Reactive and Functional Polymers xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Reactive and Functional Polymers

journal homepage: www.elsevier.com/locate/react

Prediction of the char formation of polybenzoxazines: The effect of heterogeneities in the crosslinked network to the prediction accuracy in quantitative structure-properties relationship (QSPR) model

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ARTICLE INFO

Keywords:
QSPR
Benzoxazines
Polybenzoxazines
Char formation
Thermal stability
Mathematical modelling

ABSTRACT

Molecular Operating Environment (MOE) software has great potential when combined with the Quantitative Structure-Property Relationship (QSPR) approach, and was proven to be useful to make good prediction models for series of polybenzoxazines [1–3]. However, the effect of heterogeneities in the crosslinked network to the prediction accuracy is yet to be tested. It was found that polybenzoxazines with polymerisable functional group (*e.g.* acetylene-based benzoxazines) form up to 40% higher char yield compared to their analogue polybenzoxazines due to the contribution of the polymerisable functional group (*e.g.* ethynyl triple bond) in the cross-linked network. In order to investigate the effect of the inconsistent cross-linking network, a data set consisting of thirty-three benzoxazines containing various structures of benzoxazines was subdivided into two smaller data sets based on their functional group, either benzoxazines with polymerisable functional group (acetylene-based benzoxazines set (Ace-M)) or non-polymerisable functional group (aniline-based benzoxazines (Ani-M)). Char yield predictions for the polybenzoxazines for these data sets (Ace-M and Ani-M) were compared with the larger thirty-three polybenzoxazines data set (GM) to investigate the effect of the inconsistency in crosslink network on the quality of prediction afforded by the model. Prediction performed by Ace-M and Ani-M were found to be more accurate when compared with the GM with total prediction error of 3.15% from both models compared to the GM (4.81%). Ace-M and Ani-M are each better at predicting the char yields of similar polybenzoxazines (*i.e.* one model is specific for a polymerisable functional group; the other for non-polymerisable functional group), but GM is more practical as it has greater 'general' utility and is applicable to numerous structures. The error shown by GM is considerably small and therefore it is still a good option for prediction and should not be underestimated.

1. Introduction

Thermoset resins have been used widely in aerospace applications for decades. Civil airliners, military aircraft, drones and satellites are some of the examples where thermoset polymers and composites are used extensively. A report by the European Transport Safety Council (ETSC) in 1996 stated that of 600 fatalities in aircraft accidents, 330 died as a result of the impact and 270 due to the effects of smoke, toxic fumes, heat, and resulting evacuation problems [4]. Even in the runway collision between the US Air Flight 1493 and the SkyWest Flight 5569 on February 1991, 17 of the 23 passengers killed had their seatbelts unbuckled, but tragically died from smoke inhalation while making their way to the exits [5]. This is also supported by a review from National Transportation Safety Board in New York in 1999, saying that from 1970 to 1995, 72.5% of the total fatalities in air crashes died from the post-impact incidents with almost all (95.4%) resulting from smoke inhalation and/or burns. Since 90% of civil aircraft interiors are typically made of thermoset polymers, including the decorative panels and the adhesives [6], there is a great demand in improving the thermal stability of these materials to provide better resistance to fire incidents. This can help to slow down the spread of the fire in the cabin and increase the time available for the passengers to escape from the aircraft.

The fire resistance and flame retardancy of thermoset resins can be improved by introducing highly aromatic or hetero-aromatic materials. Benzoxazines are a good example of this – a relatively new addition to

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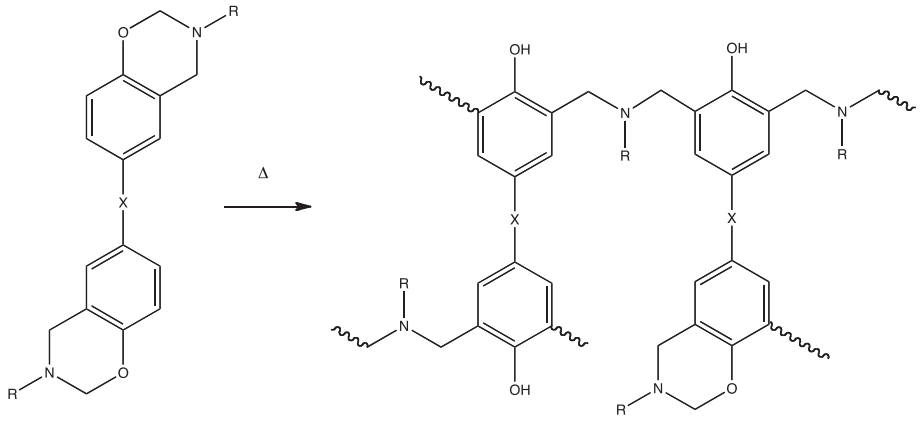
http://dx.doi.org/10.1016/j.reactfunctpolym.2017.08.002
Received 17 May 2017; Received in revised form 14 July 2017; Accepted 3 August 2017



Scheme 1. Schematic showing polymerisation of bisbenzoxazines through ring opening and crosslinking (X = alkyl, aryl or heteroatoms, R = alkyl or aryl).

the family of thermoset polymers, but with great potential especially in applications where fire resistance is important. Benzoxazines polymerise through a ring opening polymerisation mechanism (Scheme 1) to form a crosslinked network.

Depending on the structure, polybenzoxazines can form char yields (the residue remaining when combustion reaches 800 °C) of up to 81%, compared to only 30–55% formed by phenolic resins and 5–15% char yield formed by epoxy [7,8]. The amount of char produced is very important in fire resistance applications as an intumescent char will act as a protective layer (barrier) to protect the remaining underlying materials from supporting combustion [9]. This will reduce the spread of fire by reducing the diffusion rate of decomposed and flammable gases into the flame front and therefore disrupt the sustained flame and eventually stop the fire [8].

In a special edition of the Journal of Polymer Science in 2015, Ginzberg, Weinhold, and Trefonas stated that, “In the near future, modelling is expected to be an integral part of formulation design and the screening process” [10]. Modelling work was proven to be useful in predicting properties of bulk scale composites such as the temperature, decomposition, softening and failure of materials [11]. The work shows the ability of the model to give good agreement between the prediction data and the experimental data for most of the properties that were examined. Looking at the great potential of modelling in prediction work, we took the initiative to try applying the modelling work to the molecular and atomistic scale. The whole area of molecular scale modelling of thermosets was reviewed by Li and Strachan where the group was credited with publishing the first fully atomistic molecular dynamics (MD) simulation of a thermoset [12]. Quantitative structure property relationships (QSPR) have been pioneered by Hopfinger [13], Katritzky [14], and Bicerano [15], and is the source of several commercial software packages. This technique is an analogue of Quantitative Structure-Activity Relationship (QSAR), which has been widely used in drug design to develop new pharmaceuticals. In this technique, we try to relate the structure of the monomer of particular polymer to the physical, mechanical, and thermal properties of the derived polymer using mathematical methods [1–3]. However, in this current work, we are more interested in investigating the effect of inconsistency within a dataset, *i.e.* in terms of the presence of polymerisable functional groups in some of the materials in the dataset, to the prediction accuracy of a char yield prediction model.

2. Method

Molecular Operating Environment (MOE) software by Chemical Computing Group (Cambridge, UK) was used to run QSPR and generate models to calculate the predicted char yield of thirty-three benzoxazines (the training set). The Partial Least Squares (PLS) regression algorithm was used to analyse the relationship between the actual char yield (measured by experimental work) and the predicted char yield (calculated using the model). PLS was chosen because it contains the fewest number of factors therefore it provides maximum correlation with the dependent variables.

There are seven main steps to generate a model with the best final linear model equation:

1. The training data set was collected from the literature. This training set is a secondary data set and consists of thirty-three benzoxazines with corresponding actual char yields measured by different research groups.
2. All monomers were built using the builder menu in MOE and a conformational search using Low Mode Molecular Dynamics [16] was carried out on each monomer before energy minimising the lowest energy conformer of each model to convergence.
3. A series of descriptors [17] were calculated for each monomer, which cover molecular volume, shape, charge, *etc.*
4. A QSPR equation was developed to relate the descriptors to the experimentally determined char yield using PLS [18].
5. Descriptors, which play a major role in influencing the model, were chosen. The linear model equation with the highest coefficient of determination (r2) was selected and further analysis was done on this model. The descriptors were used to calculate the prediction values and the average percentage error of the data produced was calculated *in-silico*. There are over 100 parameters in the software, so a subset is chosen randomly and pruned by the process described below to leave the best set of parameters that influence the equation without over-determining the equation. During the modelling the software gave the relative importance of each variable used and at each cycle those that contribute a small amount to the prediction are deleted leaving only those have a real influence on the regression. Finally, a statement of the relative importance of the descriptors is presented. The absolute values of the normalized coefficients are printed, divided by the absolute value of the largest normalized coefficient.
6. The Leave-One-Out-Cross-Validation (LOOCV) test [19] was carried out by the model to evaluate whether it could be taken further and was capable of producing accurate prediction values. This test was done by taking out one of the materials in the training set and applying the model to that chosen material.

The experimental data for the materials used in the validation test were compared against the predicted/calculated data. The percentage error and difference error between the two values was calculated and a conclusion was made based on the comparison values.