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Curing Characterisation of Spruce Tannin-based Foams using the Advanced Isoconversional Method

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The curing kinetics of foam prepared from the tannin of spruce tree bark was investigated using differential scanning calorimetry (DSC) and the advanced isoconversional method. An analysis of the formulations with differing amounts of components (furfuryl alcohol, glycerol, tannin, and a catalyst) showed that curing was delayed with increasing proportions of glycerol or tannins. An optimum amount of the catalyst constituent was also found during the study. The curing of the foam system was accelerated with increasing temperatures. Finally, the advanced isoconversional method, based on the model-free kinetic algorithm developed by Vyazovkin, appeared to be an appropriate model for the characterisation of the curing kinetics of tannin-based foams.

Keywords: Cure kinetics; Differential scanning calorimetry; Foam; Spruce bark tannin

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INTRODUCTION

Renewable resources can provide partial or, in some cases, complete substitutes for petroleum-based polymers through the design of bio-based polymers. Bio-based polymers can compete with, or even surpass, existing petroleum-based materials on a cost-performance basis, possessing high eco-friendliness values as well (Raquez *et al*. 2010).

Wood and bark are the two most common natural renewable resources that can be most easily used for creating bio-based polymers. Bark is less attractive for commercial use and is typically a waste product that is used for burning. Nevertheless, because of its diverse chemical structure, bark has a high potential for use as a raw material for many products (Gričar 2011). It contains natural protective compounds called tannins, which, because of their high reactivity, are also suitable for the production of foams (Link *et al*. 2011; Tondi and Pizzi 2009). Tannin-based foams are made through the polycondensation of polyflavonoid tannins and formaldehyde in combination with the autocondensation of furfuryl alcohol (Pizzi *et al*. 2012). The resulting thermosetting material can be used as a thermal or sound insulator, an absorber of metal ions (Tondi *et al*. 2009), a dye or a pharmaceutical compound (Sanchez-Martin *et al*. 2013), or a material with good resistance to chemicals and fire (Meikleham and Pizzi 1994; Tondi and Pizzi 2009).

In thermosetting systems (*e.g.*, tannin-based foams), it is important to consider the cure kinetics, that is, how the cure transition phenomena (*e.g.*, gelation and vitrification) relates to the reaction time and temperature. A good understanding of cure kinetics, *i.e.*, the consolidation of the material from the start of crosslinking to a viscous state, through a rubbery gel into an elastic solid (Huang and Patham 2013), makes it possible to tailor the

properties of the cured polymer.

During the formation of thermosetting foams, monitoring the curing kinetics is of the upmost importance, as it must be balanced with the kinetics of the foaming process (Basso *et al*. 2013). Thus, knowledge of curing kinetics is necessary for better control of the process, as well as for the quality of the final product (Alonso *et al*. 2006). This process can be monitored by certain methods that either record the concentrations of the unreacted functional groups or measure the physical or viscoelastic properties associated with the curing reaction (*e.g.*, the shear or flexural modulus). These monitoring methods also measure the viscosity, shrinkage, conductivity, and changes in the heat flow during the formation process of the foams (Lipshitz and Macosko 1977).

Cure kinetics are commonly determined by DSC or TGA measurements, which can be performed under either isothermal or dynamic conditions (Um *et al*. 2002). Furthermore, cure kinetics are modelled based upon two different approaches: model-based kinetics (such as the nth-order model) or model-free kinetics (MFK), such as the Vyazovkin method, and advanced model-free kinetics (AMFK) (Vyazovkin and Wight 1997). The model-based approach assumes constant activation energy throughout the entire process, whereas model-free kinetics assume that the activation energy changes during the process, independent of the temperature. The latter is better suited to describe and predict the curing process in tannin-based thermosets, as it involves numerous consecutive reactions and therefore cannot be described with a single activation energy. For similar phenolic thermosets, MFK has been renowned as being far superior in modelling accuracy in comparison to any of the other model-based approaches (Wang *et al.* 2005, 2007). Establishing a dynamic or non-isothermal experiment is more convenient than establishing an isothermal experiment. A combination of dynamic heating and isothermal experiments can be used to overcome the experimental challenges inherent when using AMFK (Vyazovkin and Wight 1997).

The cure kinetics of foams have been infrequently researched and rarely described in the literature. Only a few studies on the curing of polyurethane foams have been conducted and published, where differential scanning calorimetry was used as an investigation method. Characterisation of their curing has been interpreted by means of different methods, such as the Kissinger method (Peng *et al*. 2000) or MFK (Daniel-da-Silva *et al*. 2008). The lack of information involving the curing of polyurethane foams is most likely related to experimental difficulties encountered in the monitoring of the rate of a chemical reaction during the expansion and foaming of a polymer. In the case of tannin-based foams, no kinetic studies using DSC have been reported.

Given the apparent lack of information concerning tannin-based foams, the aim of this work was to assess the impact of tannin-based foam formulation on its cure kinetics, using AMFK as the standard. To this end, the Vyazovkin isoconversional method (Vyazovkin 1996, 1997) was used, based on a series combination of isothermal and dynamic-isothermal experiments. The change in activation energy in the cure conversion was thus monitored for various formulations. In particular, the influence of the content of the catalyst, glycerol, and tannin in the formulations was investigated.

EXPERIMENTAL

Effects of temperature and composition on the curing of tannin-based foams was studied by differential scanning calorimetry, measuring the heat flow during the reaction.

Materials

Condensed tannins were extracted from spruce bark (*Picea abies* L.) in an unpressurised hot water treatment plant. Crude tannin, with a purity of a 50%, was produced in the laboratories of VTT, the Technical Research Centre of Finland, in accordance with the procedure described by Kemppainen *et al*. (2014). Other reagents, such as furfuryl alcohol (98%) and a water solution (65%) of a monohydrate of toluene-sulphonic acid (pTSA), were supplied by the Merck Company. Glycerol (99.5%) was produced by Kemika Inc. (Zagreb, Croatia).

The effects of the overall content of glycerol, tannin, and catalyst on the cure reaction were investigated. Four formulations of foams were prepared with varying compositions (Table 1). The reference composition (where the ratio of furfuryl alcohol to glycerol to tannin to catalyst (pTSA) = 5:2:5:3) was the same for each set of measurements. In total, 10 different compositions of foams were analysed. Each composition was designated with a label, which is stated below in the figures and tables. The sequence of digits determines the weight in grams of the individual components in the following order: furfuryl alcohol, glycerol, tannin, and pTSA, as seen in Table 1.

Table 1. Composition of the Foams and Types of Measurements

NAME	Furfuryl alcohol (g)	Glycerol (g)	Tannin (g)	Catalyst - pTSA (g)	Set of measurements
5:2:5:3	5	2	5	3	Reference
5:0:5:3	5	0	5	3	Variation of the glycerol
5:1:5:3	5	1	5	3	
5:3:5:3	5	3	5	3	
5:2:3:3	5	2	3	3	Variation of the tannin
5:2:4:3	5	2	4	3	
5:2:6:3	5	2	6	3	
5:2:5:2	5	2	5	2	Variation of the catalyst
5:2:5:4	5	2	5	4	
5:2:5:5	5	2	5	5	

Methods

Preparation of the foams

Tannin-based foams were prepared in the following manner: furfuryl alcohol and glycerol were first mechanically stirred at a speed of 1000 rpm for 30 s. Mixing was carried out with IKA RW 20 digital blender using propeller stirrer shaft with 4-blades. Subsequently, tannin was added and the mixture was stirred for another 60 s. A catalyst (65% water solution of pTSA) was then added to the homogenised mixture, followed by the stirring of the mixture for 20 s. The mixture was not a clear solution, because tannin was not totally dissolved in it. The mixture was then inserted into an aluminium DSC crucible, sealed, and placed in the high-pressure chamber of a differential scanning calorimeter to measure the heat of reaction during the curing process.

Differential scanning calorimetry (DSC)

Different temperature programs, with heating rates similar to real conditions found during the formation of foam, were used (Fig. 1). Modelling of curing according to the AMFK approach allows a combination of dynamic and isothermal heating experiments.
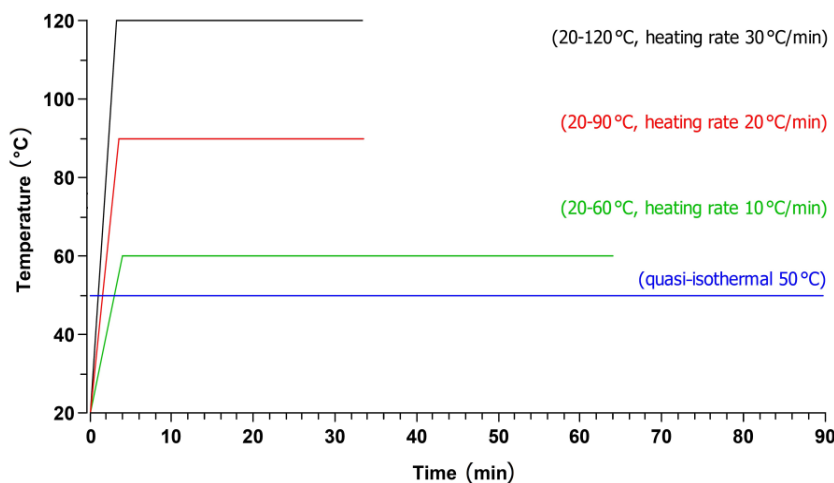

Fig. 1. Temperature programs used during the DSC measurements

The DSC measurements were made to investigate the rate of the chemical reactions occurring during foam formation. The measurements were taken using a Mettler Toledo HP DSC 1 differential scanning calorimeter, in 40-µL aluminium crucibles, with lids that were pierced and sealed. A nitrogen-rich (N_2) atmosphere, at a pressure of 20 bars, was used to move the water evaporation point to a higher temperature. In addition, the nitrogen-rich atmosphere also prevented overlapping between the endothermic signal of the water evaporation and the exothermic signal of the chemical reaction of polycondensation and autocondensation during curing. The sample masses for the DSC measurements fell between 18.17 and 22.70 mg. The weighing process was performed using a Mettler Toledo XS 205 balance. The DSC measurements were conducted using four different methods. The first three methods combined dynamic and isothermal conditions, where the samples were heated from 20 °C to 60, 90, or 120 °C, with heating rates of 10, 20, or 30 °C/min, respectively. Finally, the first three methods were held isothermally at their final temperatures for 30 or 60 min. The fourth measurement was conducted under quasi-isothermal conditions at 50 °C. The specimen was heated at a rate of 100 °C/min to the final temperature (50 °C) and maintained at this temperature for another 90 min. Using this procedure, the reaction was performed to its fullest extent. Each specimen was scanned twice, once during the curing process and once when in its final cured state. The normalised values of the heat flow obtained from measurements of the cured state of the samples were subtracted from the previous measurement (taken during curing) to exclude the thermal effect due to temperature changes during the process. A horizontal line was used as the baseline for the integration of dissipated heat. All the measurements of heat flow were performed twice, and each curve used in the calculations represents an average value. The DSC thermograms were processed using Mettler Toledo STAR V10.0 software as well as an Advanced Model Free Kinetics (AMFK) module to calculate both the degree of conversion and the activation energy during the curing reaction. The curve of the activation energy represents the basis for further predictions of the conversion of foams under isothermal conditions.

The kinetic evaluation method

In the dynamic curing process studied by DSC, the degree of conversion, α, can be determined from the exothermic signal using the equation:

$$\alpha = \frac{H_t}{H_{tot}}$$ (1)

where H_t is the heat dissipated from the reaction at time t and H_{tot} is the complete heat of reaction. The time derivative of Eq. 1 is as follows:

$$\frac{d\alpha}{dt} = \frac{1}{H_{tot}} \cdot \frac{dH_t}{dt}$$ (2)

where $d\alpha/dt$ is the reaction rate and dH_t/dt is the heat flow. The rate of reaction can also be written as a function of the temperature T:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha)$$ (3)

where $f(\alpha)$ is the reaction model and $k(T)$ is the rate constant. The rate is usually expressed by the Arrhenius equation:

$$k(T) = A \cdot \exp\left(-\frac{E}{RT}\right)$$ (4)

where A is a pre-exponential factor, representing the number of collisions between reagents per unit of time, E is the activation energy, R is the gas constant, and T is the absolute temperature (Poorabdollah *et al*. 2013).

In MFK, the activation energy is allowed to fluctuate as the reaction progresses. The fluctuation allowance is based on the assumption that there is not one solitary reaction model that can be used to adequately describe the reaction kinetics over the course of the reaction. It is well-established that, in the case of the complex set of reactions involved in the curing of phenolic resins, MFK is more appropriate than kinetic models (Wagner 2009; Wang *et al*. 2005). In these methods, known as isoconversional methods because they are based on the isoconversional principle, it is assumed that the reaction rate is (at a constant conversion degree) a function of temperature only, as depicted in the following equation (Poorabdollah *et al*. 2013; Sbirrazzuoli and Vyazovkin 2002; Vyazovkin and Sbirrazzuoli 2006).

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_\alpha = \left[\frac{\partial \ln k(T)}{\partial T^{-1}}\right]_\alpha + \left[\frac{\partial \ln f(\alpha)}{\partial T^{-1}}\right]_\alpha$$ (5)

where the subscript α indicates isoconversional values that are related to a specified conversion degree. If the conversion degree (α) is constant, then $f(\alpha)$ is constant as well, meaning Eq. 5 can be rewritten as follows:

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_\alpha = -\frac{E_a}{R}\bigg|_\alpha$$ (6)

It is clear that the activation energy, E_a, can be evaluated without determining any particular form of the reaction model. This is why isoconversional methods are frequently called "model-free" methods (Poorabdollah *et al*. 2013).

To obtain the temperature dependence of the isoconversional rate, either a series of three to five measurements at different heating rates should be performed, or a series of measurements at different constant temperatures have to be used.

One of the most precise methods of determining temperature dependence was developed by Vyazovkin (1996). Vyazovkin's method is based on the direct numerical integration of Eq. 2. The conversion dependence of the activation energy can be determined by minimising the following function (Eq. 7), where, in the case of an arbitrary temperature program, the typical function of integration over temperature is replaced by integration over time. The resulting method can be used to handle data obtained from any temperature program (Vyazovkin 2008).

$$\varphi(E_a) = \sum_{i=1}^{n}\sum_{j\neq i}^{n} \frac{J[E_a, T_i(t_\alpha)]}{J[E_a, T_j(t_\alpha)]} \qquad (7)$$

where,

$$J[E_a, T_i(t_\alpha)] = \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[-\frac{E_a}{RT_i(t)}\right] dt \qquad (8)$$

In practice, this algorithm is integrated using the Mettler Toledo STAR V10.0 software, with the function "Advanced Model Free Kinetics (AMFK)".

RESULTS AND DISCUSSION

Effect of Composition

As expected, the curing of foam resulted in an exothermal signal when the sample was exposed to different temperature programs, as shown in Fig. 1. The signal occurred earlier and became narrower with higher heating rate intervals and higher ending temperatures (Fig. 2). Increasing temperature results in increased mobility of the molecules, subsequently increasing the reactivity of the system as well. Additionally, the heat of the reaction depends on the catalyst content. In cases where the catalyst quantity of the mixtures was equal to that of the reference mixture, the heat of cure was approximately 272 J/g (variation of glycerol or tannin). When varying the total amount of the catalyst, the heat of cure ranged from 180 to 280 J/g.
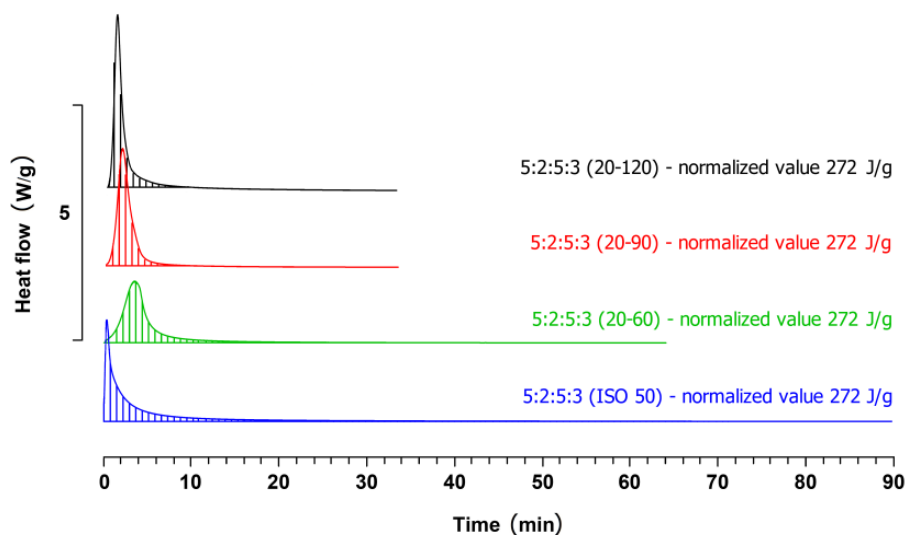

Fig. 2. DSC thermograms showing the cure exotherm signal of the reference foam composition for different heating programs, as described in Fig. 1

The heat of reaction depended on the amounts of the individual components (Fig. 3), which was most apparent in the case of the isothermal mode at 50 °C. Increasing the proportion of glycerol or tannin decreased the overall heat of reaction. A possible reason for the decrease in heat can be found by decreasing the amount of furfuryl alcohol. Autocondensation of the furfuryl alcohol is an exothermic reaction. Therefore, decreasing its relative proportion, while increasing the proportion of glycerol or tannin, can decrease the overall heat of reaction. This effect was more apparent when the amount of tannin was increased. This indicates that the tannin content had a slightly greater impact on the elimination of possible reaction locations than glycerol.
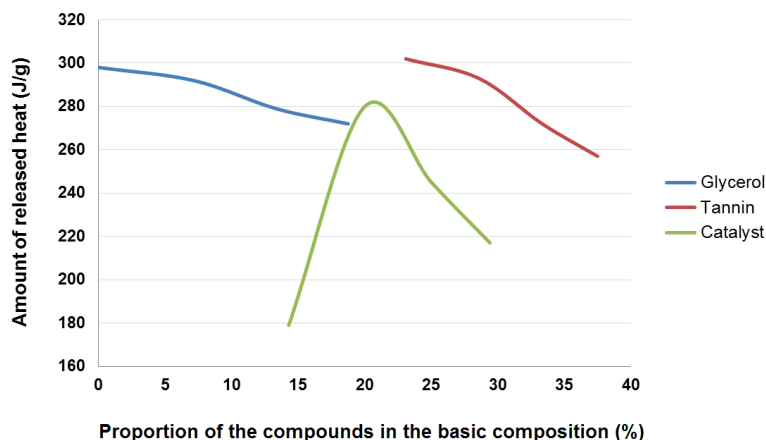
Fig. 3. The normalised heat of reaction during isothermal DSC measurements for different amounts of the foam constituents

Regarding the proportion of the catalyst, the maximum emitted heat was recorded when the catalyst content was about 20%. By decreasing or increasing the proportion of catalyst from this value, the amount of heat was greatly reduced. It can be concluded that adding 20% catalyst to the foam composition was the optimum amount. Any proportion of catalyst added below 20% resulted in a lower amount of heat emitted in the reaction, as a higher proportion of the catalyst is required for maximum cross-linking of the foam. Consequently, the maximum amount of heat was not reached.
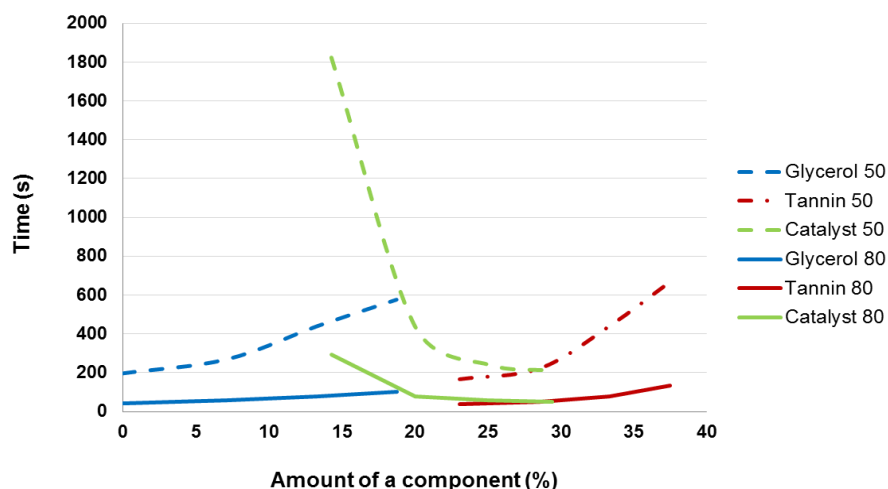
Fig. 4. The time (in seconds) required to achieve an 80% conversion - dependence of the foam formulation amounts of the different compounds for two isothermal temperatures

In the case of proportions which were higher than 20%, a drop in the total heat could be the result of increased intake of water into the system, as the catalyst was a water solution of toluene-sulphonic acid monohydrate.

Another approach to visualise the impact of formulation on cure kinetics is to assess the time needed to completely reach a specified degree of conversion with a given temperature program. At 50 °C, approximately 440 s were needed to achieve an 80% conversion (Fig. 4) of the reference composition. A small increase in the temperature, from 50 to 60 °C, shortened the curing time by almost one half. Additionally, at 90 °C, only 80 s were needed to achieve the same degree of conversion.

Increasing the proportion of glycerol or tannin resulted in the prolongation of the time required to attain 80% conversion. The addition of glycerol (up to 20%) extended the overall time by a factor of three. A slightly greater effect on the increase in the required time could be observed when the proportion of the tannin was increased. An increase of 15% in the proportion of the tannin (*e.g.*, from 23 to 38%) prolonged this time by about 500 s.

At lower temperatures (50 °C, for example), increasing the proportion of the catalyst to 25% resulted in a significant reduction in the amount of time needed to reach 80% conversion. An increase of 5% of the catalyst (from 15 to 20%) reduced the time by approximately 1400 s. In the case of higher proportions (between 25 and 30%), the detected differences were insignificant. The inflection point represents the optimum proportion of the catalyst, which, in the present case, lay between 22 and 23%. A similar trend can be observed when incorporating higher temperatures (80 °C) as well. Increasing the proportion of the catalyst reduces the activation energy of the reaction, as the number of collisions between molecules increases, which results in a faster reaction.

Raising the temperature reduces the optimum proportion of the catalyst that is needed. Higher temperatures increase the energy of the atoms, which is reflected in the reduction of bond breaking difficulty in new reactions. According to AMFK predictions, the optimal amount of the catalyst is 22% at 50 °C; however, when the temperature is increased to 80 °C, the optimal amount falls to 20%. Therefore, to determine the optimal quantity of the catalyst, it is necessary to take into account the temperature conditions during the reaction (or production), which strongly affect the proportions of the individual components.

Fig. 5. Picture of a spruce tannin-based foam with the reference composition

Prediction Modelling with AMFK

As expected, the total activation energy varied with the degree of conversion (Fig. 6). In a lower range of conversion, more energy was needed for the reaction to proceed. When the degree of conversion ranged from 20 to 60%, the activation energy was more or less constant and reached its minimum when the degree of conversion was nearing the maximum of the range. The shape of the curve was similar for all the tested compositions. The value of the activation energy for the reference composition of foam was within the range of 30 and 80 kJ/mol of the substance (mixture).
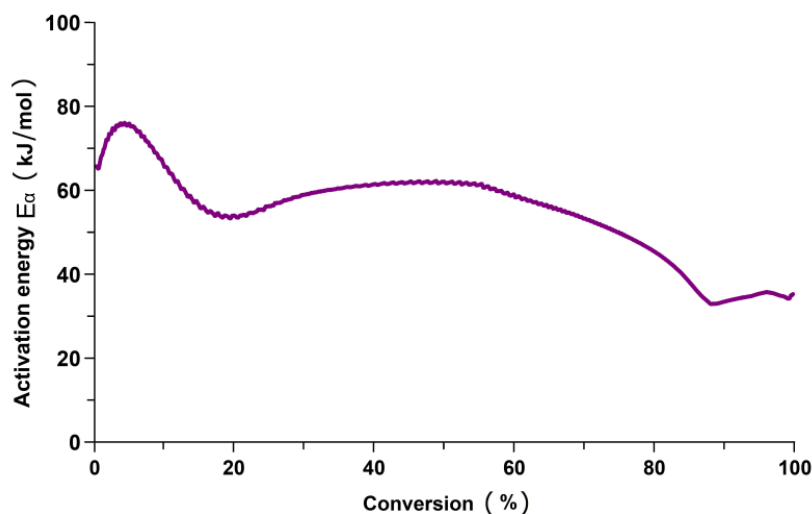

Fig. 6. Dependence of the degree of conversion on the activation energy for the reference foam composition

Complex reactions involving multiple parallel reactions or changes cause variation in the activation energy. Increasing the function (E_a) (*i.e.*, its value) reveals the presence of, and competition between, parallel reactions. Decreasing the function suggests the terminal stage of the reactions. A concave, decreasing curve (of E_a) suggests a terminal stage reaction, whereas a convex, decreasing curve indicates a change in the limiting stage (Wang *et al*. 2005).

In Fig. 6, at least 3 stages of the curing process can be observed: (1) From the onset of the reaction up to 5% degree of conversion, E_a increases, indicating the presence of competing parallel reactions. This is expected, as both the autocondensation of the furfuryl alcohol (Guigo *et al.* 2007) and the hydroxymethylation of the polyflavonoid are likely to occur in the first stages of the cure; (2) From 5% to 20%, E_a decreases sharply, indicating a reversible intermediate stage; and (3) From 20% to 80%, the convex, decreasing curve suggests a change in the limiting stage. The cure might become a diffusion controlled-process.

This behaviour is generally similar to that previously observed for the condensation and curing of phenol-formaldehyde resins under basic conditions (Wang *et al*. 2005).

With this modelling information, predictions involving the degree of conversion can be made for any temperature program. A selection of predictions for isothermal cure programs is presented in Fig. 7. Under isothermal conditions, predictions of conversion should be based on the calculated activation energy. The time dependency of conversion for the reference composition, at temperatures ranging from 40 to 100 °C (with 10 °C intervals), are depicted with solid lines in Fig. 7. The dashed lines represent the

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experimental data of the reference composition when exposed to an isothermal temperature of 60 or 70 °C (Fig. 7).
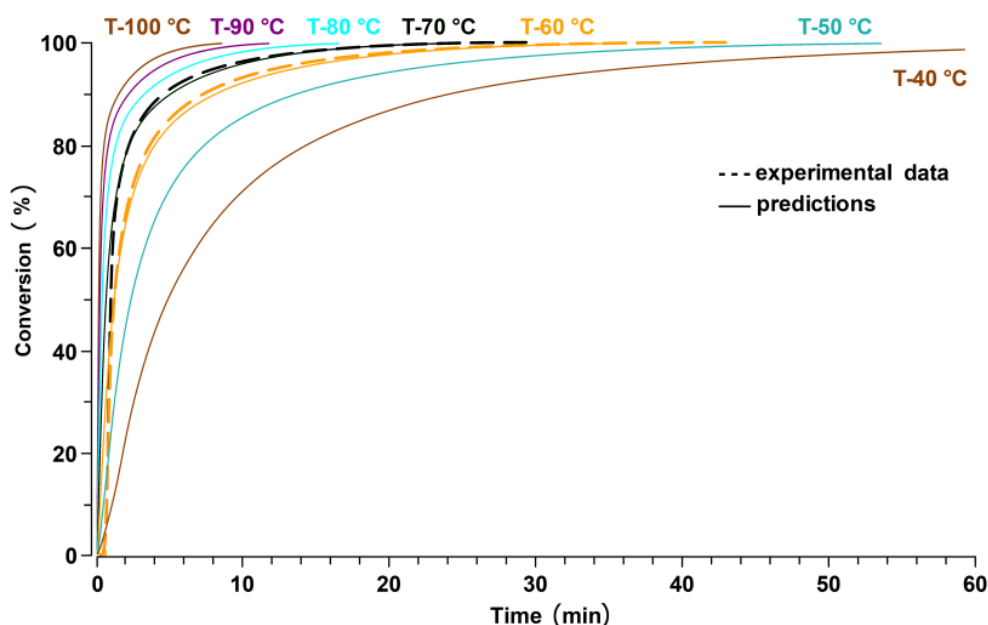

Fig. 7. Prediction of conversion for different isothermal temperatures in the case of the reference foam composition and comparison with the experimental data for two isothermal temperatures (60 and 70 °C)

It is evident that the prediction curves aligned with the experimental data very well. The main limitation was that the experimental data used for the model construction were similar to those used in the prediction. However, it can still be concluded that the Vyazovkin advanced isoconversional method is a suitable method for the characterisation of the curing of tannin-based foams. Predictions of the conversion modulated by AMFK are shown for other studied foam compositions in Tables 2, 3, and 4.

Table 2. Time Required (s) to Achieve a Certain Degree of Conversion – Depending on the Amount of Glycerol for Two Isothermal Temperatures

		Type of composition							
		5:0:5:3		5:1:5:3		5:2:5:3		5:3:5:3	
		50 °C	80 °C	50 °C	80 °C	50 °C	80 °C	50 °C	80 °C
Conversion	0.10	15.0	1.7	18.0	1.5	26.4	2.8	33.0	3.8
	0.20	27.6	3.2	36.0	3.9	48.6	6.6	59.4	9.6
	0.30	41.4	5.8	52.2	7.8	71.4	10.2	86.4	15.0
	0.40	54.6	9.0	70.2	12.6	100.2	14.4	120.6	21.0
	0.50	70.8	13.2	94.2	17.4	139.2	19.8	165.6	28.8
	0.60	94.8	17.4	127.8	24.6	195.6	28.2	232.2	40.2
	0.70	132.0	24.6	177.6	35.4	282.0	43.2	345.0	60.6
	0.80	196.8	40.2	269.4	57.0	440.4	76.8	576.6	103.8
	0.90	337.2	85.8	498.0	114.6	819.6	195.6	1205.4	236.4

Table 3. Time Required (s) to Achieve a Certain Degree of Conversion – Depending on the Amount of Tannin for Two Isothermal Temperatures

		Type of composition							
		5:2:3:3		5:2:4:3		5:2:5:3		5:2:6:3	
		50 °C	80 °C	50 °C	80 °C	50 °C	80 °C	50 °C	80 °C
Conversion	0.10	13.8	1.3	18.0	1.7	26.4	2.8	40.8	6.0
	0.20	25.2	2.5	33.6	3.9	48.6	6.6	72.0	12.6
	0.30	37.8	4.8	48.6	7.2	71.4	10.2	107.4	19.2
	0.40	49.8	8.4	64.2	11.4	100.2	14.4	150.6	27.0
	0.50	63.6	12.0	84.6	16.2	139.2	19.8	208.8	37.8
	0.60	83.4	16.2	112.2	21.6	195.6	28.2	292.8	53.4
	0.70	114.6	23.4	153.6	31.2	282.0	43.2	426.6	80.4
	0.80	166.8	37.2	222.6	51.0	440.4	76.8	669.0	134.4
	0.90	274.2	76.2	372.0	106.8	819.6	195.6	1225.2	278.4
	0.99	696.0	295.8	989.4	384.6	2411.4	723.6	3567.0	1008.6

Table 4. Time Required (s) to Achieve a Certain Degree of Conversion - Depending on the Amount of Catalyst for Two Isothermal Temperatures

		Type of composition							
		5:2:5:2		5:2:5:3		5:2:5:4		5:2:5:5	
		50 °C	80 °C	50 °C	80 °C	50 °C	80 °C	50 °C	80 °C
Conversion	0.10	84.6	21.0	26.4	2.8	13.2	1.2	10.8	1.1
	0.20	165.6	39.0	48.6	6.6	25.8	2.3	19.8	2.0
	0.30	273.0	58.8	71.4	10.2	40.2	4.7	30.6	3.3
	0.40	421.2	84.6	100.2	14.4	55.2	8.4	43.2	5.8
	0.50	625.8	117.0	139.2	19.8	73.2	13.2	57.6	9.6
	0.60	905.4	159.0	195.6	28.2	102.0	19.2	80.4	15.0
	0.70	1286.4	215.4	282.0	43.2	149.4	30.6	123.0	24.6
	0.80	1823.4	294.6	440.4	76.8	242.4	58.2	210.6	51.0
	0.90	2689.2	414.6	819.6	195.6	531.6	163.8	498.0	160.8
	0.99	4701.6	697.8	2411.4	723.6	2721.0	796.8	3110.4	810.0

CONCLUSIONS

1. It was demonstrated for the first time that the cure kinetics of tannin foams can be monitored by differential scanning calorimetry (DSC) and modelled using the Vyazovkin advanced isoconversional method.

2. The results show that the curing process is delayed when the proportion of glycerol or tannin in the mixture is increased. However, for the catalyst, it was observed that an optimum amount exists.

3. The optimal proportion of the components used depends on the temperature conditions.

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