotropic elastic constants for (**2**), as calculated by Materials Studio and Cerius^2, are shown in Table 1. Although there are no empirical data available for (**2**) specifically, if Young's moduli of epoxies (~2.6 GPa), phenolics (4.1–8.4 GPa) and melamine polymers (~8.9 GPa) are considered, it can be theorised that the values produced by Materials Studio are likely to be closer to the empirically measured value [13].

4. Summary and Conclusions

Two molecular models were imported into Materials Studio from previous work conducted at the University of Surrey. These models were individually geometry optimised and then used in MD simulations to predict the glass transition temperatures of both materials. A range of mechanical properties were also calculated, including bulk modulus, Young's modulus, Poisson's ratio and the Lamé constants, λ and μ.

Table 2. R^2 data for best fits.

R^2 values	Below T_g	Above T_g
(**1**)	0.958	0.963
(**2**)	0.989	0.994

The new data produced in Materials Studio have varying compatibility with previous data from Cerius[2]. The main emphasis of this work was with regard to predicting glass transition temperatures, and it is within this area that the best results were achieved. The predictions are high in comparison with empirical data, but this is to be expected with defect-free systems, and it is clear to see how the model can be improved by adding defects in the structure, so it is more consistent with a natural system. The same explanation can be given for why Young's modulus predicted by Materials Studio is slightly higher than the empirically measured value.

The effective isotropic elastic constants do not compare very well between Materials Studio and Cerius[2], with calculations giving quite different results. Although there is not a wealth of empirical data with which to compare these figures, from what is available, it is encouraging to see that Materials Studio does appear to be producing the more accurate results.

4.1 Further Work

It is clear that there is still much room for improvement within the methods used to predict the glass transition temperature and mechanical data. Obviously, it would be ideal to run simulations on supercells with nanometre length sides for a number of nanoseconds using the best levels of precision available within the choice of force fields. However, these experiments will always be limited by the processing power available and such an experiment would take many years even on a high-end supercomputer. It would be advisable to begin any further work by determining the most efficient use of processing power by applying principal components analysis or a similar statistical technique to the many variables. By doing this, the optimum settings can be determined under which to run the simulation.

One factor that has been mentioned already during the report is the temperature range over which the experiments are conducted. MD is used to simulate an experiment that is normally undertaken between ambient and *ca*. 300°C; however the simulation carried out in the previous work ranged from −173 to 427°C and the recent work from −73 to 427°C. If the simulations are conducted in the temperature range over which the physical experiment is more traditionally performed, the results would surely be more representative of the empirical data attained from said experiment.

Although investigations into the use of larger supercells were limited to one trial, the results are noteworthy because it was the only factor that significantly reduced the SD of the cell volume. Certainly, if more powerful computing resources are made available, it would be beneficial to utilise a $4 \times 4 \times 4$ unit supercell in MD simulations.

It was mentioned in the discussion of the results how the defect-free benzoxazine model will always have higher values for glass transient temperature and Young's modulus. In future work, it would be an improvement to the model if a number of defects and solvent molecules were introduced into the molecule to make it more representative of the true polymer. Although previously it was difficult to navigate within the large supercell to introduce such defects, recent work with 3D visualisations has allowed modifications within the supercell to be made with great ease, and this forms the basis of the current work.

We have adopted a number of these more advanced ideas into the evolution of our thermoset modelling technique.

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