Predictive model for segmented poly(urea)

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Abstract. Segmented poly(urea) has been shown to be of significant benefit in protecting vehicles from blast and impact and there have been several experimental studies to determine the mechanisms by which this protective function might occur. One suggested route is by mechanical activation of the glass transition. In order to enable design of protective structures using this material a constitutive model and equation of state are needed for numerical simulation hydrocodes. Determination of such a predictive model may also help elucidate the beneficial mechanisms that occur in polyurea during high rate loading. The tool deployed to do this has been Group Interaction Modelling (GIM) – a mean field technique that has been shown to predict the mechanical and physical properties of polymers from their structure alone. The structure of polyurea has been used to characterise the parameters in the GIM scheme without recourse to experimental data and the equation of state and constitutive model predicts response over a wide range of temperatures and strain rates. The shock Hugoniot has been predicted and validated against existing data. Mechanical response in tensile tests has also been predicted and validated.

1 Introduction

Elastomers made by co-polymerisation of poly(urea) and poly(urethane) have been shown to be very beneficial in blast mitigation and in protection against bullet/fragment impact by being used as a rear face coating or in sandwich materials [1–3]. Their properties have been measured [3–6] and molecular simulations carried out [1,2] in order to understand the mechanisms that operate under impact conditions and, particularly, the energy absorption that is seen.

Group Interaction Modelling (GIM) [7] has been shown to predict the equation of state for any polymer [8] and, more recently, the general mechanical properties of any polymer [9]. The techniques used in GIM will be deployed in predicting the properties of one such copolymer and, with validation, should help shed light on the origin of beneficial properties as well as highlighting changing response of the polymer during impact.

The segmented copolymer made from polymerising diphenyl methane, poly(tetramethyleneoxide)-diphenyl with urea linkages is a large molecule with the mer unit made from disparate functional groups. There is a hard segment, Fig. 1 and a soft segment, Fig. 2. The phenyl and carboxyl groups are normally appended to the urethane chain as part of the soft segment but we have chosen here to consider it part of the hard segment due to its effective glass transition temperature. There is hydrogen bonding between the hard segments that acts to pin together these segments on neighbouring chains. This gives a similar effect to particle reinforcement in composite materials. The value of n in the soft segment can vary between 12 and 14. This long urethane chain is amorphous in nature and should be able to rotate freely in "crankshaft" mode.

In the first instance the value of n is taken to be 14 and the parameters for the functional groups determined from this chemical structure and tables in [7] alone. The parameters are given in Table 1.

2 Shock properties

The equations of state of each segment are calculated directly from the GIM parameters. Assuming pressure equilibrium between segments allows determination of the equation of state of the "composite" and prediction of the Hugoniot [8], Fig. 3. This prediction, however, required an assumption that the shock process suppressed either the free rotation expected of a long amorphous urethane chain or the extra degrees of freedom associated with a polymer above its glass transition.

It should be noted that the prediction is of a curved line that agrees with the ultrasonic wave speed at $U_p = 0$.

A comparison can also be made with the longitudinal stress measurements. This requires prediction of the C_{11} stiffness coefficient and thus needs to include a pressure dependence of the elastic modulus. A generally good prediction of this pressure dependence for most polymers is [7]:

$$K = K_0 + 6P \qquad (1)$$

where K_0 is the zero pressure bulk modulus and P is the pressure. Figure 4 shows the predictive comparison with data [3]. The pressure hardening derives from the shape of the potential energy function associated with van der Waals bonding and does not require any assumption of free volume.

The zero pressure bulk modulus under shock is predicted by the model to be $K_0 = 2.8$ GPa. At low rates this reduces to $K_0 = 1.8$ GPa. This should be compared to measured bulk modulus at low rates of 2 GPa [5] and demonstrates the fewer relaxations available in the shock event.

3 Mechanical response

The GIM parameters also allow direct prediction of the loss tangent as a function of temperature, Fig. 5. This misses out the higher temperature loss peaks associated
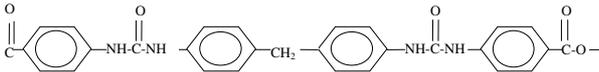
Fig. 1. Chemical formula of the hard segment.

$$-\{-CH_2-CH_2-CH_2-CH_2-O-\}_n-$$

Fig. 2. Chemical formula of the soft segment.

Table 1. GIM parameters.

	Soft Segment	Hard Segment	
V_w	644	264	cc/mol
M	1008	506	g/mol
L	105	33	angstrom
E_{coh}	340200	324500	J/mol
theta	550	550	K
N	140	41	
N_c	210	95	
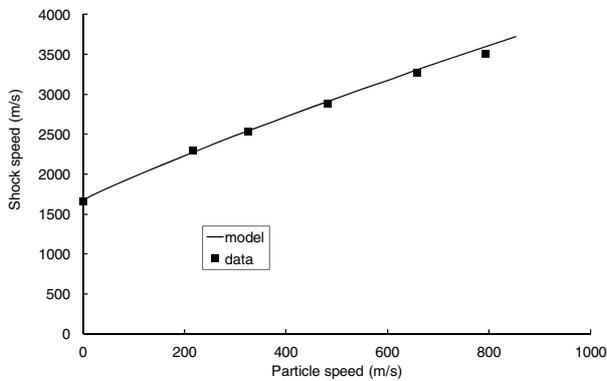
Fig. 3. Hugoniot prediction compared with data [3].

Fig. 4. Longitudinal stress prediction compared with data [3].

Fig. 5. Loss tangent prediction compared with data [5].

Fig. 6. Prediction of mechanical response at 10 000 /s compared with data [5].

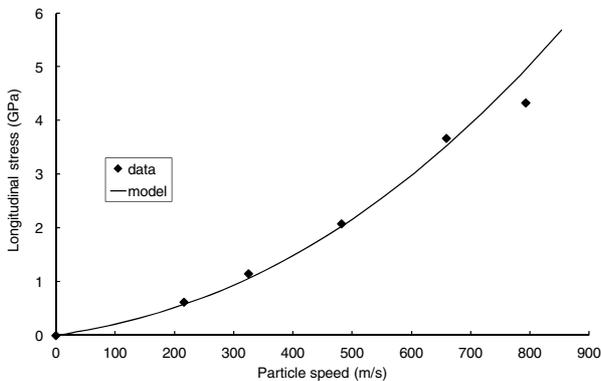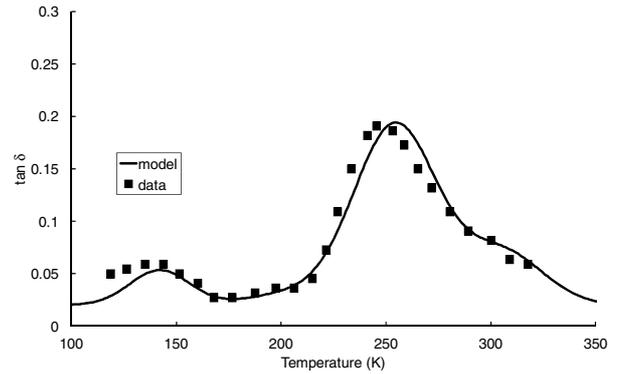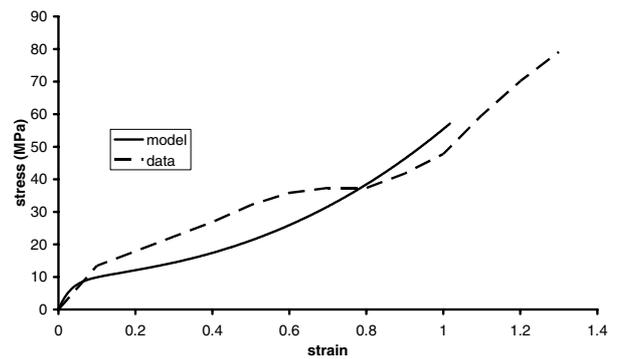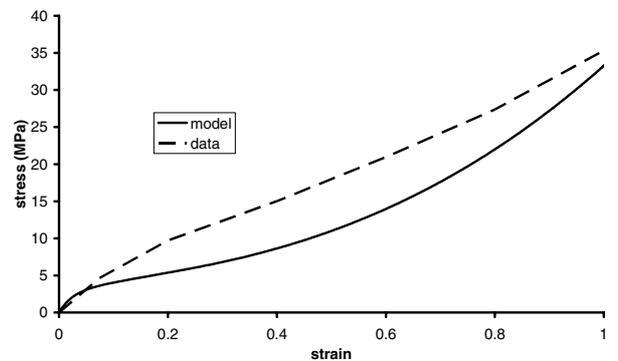Fig. 7. Prediction of mechanical response at 100 /s compared with data [5].

with the hard segments and some of the interactions between hard and soft segments. Changing the stoichiometry of the mixture with more hard segments will shift the balance of loss to a higher temperature as mixed interactions between soft and hard segments, with a higher glass transition, become more likely. This will make the polymer stiffer at room temperature because fewer of the total degrees of freedom will have been developed and will allow more energy to be absorbed. This is seen in practice [5]. There is a balance to be made between energy absorbance and glassy behaviour where the reduced fracture strain removes the beneficial nature of the polymer coating.

GIM shows how to move from the prediction of the loss to a prediction of the non-shock stress-strain response of the polymer. The response at two strain rates is predicted by the model and compared with data in Figs. 6 and 7.

Fracture is also predicted by considering the amount of mechanical work that is equivalent to the configurational energy contained in the degrees of freedom liberated through the glass transition. At 10 000 /s this translates to a failure strain of 1.2 compared to the experimental value of 1.3; for 100 /s it suggests 1.5 compared to an experimental value of 1.7.

4 Summary

Group Interaction Modelling has been used to generate a model for segmented poly(urea) and has shown good agreement when compared with mechanical properties measurement from literature both in the shock regime and at low rates. Its basis in the chemical structure allows physical understanding of the basis for those properties and how they may change with stoichiometry. This would allow an optimum structure to be designed for the specific application of blast/ballistic protection.

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