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Intelligent Polymer Design using High Throughput Modelling

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1. Summary

Group Interaction Modelling of polymer properties has been extended to take advantage of high throughput techniques. This allows the accurate prediction of non-linear polymer properties over a larger range of variables than previously possible. Further, the extended high throughput model framework includes a basic Multi Classifier System that facilitates ranking of the output data, depending on user preference. The model work in two modes; forwards allowing prediction of polymer properties for a range of variables, but also in reverse, allowing material suggestions to be generated for a particular property profile requirement. The model now covers a broader range of polymer types, including amorphous and semi-crystalline thermoplastics and thermosets.

2. Introduction

The overall objective of this research was to develop a high throughput version of the previously established Group Interaction Modelling (GIM) technique. GIM is a research tool for predicting a range of polymer properties as a function of most state variables and quantities. It uses the intermolecular energy of interaction between characteristic groups of atoms in adjacent polymer chains to model non-linear thermo-mechanical properties (e.g. bulk and tensile modulus, heat capacity, density, volume, loss tangent, glass transition temperature).

Here, GIM has been extended to incorporate a high throughput framework which predicts the thermo-mechanical properties of aromatic, aliphatic, amorphous and semi-crystalline polymers via the use of a basic Multi-Classier Systems (MCS). This allow property maps to be generated which it is anticipated will assist researchers and end users in making decisions regarding the best polymer for a given a set of properties, and vice versa.

The need to implement an ensemble of diverse decision making agents was prompted by the increasing polymeric database of the framework which has the potential to generate vast amounts of output. Having large amounts of data without the means to interrogate it renders the system effectively redundant. In the process of scoping new materials or requesting a material with specific properties, the algorithm faces competing human demands and therefore requires the means of negotiating these requests. By using a hierarchical topology, the MCS reduces the number of possible classes to which the input data belongs, and as the data passes through more classifiers/agents the decisions become more focused. The base combiner is a majority voting function, which presents the user with rankings by polling all the classifiers to determine which class is the most popular.

The high throughput version of GIM now incorporates classes of polymers which had been relatively untested (in model terms). Previously, the polymers used to extensively test GIM or predict properties for scientific purposes were limited to a relatively small number of model thermoplastics and thermosets. The thermoplastics were primarily polycarbonate of Bis-A, polystyrene and polyethylene but a larger list of roughly 250 thermoplastics has been used to validate a relatively small number of predicted properties. The thermosets were limited to single properties of epoxies and blends of epoxies where crosslinking is a significant factor.

In this work, the use of a high throughput model has allowed GIM to be applied to polymer classes instead of individual polymers, and also automatically predict a relatively large number of properties within these classes. Work has continued on epoxy resins to begin with but this was extended to other classes later in the project. Firstly, nylons were chosen because they are a commonly used semi-crystalline polymer with widespread hydrogen bonding and have a range of chemical structures (nylon x and nylon x, y). Hence, a range of properties for a range of nylons have been predicted using the high throughput model which typically compare well with experimental data.

Secondly, the properties of a range of acrylates have been predicted. This follows on from the nylon work but here model validation has been challenging. This is because of the diversity found within this polymer class and also gathering consistent, reliable experimental data (either measured in house or obtained from academic literature) has been difficult. Correspondingly, only limited results are presented here.

3. Computational and Scientific Progress

Group Interaction Modelling (GIM) provides a multiscale framework for predicting the complex mechanical properties of polymers through a series of predictive analytical equations. Unlike phenomenological models with high numbers of fitting parameters, the independently calculated thermo-mechanical properties in GIM do not have to be obtained by fitting the experimental data they are trying to predict. GIM is designed to complement detailed numerical molecular dynamics calculations where high computational costs restrict both the time and length scales of the simulations.

Informed and novel materials discovery is possible by combining GIM with intelligent data mining and database construction. A high throughput development of GIM is a simple, yet powerful concept: create a large polymer database of mer units containing descriptors of their chemical structures, generate a database of the calculated thermomechanical properties of existing and hypothetical materials, and then intelligently interrogate the database in the search of materials with the desired properties. The practical implementation of high throughput GIM therefore requires 4 steps:

1. Chemical structure database: building up a database of components characterised by their structural unit;
2. Property prediction: thermomechanical property calculations of materials;
3. Rational materials storage: systematic storage of the information in database repositories;
4. Materials characterisation and selection: data analysis aimed at selecting novel materials or gaining new physical knowledge.

All 4 stages are linked and necessary, but the last one is the most challenging and potentially rewarding. Extracting the relevant information from a vast database of properties, requires a deep understanding of the problem at hand. The intelligent ranking, comparison, and searching of a database is implemented by means of ‘descriptors’. These are empirical quantities, not always observable, connecting the calculated mer unit parameters (e.g. crosslinking) to material properties (e.g. modulus). Once a good descriptor is identified, the search for better materials within the repository can be performed intrinsically or extrinsically, depending on whether the optimum solutions are already included in the set of calculations or not. Intrinsic searches include just step 4, require only fast descriptors, and may employ various informatics techniques. Extrinsic searches involve all four steps, as the search for an optimal solution implies iterations leading to an expansion of the repository.

3.1 Group Interaction Modelling (GIM)

Whilst molecular mechanics and dynamics are becoming a standard tool for hierarchical polymer characterisation, the time, temperature and length scales are not easily applicable to real engineering problems[i,ii]. Continuum level descriptions of polymer properties have been investigated in the literature to describe the macroscopic and microscopic responses of polymers. Continuum models are classified into thermodynamic consistent and phenomenological approaches. A number of phenomenological approaches exist based upon spring and dashpot elements[iii,iv,v,vi]. The main deficiency associated with these continuum level modelling approaches is the high number of material parameters which need to be found through calibration process between simulations and experimental data. In the case of molecular level models, most recently a plasticity theory was developed by considering the rate dependence of the glass and beta transition loss peaks and storage modulus in PC and PMMA[vii].

The Group Interaction Modelling (GIM) framework provides a multi-scale approach which is developed based upon the premise that the macroscopic mechanical responses of polymers are a direct consequence of energy stored and dissipated at the molecular level during a thermomechanical loading[viii,ix,x,xi,xii]. Energetic descriptions of the deformation mechanisms in polymers have been discussed[xiii,xiv,xv], and are generalised in GIM in order to incorporate the molecular chemistry and physical structure into the prediction of the macroscopic constitutive properties and behaviour of polymers.

An overview of GIM is provided below.

1. Identify the characteristic structural group
    - Single mer unit or fractional mer unit content e.g. 60% Polymer A, 40% Polymer B
2. Assign input parameters to the structure
    - Dimension parameters such as volume and length
    - Energy parameters
3. Calculate input energies
    - Cohesive energy, thermal energy, configurational energy and mechanical energy
4. Combine input energies into a potential function
    - Relates interaction energy of adjacent mer units (E) to the separation distance between them (r)
    - Allows molecular level parameters to be transformed into bulk physical properties
5. Solve the potential function to give an equation of state
    - Provides typical PVT/PVE type relationships to allow property prediction
6. Calculate physical properties
    - Derive a series of linked equations allowing prediction of thermo-mechanical properties based on the input parameters
    - Potential function approach provides physical basis for properties at a given temperature, pressure etc.

In GIM, a simplified hexagonal geometry is assumed where a central polymer chain is surrounded by six neighbours and interacts with them via a potential function (energy, E, vs. separation distance, r). The length of the polymer chains, L, is assumed to be long and invariant such that the volume of the polymer chains, V, is proportional to r^2.

GIM uses a mean field potential function approach to predict the thermal, volumetric and mechanical properties of polymers. The method uses a simple contribution based approach to calculating the total energy of the system, E. Interactions between neighbouring polymer chains are defined using a modified Lennard-Jones potential function (as shown below). Simultaneously, the total energy is also expressed in terms of several thermodynamic energy contributions (also shown below).

$$E = E_{coh}\left[\left(\frac{V_0}{V}\right)^6 - 2\left(\frac{V_0}{V}\right)^3\right] = E_{coh} + H_T + H_C + H_M$$

The equation above is presented in molar terms, but could just as easily be given in molecular terms. The total energy is therefore comprised of cohesive energy, E_{coh}, thermal energy, H_T, mechanical energy, H_M, and configurational energy, H_C, contributions. E_{coh} quantifies the attractive forces holding the polymer chains together and the other terms are repulsive acting to break the chains apart. H_T is related to the molecular level temperature variations through heat capacity, C; H_C is calculated based upon the level of the cohesive energy for different molecular configurations (e.g. amorphous or semi-crystalline); H_M is only required when a mechanical field is being applied to the system and is generally set to zero.

The total energy equation given above can be solved as a quadratic in $(V_0/V)^3$ as the starting point for the derivation of a series of linked constitutive equations for predicting polymer properties. The details of these equations are provided elsewhere, with one exception. The glass transition temperature, T_g, is a key property of the polymer which is important to be able to predict accurately, but also provides a useful test of whether the model is functioning correctly. In GIM, the equation below is used to predict T_g.

$$T_g = 0.224\theta_1 + \frac{0.0513E_{coh}}{N}$$

This equation allows the glass transition temperature of an amorphous polymer to be estimated from just three parameters. These are θ_1, the 1D reference temperature (which is often taken a value of 550K for aromatic polymers), E_{coh} and N, the skeletal degrees of freedom. These parameters provide information about the vibrational energy of the chain (via θ_1), the skeletal modes of vibration (via N) and the cohesive energy holding the system together (via E_{coh}).

In order to use GIM to predict polymer properties, several fundamental parameters are required as input which are based on the representative mer unit. These are the degrees of freedom, N, the cohesive energy at absolute zero, E_{coh}, the van der Waal's volume, V_w, the length, L, the molecular weight, M, and the 1D reference temperature, θ_1.

The parameters are well defined for each mer unit, and the variation of N with temperature through the any transitions (e.g. glass transition) is important to accurately characterise. The values of these parameters can be obtained from a variety of sources, including contribution tables, connectivity indices or molecular modelling. Once the input parameters are known, the linked constitutive equations are used to predict polymer properties. This section has described a linear approach to predicting polymer properties with GIM. The next step is to implement this into a high throughput approach as described below.

3.2 High Throughput Group Interaction Modelling

The high throughput extension to GIM is similar in concept to Drug Discovery tools. The exception to this comparison is the screening process which is essentially redundant because a more targeted approach is required to model specific polymers of interest. The intelligent molecular matching is linked to an in house database, validated at implementation by experimental results either measured in situ or collated from academic publications.

The implementation of the high throughput GIM is designed to work in two modes (see Figure 1), so-called forward and reverse approaches. The forward approach is a parallelized adaptation of GIM which starts from the constitutive mer unit database. It uses input parameters (degree of freedom, cohesive energy etc.) and model variables (degree of cure, composition, temperature, strain rate etc.) to predict the thermo-mechanical properties (loss tangent, bulk and tensile modulus, heat capacity, density, volume etc.) which in turn defines polymer performance.

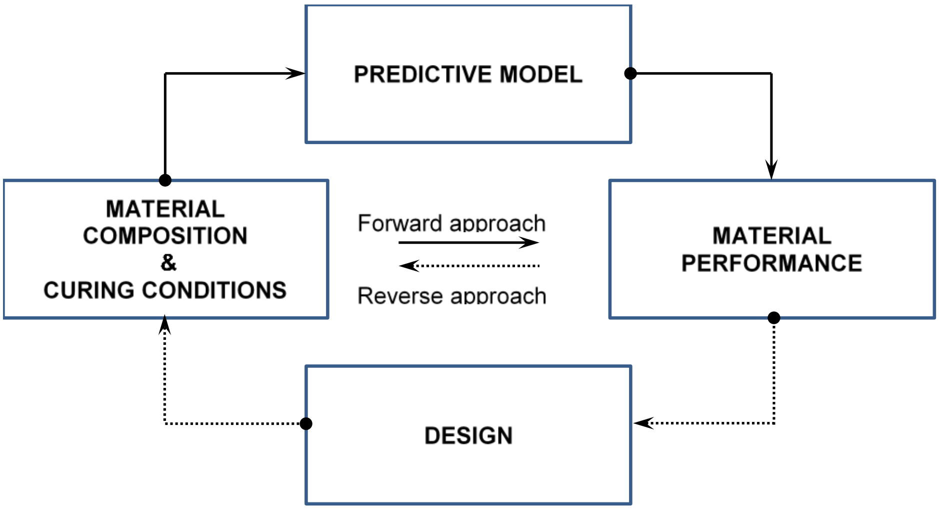


Figure 1 High throughput implementation for Group Interaction Modelling (GIM).

In contrast, the reverse approach uses the knowledge acquired through the predictive model and, starting from a given material performance, links back to the material design and mer unit information. With this approach, and an increasing parameter database, the high throughput GIM can narrow down a materials composition and processing conditions to relatively small number of candidates. These candidates can then be screened by a human and formulated in the lab or manufacturing facility as required.

In order to benefit from local knowledge, the initial attempt at a high throughput version of GIM was implemented using high performance epoxy resins as the model polymer system. Additionally, there is considerable industrial interest in these polymers, they are relatively easy to combine into binary and ternary blends and there is a wide range of in-house and literature based experimental data for validation purposes.

Figure 2 shows a schematic representation of the high throughput model using the ‘forward approach’ discussed earlier. Rather than performing sequential calculations for each system, the data is treated simultaneously, where each individual ‘square’ (Figure 2, bottom left) on the molar fraction axis represents a unique polymer, here a unique epoxy blend. The squares are chemically distinct and are defined by their constituent, parameterised mer units. The remaining axes represent the predicted properties over temperature and strain rate. By adding another variable, such as degree of cure (DOC), a series of objects is created along another axis. Similarly, more variables can be added (such as varying the curing agent (DDS, DDM, TETA) and ultimately the number of descriptors is increased. The predicted polymer properties can then be plotted against any of the variables required (Figure 2, right).

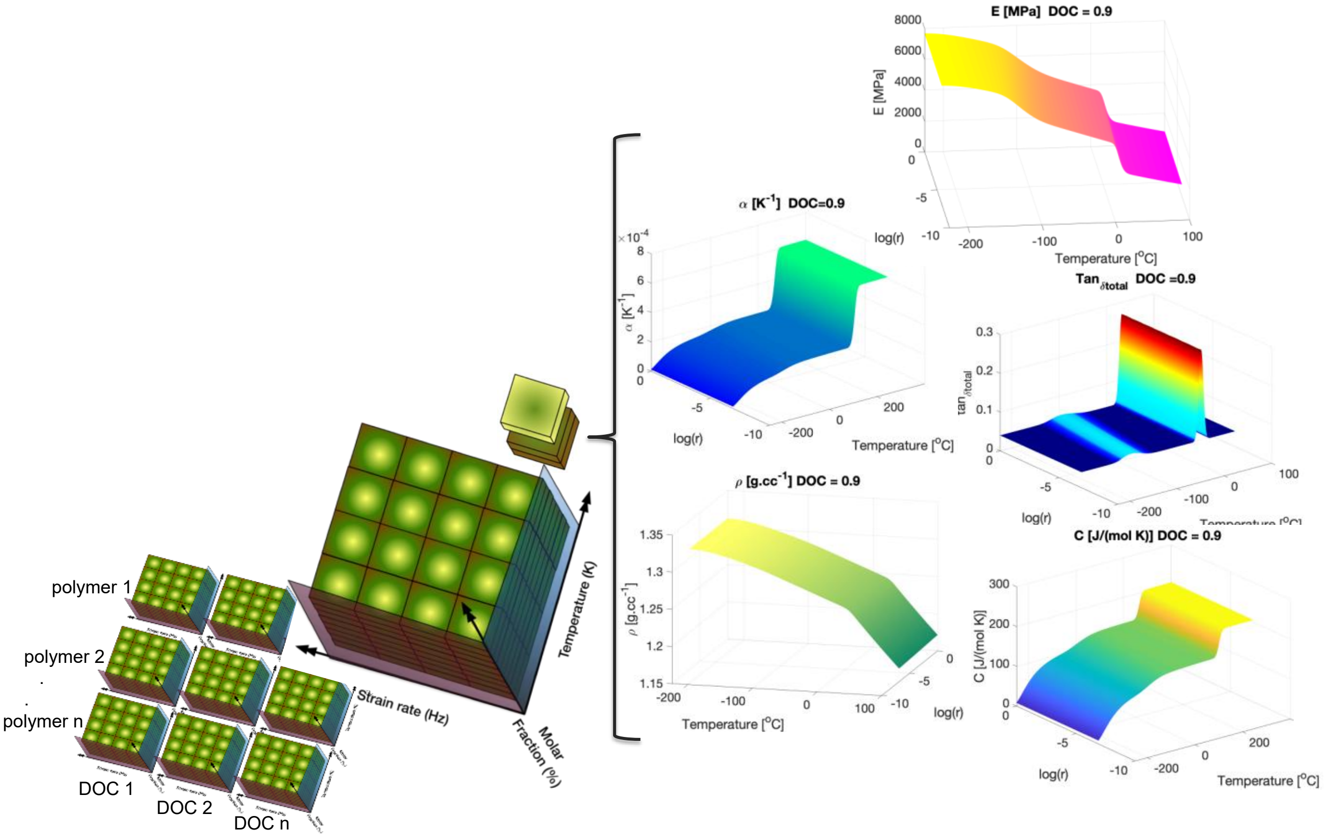


Figure 2 Schematic representation of the ‘forward approach’ using high throughput GIM.

The properties of each system are grouped together, but linked back to the corresponding input data, which allows the reverse process to be performed. The tool currently generates data files, predefined figures and a classification tool that ranks and compares chosen systems and their linked properties.

Due to the parallel implementation and low CPU requirement of GIM, the high throughput framework described here can generate vast amounts of data, more than would be feasible to match experimentally. Therefore, in order to make sense of the output, a Multi-Classifier System (MCS) is implemented. This is important for two reasons; firstly, to rank and compare the large amounts of data and, secondly, to enable the previously discussed 'reverse approach' to be used.

The output of GIM in it's simple, linear form (see previous section) would be a single value of a given property for a given set of variable values. Whilst this is of use, it is far more powerful to predict the variation of a given property as a function of a range of variables. Figure 3 shows two selected properties, density and tensile modulus, plotted against temperature for a binary blend of two commonly used high performance epoxy resins. The two properties are chosen from a longer list as they are relatively straightforward properties to measure experimentally. That said, obtaining such a wide range of experimental density and tensile modulus values as shown in Figure 3 would be prohibitively expensive. As such, experimental comparisons with this predicted data are limited to a few points. Whilst these comparisons are good, they aren't shown on the figures for clarity purposes.

It is clear from Figure 3 that a rich variety of data can be determined using the high throughput approach to GIM in a relatively short time period. The property vs. temperature data shown describes the influence of crosslinking, degree of cure, composition and strain rate. As the underlying polymer physics is encapsulated within GIM, the density plots show the expected gradient changes at the glass transition, whilst step changes are seen at similar points in the tensile modulus. In epoxy resins, the three main factors governing performance are the chemistry of the epoxy/hardener, epoxy/hardener ratio and cure schedule. The data presented in Figure 3 provides this data and more besides, and therefore represents a powerful addition to our understanding of these polymers.

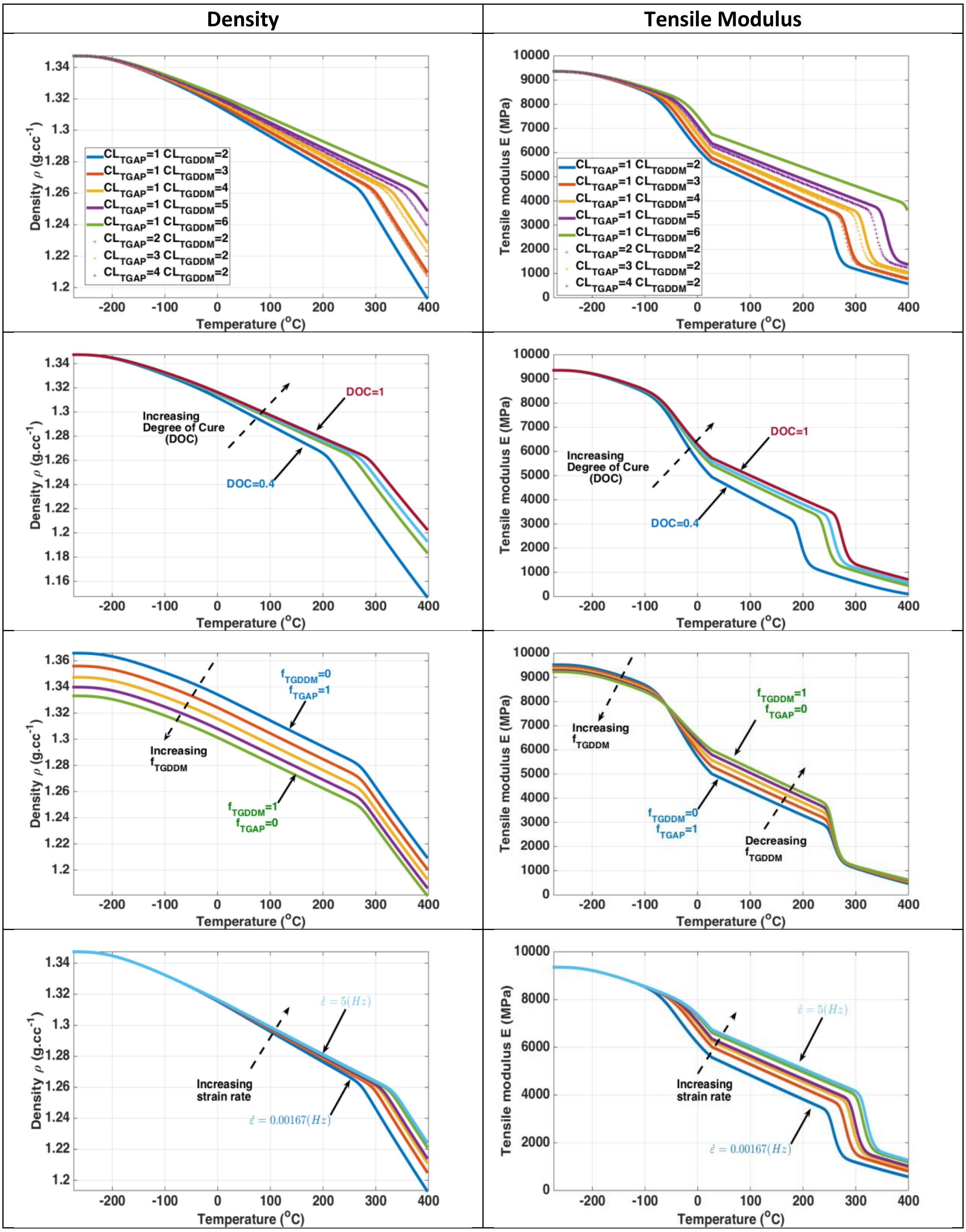
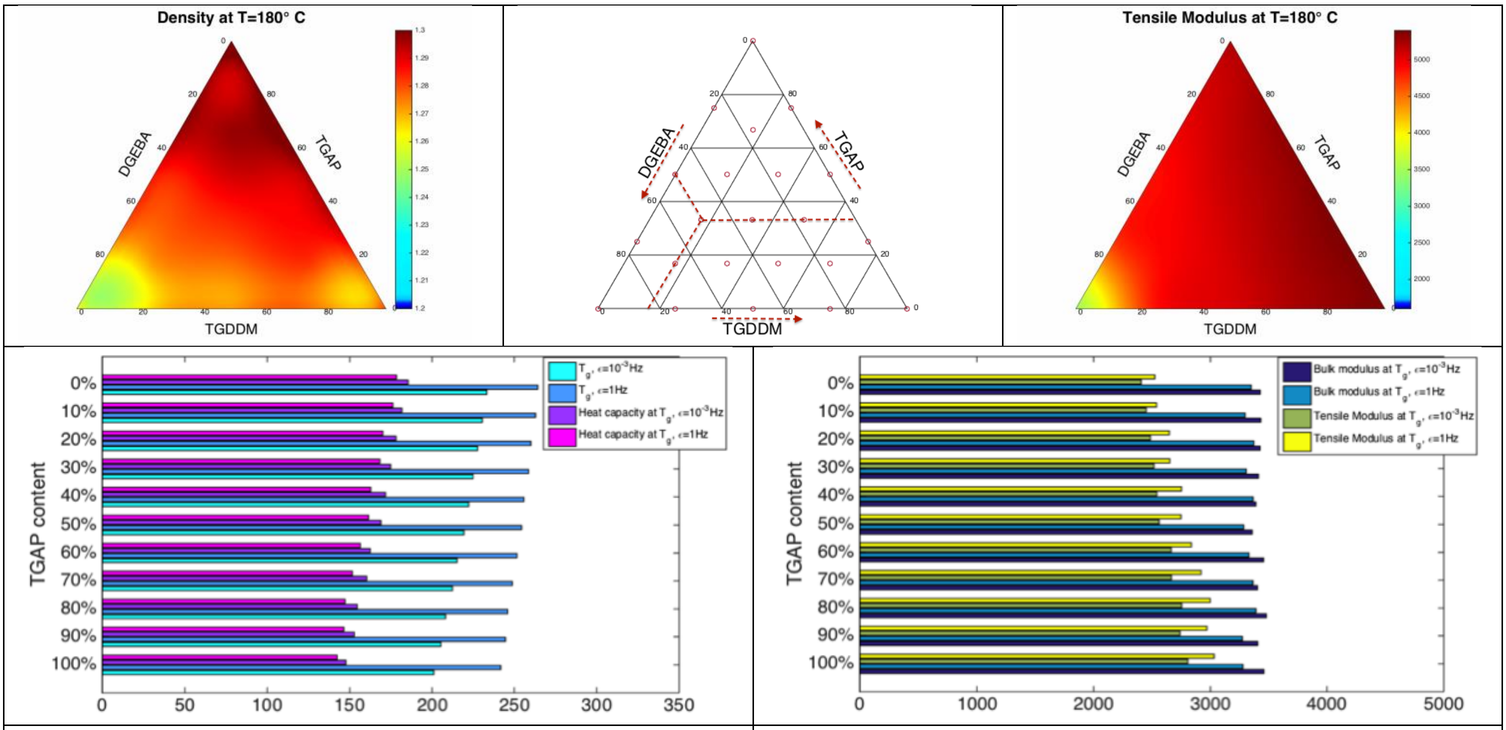


Figure 3. Predicted density (left column) and tensile modulus (right column) versus temperature for a binary blend of two epoxy resins (triglycidyl p-aminophenol (TGAP) and tetraglycidyl. 4,4'-diaminodiphenyl methane (TGDDM) cured with a diaminodiphenyl sulfone (DDS)). The plots are shown as a function of (1) crosslinking (2) degree of cure (3) composition and (4) strain rate.

Moving on, the high throughput model can be used to investigate more and more complicated systems. Figure 4 is an illustration of the classifying, ranking and comparing of properties for a range of epoxy resin ternary blends. In this case, the MCS can help the user decide on the best composition across an epoxy ternary blend. The MCS ranks the thermo-mechanical properties of the blend across all available combinations, shown here at relatively low resolution (10% variation in composition). All the input parameters, mentioned in the sectioned above, can be varied at a level of granularity favoured by the user.

The top row in Figure 4 now shows density and tensile modulus predictions as a function of the ternary blend composition (the schematic is also provided as a guide tool). The middle row shows an example of ranking across glass transition temperature, heat capacity, bulk and tensile modulus at two different strain rates. The MCS system presents the user with best choices across all properties, however for illustrative purposes, we present here simplified graphs. The final row shows the rankings, as calculated by each agent, and aided by a hieratical topology and a majority voting function sums the final result for the user.



MCS agent 1

Epoxy	DGEBA	TGAP	TGDDM
Ranked 1	0	0	1
Ranked 2	0	0.1670	0.833
Suggested	0	0	1

MCS agent 2,3

Epoxy	DGEBA	TGAP	TGDDM
Ranked 1	0.33	0.33	0.333
Ranked 2	0.50	0.1670	0.333
Suggested	0.3889	0.277	0.333

Figure 4. Predicted density and tensile modulus for a ternary blend of diglycidyl ether bisphenol A (DGEBA), triglycidyl p-aminophenol (TGAP), tetraglycidyl. 4,4'-diaminodiphenyl methane (TGDDM) cured with a 4,4'- diaminodiphenyl sulfone (DDS). Followed by as illustration of the use of Multi-Classifier Systems, ranking and informing the user decision on which ternary blend is best across a range of properties.

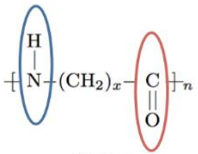
Besides aiding in classification and ranking, the immediate advantage of using MCS is that they act as an indexed link between material properties and the constitutive mer unit information. This, in effect gives the user the ability to alter existing polymer formulations, determine or narrow down the material composition and curing conditions and, given a big enough database, could reverse engineer material composition.

3.3 Using High Throughput Group Interaction Modelling with Other Polymer Classes

The development of the high throughput version of GIM to this point in Sheffield has relied on the polymer structure lacking any significant crystallinity; polymer properties have been successfully predicted for amorphous epoxy resins. Clearly, there are many polymers, particularly thermoplastics, which exhibit crystalline behaviour, ranging from relatively low levels up to highly ordered structures. GIM was originally developed with thermoplastics in mind, some of these are entirely amorphous but there are also a large number of semi-crystalline polymers. In order to account for this, a variable is required which can describe the relative order and disorder found in semi-crystalline polymers. Hence, the configurational energy is high for amorphous polymers, low for crystalline polymers and varies between these extremes for semi-crystalline systems.

There are a number of suitable model systems for testing the predicted output from the high throughput version of GIM when applied to semi-crystalline polymers. Among these, the polyamides (nylons) and polyacrylates seemed the most applicable. Both have a range of chemical structures available (leading to varying degrees of crystallinity), both have different types of bonding present (requiring model development leading to improved predictions) and both are commonly-used polymers (with a reasonable range of literature property values available for validation).

The simplest form of nylon is nylon x as shown in the chemical structure below. The value of x can be varied from low to high to provide a range of different nylons with varying properties. In modelling terms, the different structures generated by varying the value of x are parameterised and stored in input arrays prior to property prediction, similar to the process shown in the previous section. Nylons have both an amine and carbonyl group in their repeat unit which leads to extensive hydrogen bonding along the polymer chain. Properties are partly determined by the hydrogen bonding, so this must be incorporated into the model (cohesive energy is increased to account for this). The degrees of crystallinity in each nylon are a requirement for the model so average literature values were used where available.



$$\left[\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-(\mathrm{CH_2})_x-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\right]_n$$

Nylon x

Figure 5 shows the predicted glass transition temperature and melting temperature for nylon x where x=6-12. There are nylons with both lower and higher values of x but there is very little experimental information available for these polymers, despite them being relatively easy for the model to predict. The experimental melting temperatures are shown with a minimum and maximum range as these values tend to be reported as a range instead of a single value (the crystalline segments exist in a variety of environments; hence a range of melting energies are required). Overall the agreement between the model predictions and experimental values is very good.

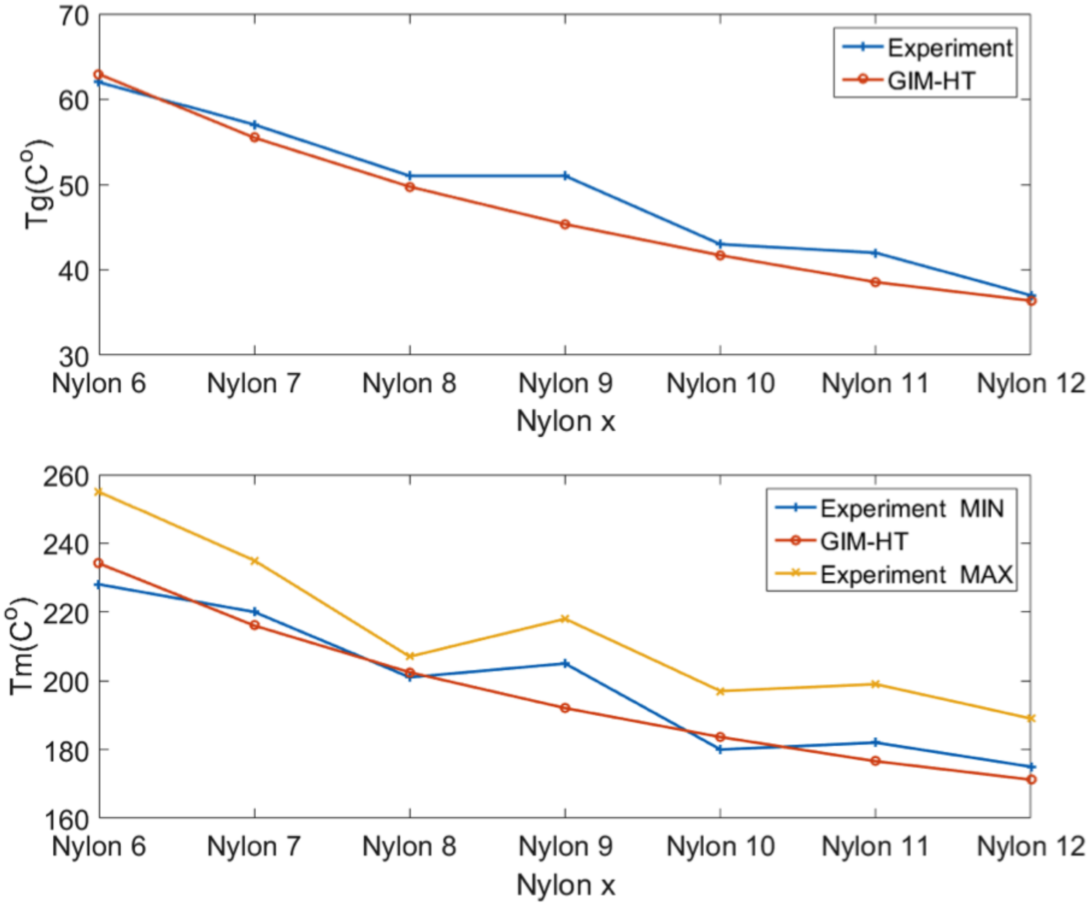
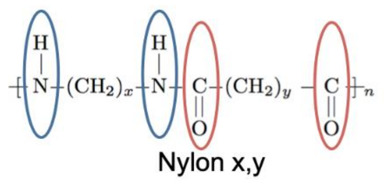


Figure 5. Predicted glass transition and melting temperatures for Nylon x.

For the glass transition temperature, there is poorer agreement for nylon-9 and nylon-11. This may be due to there being fewer experimental measurements for these nylons, or perhaps a particular aspect of the chemical structures exists when x=9 or 11.

For the melting temperature, agreement is good, but the predictions tend to be on the low side. This suggests the degrees of crystallinity used may need to be revisited. If the model used slightly higher degree of crystallinity, the melting temperature predictions would also be higher, and sit within the experimental ranges better. Again, there is a minor issue for x=9 or 11, the reasons for which will be similar to those suggested for the glass transition temperature earlier.

Next, a slightly different chemical structure of nylons is nylon x, y as shown in the chemical structure below. Now, there are two chemical structure variables, x and y, which can vary independently. Similar to nylon x, nylon x, y has both amine and carbonyl groups present so hydrogen bonding must be accounted for. It is a semi-crystalline polymer so the degree of crystallinity again needs to be acquired from literature values.



$$-\!\!\left[N(H)-(CH_2)_x-N(H)-C(=O)-(CH_2)_y-C(=O)\right]\!\!-_n$$

Figure 6 shows the variation of glass transition temperature with x and y. As for nylon x, agreement between the model predicted and experimental values is very good. There is a small anomaly for nylon 10,10, but again this is not a common polymer (lack of literature values) or there may be some unknown peculiarity with this polymer not yet accounted for in the model.

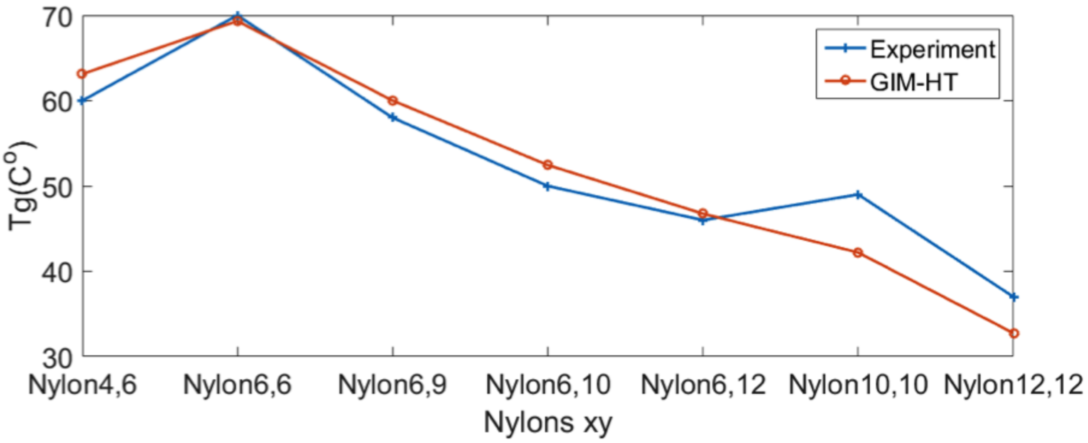


Figure 6. Predicted glass transition temperatures for Nylon x,y

Figure 7 shows the predicted and experimental data in a different format. The plots show the variation of glass transition temperature with the various GIM parameters for nylon x and nylon x, y; the points are the predictions, the line are the experimental ranges. Generally, agreement is good.

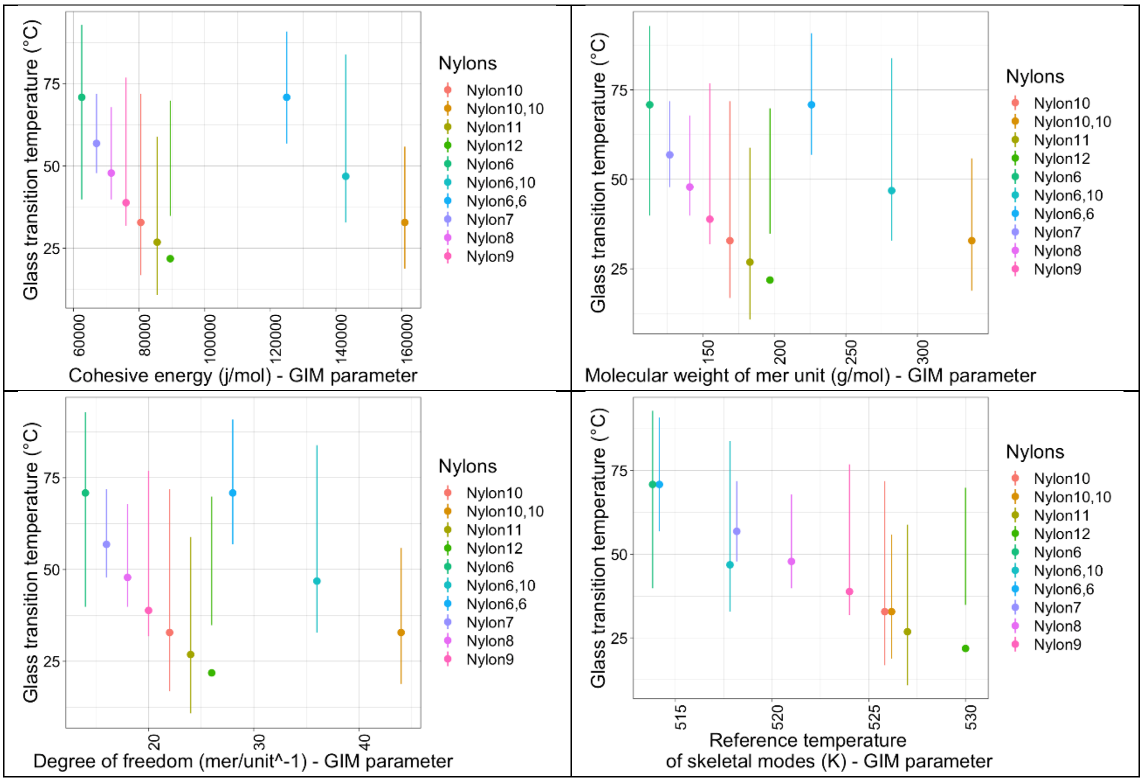


Figure 7. Predicted glass transition temperatures for nylon x and nylon x,y against various GIM parameters (cohesive energy, molecular weight, degree of freedom and skeletal mode reference temperature). Points show predicted values; lines show experimental value ranges.

The final class of polymers which were investigated are the polyacrylates. Figure 8 shows a similar plot to Figure 7, providing variation in glass transition temperature for a range of acrylates. It should be noted that this work is ongoing, and as such the agreement between experiment and model is not as good as in previous sections in this report. Despite this, the results are encouraging.

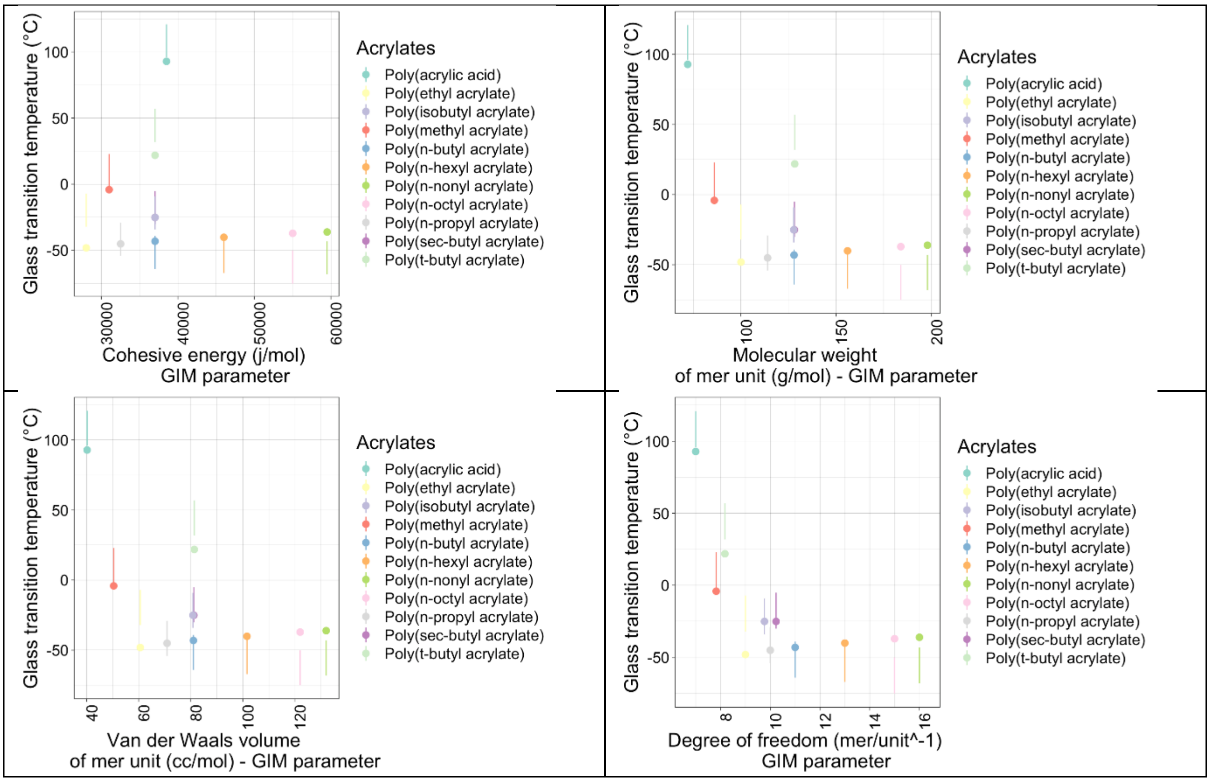


Figure 8. Predicted glass transition temperatures for acrylates against various GIM parameters (cohesive energy, molecular weight, degree of freedom and skeletal mode reference temperature). Points show predicted values; lines show experimental value ranges.

4. Conclusions

The results shown in this report represent a brief overview of the progress made during the project to develop a high throughput version of Group Interaction Modelling. The development has ranged from predicting polymer properties of amorphous, thermoset epoxy resins to semi-crystalline, thermoplastic polyamides and polyacrylates.

The model predicted values are generally in very good or excellent agreement with experimental values. The work on epoxies has more examples of predicted properties and their comparison with experiment as this is the primary research area of the research group. The work on polyamides and polyacrylates is comparatively limited in scope, primarily due to a lack of experimental data, either available in-house or in publically available literature. However, the early values very much indicate that the model is, in large part, working and capable of predicting experimental values where available. Accordingly, a relatively small amount of work would be needed to finish off this part of the project. The application of the model to other classes of polymers is also possible; the polymer types were chosen to cover a range of types but is clearly not exhaustive.

The number of properties predicted via the examples provided in the report is limited due to a desire to restrict properties to those ‘useful’ to industry and where experimental data is available. As such, the examples provided are (in a sense) proof of concept projects to show that the process can work.

Further work would necessarily expand on the properties available and take full advantage of the high throughput capacity of the model framework. This would allow the full forward and reverse aspects of the model to be more completely utilised than it has up to now.

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