

PREDICTING THE MATERIAL PROPERTIES OF A POLYURETHANE MATRIX (A COMPOSITE WITHIN A COMPOSITE)

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Abstract

The material properties of a polyurethane matrix are predicted using Group Interaction Modelling (GIM) and compared to experimental data. GIM is able to predict the properties of the hard (crystalline) and soft (amorphous) domains present in thermoplastic polyurethanes by parameterising their different molecular structures. This leads to the accurate prediction of non-linear properties such as the strain rate dependent secondary transitions (e.g. glass transition temperature) or the two phase nature of the stress-strain curve. The latter contains two linear parts (due to the soft block only and the soft and hard block together) joined by a transition governed by the onset of hard block. With the two phase nature of the polyurethane matrix, the system as a whole can be thought of as a 'composite within a composite'.

1 Introduction

Dyneema is a commercial brand of Ultra-High Molecular Weight Polyethylene (UHMWPE) fibres [1]. Some grades of Dyneema are a composite system consisting of UHMWPE fibres held in a thermoplastic polyurethane matrix and are used as armour in various military scenarios. The polyethylene fibres are very strong, lightweight, durable, relatively easy to process and display excellent energy absorption characteristics under ballistic impact. The polyurethane matrix not only acts as glue holding the fibres in place but also has a role to play in energy absorption.

The matrix used in Dyneema is a polyether based thermoplastic polyurethane (TPU) which generally display rubber-like elasticity and have good hydrolysis and microbial resistance. Many TPU systems are referred to as 'hard block soft block' in which two distinct domain types exist within the polymer structure. The hard block consists of the urethane segments which are able to hydrogen bond with each other across adjacent polymer chains leading to increased order (higher crystallinity) and a higher modulus and density. The soft block consists of the polyol segments which are largely amorphous (lower crystallinity) leading to a lower modulus and density.

Group Interaction Modelling (GIM) is a technique that uses the interaction energy between groups of atoms in adjacent polymers as the basis for predicting bulk thermomechanical and engineering properties [2]. This paper summarizes the development of GIM for use on

multiple domain polymers and its application to thermoplastic polyurethanes, including those used in Dyneema composites.

2 Group Interaction Modelling (GIM)

A brief description of GIM will be provided here (more detailed information is available in the literature [3,4]). A potential function is used to define the interaction energy, E_{total} , between two adjacent polymers. The function is based on the Lennard Jones function assuming volume, V , is proportional to the square of the interchain distance (see equation 1).

$$E_{total} = E_{coh} \left[\left(\frac{V_0}{V} \right)^6 - 2 \left(\frac{V_0}{V} \right)^3 \right] \quad (1)$$

This potential function is solved as a quadratic in $(V_0/V)^3$ in order to provide a simple relationship between energy and volume. This is then used to derive a series of linked constitutive relationships for predicting all other properties.

The parameters used to populate the property prediction equations are obtained by defining the representative repeat mer unit for the polymer. For a given parameter, each distinct chemical function group makes a contribution to the mer unit whole. Dimension parameters such as mass, length, van der Waal's volume, V_w , are obtained from group contribution tables along with energetic parameters such as the cohesive energy, E_{coh} , and degrees of freedom, N .

The majority of isotropic polymers undergo a single glass transition where large scale movement between adjacent chains becomes possible with increasing temperature. When a polymer exists as a number of separate phases (such as the hard block soft block domains in most TPUs) the system can display more than one transition, one for each domain type. In order to include this non-linear behavior in GIM, the location and magnitude of each transition is calculated based on the molecular events that cause it. A predicted loss profile is obtained which is comparable to those obtained experimentally using dynamic mechanical thermal analysis (DMTA). The temperature at which a secondary phase transition occurs is affected by the strain rate at which the system is perturbed. The GIM equations which predict the loss profile are frequency dependent which allows strain rate dependence to be predicted.

3 Predicting the Properties of a TPU with GIM

The Dyneema TPU matrix phase was extracted from the composite and chemically analysed to obtain the structure of the hard block and soft block domains. The ratio of hard block to soft block was measured as approximately 1:10 by weight which corresponds to 1:4 molar ratio. From this a table of GIM parameters can be assembled (see table 1) for use in the property prediction equations.

	N	E_{coh} (J/mol)	V_w (cm ³ /mol)
Hard Block	22	123,500	148.2
Soft Block	10	24,300	45.9
TPU Mer Unit	13	49,100	71.5

Table 1. GIM parameters for hard block, soft block and the TPU mer unit as a whole.

GIM uses the data in Table 1 to predict a transition temperature and total loss for both the hard and soft blocks within the TPU. The full loss profile as a function of strain rate is then plotted using normal distribution functions to describe the peaks (see Figure 1). The group of

peaks at lower temperature (~ -50 °C) corresponds to the glass transition of the soft block. The group of peaks at higher temperature (~ 120 °C) corresponds to a transition within the hard block assumed to be due to changes in order/disorder as the temperature is varied. Both peaks increase with strain rate as the molecules become increasingly less able to dissipate energy due to the shorter time scales.

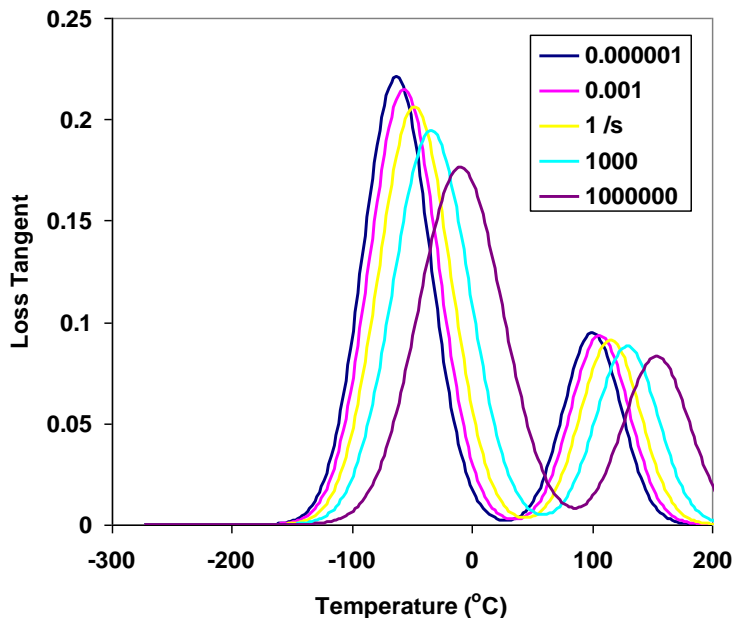


Figure 1. GIM predicted loss tangent profile as a function of strain rate for the Dyneema TPU matrix.

An experimental loss profile has been recorded for the same TPU using a Perkin Elmer DMA 8000 (see Figure 2). The experiment was performed with the sample in a steel ‘Material Pocket’ so the results are somewhat noisy and any modulus measurements are irrelevant. However, the peaks in the loss tangent are very similar to those predicted using GIM, with lower temperature soft block and higher temperature hard block peaks clearly visible.

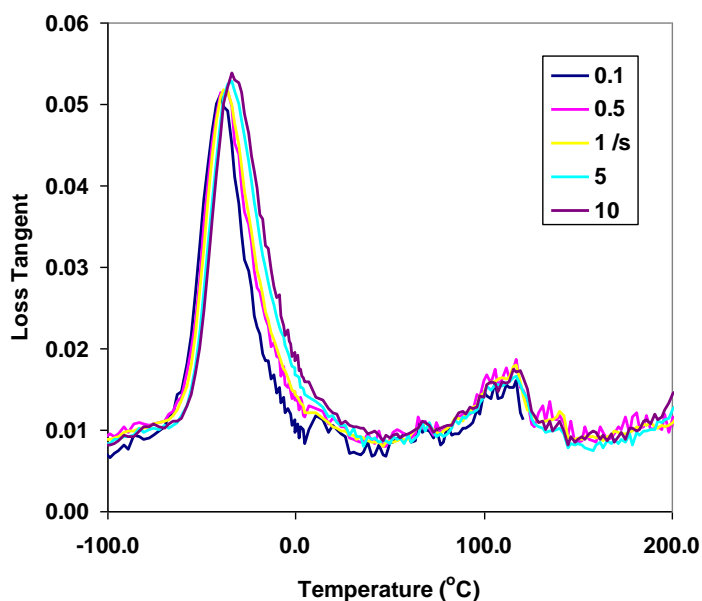


Figure 2. Experimental loss tangent profile as a function of strain rate for the Dyneema TPU matrix.

The GIM predicted tensile modulus as a function of strain rate is shown in Figure 3. There are two distinct transitions occurring, the lower temperature for the soft block and the higher temperature for the hard block. At very low temperature the TPU is a stiff glass which changes to a soft rubber through the soft block glass transition. As the temperature is increased, the hard block transition further softens the polymer until melting occurs around 160 °C.

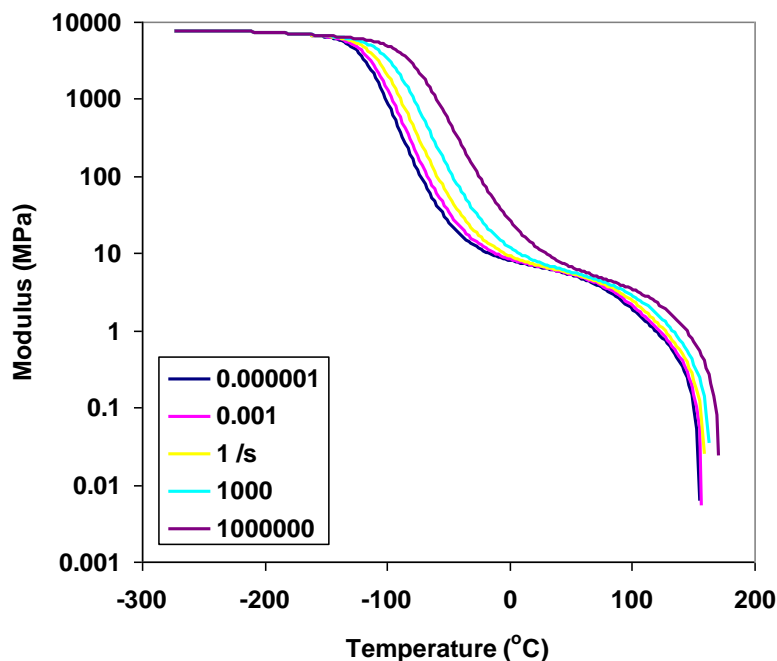


Figure 3. Experimental loss tangent profile as a function of strain rate for the Dyneema TPU matrix.

A summary comparison of the predicted and experimental data is given in Table 2. The GIM transition temperatures compare well with experimental values across a range of strain rates (not shown). The room temperature tensile moduli also compare well and all predictions are within typical experimental error.

	GIM	Experiment
Soft Block Transition T	-48	~ -40
Hard Block Transition T	116	~ 120
Tensile Modulus (MPa)	6.75	6.58

Table 2. Comparison of GIM predicted and experimental properties at 1/s strain rate.

Finally, the room temperature TPU tensile stress-strain curve is predicted (see Figure 4). The stress strain curve for a two phase TPU can be rationalised by considering it to consist of two linear sections which correspond to two different processes occurring in the polymer. The initial linear section from 0% strain is the soft block being stressed alone. After roughly 50% strain, the hard block segments are now also being stressed and the second linear section is observed which continues until failure. The slopes of each section are predicted using the parameters for either the soft block alone or the soft and hard blocks together. The link between the two linear sections is predicted using the onset of the hard block transition, as governed by the loss tangent profile in Figure 1. An experimental tensile stress-strain plot is included in Figure 4 for comparison purposes. The agreement between model and experiment is excellent.

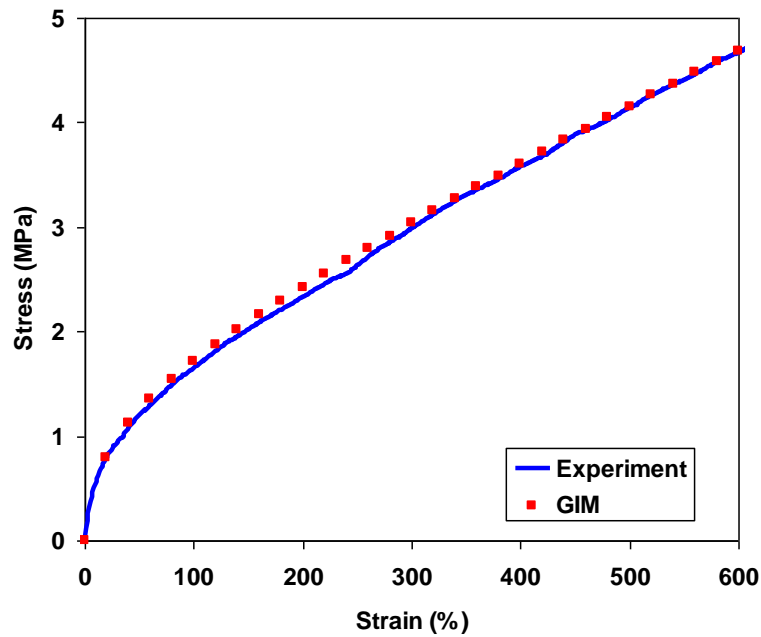


Figure 4. Comparison of GIM predicted and experimental tensile stress-strain curve.

4 Conclusions

Group Interaction Modelling has been developed to predict the properties of a thermoplastic polyurethane consisting of a two phase, hard block soft block, architecture. The model predicts a range of properties as a function of temperature and strain rate with good accuracy. This type of model can now be used to quickly predict non-linear material properties for any polymer for use in larger scale models (such as finite element).

References

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