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On the curing of a vinylester–urethane hybrid resin

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Abstract

Curing kinetics of a vinylester–urethane hybrid (VEUH) resin consisting of vinylester resin (VE) diluted in styrene and novolac type polyisocyanate (NPI) have been studied by differential scanning calorimetry (DSC). As VEUH is crosslinked via free radical polymerisation between the vinyl functions of styrene and VE, and polyaddition reaction between the secondary –OH groups of VE and –NCO of NPI, it was necessary to study these reactions separately. This was achieved by studying the curing with and without incorporating the NPI. The curing reaction was monitored by measuring the heat of reaction under isothermal and dynamic temperature conditions. Models describing the curing were developed, which are in good agreement with the experiments. A comparison between the curing of the VEUH and the VE resin without NPI leads to the conclusion that the curing of the VEUH as accessed by DSC is dominated by the radical polymerisation of styrene with VE although the two reactions are not time separated. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Vinylester–urethane hybrid resin; Curing kinetic; Modelling

1. Introduction

The vinylester–urethane hybrid (VEUH) resin used in this study consists of vinylester (VE) diluted in styrene and a novolac type polyisocyanate (NPI). VE was produced by reacting a bisphenol-A type epoxy resin with methacrylic acid [1]. So this VE resin has terminal vinyl functions and secondary hydroxyl groups. During curing the vinyl function of the VE can undergo a radical reaction with the styrene and its hydroxyl group can react with the isocyanate of NPI [2]. The result is a crosslinked network with very good mechanical and thermal properties and high resistance to corrosion [3]. Due to the combination of the radical polymerisation and urethane chemistry VEUH resins are very versatile and their property profile can be easily tailored to special needs [4]. It should be noted that the curing is not accompanied by any phase separation.

For processing VEUH the understanding of the curing behaviour is required. For simulation of the different operations, i.e. mould filling in the resin transfer moulding, mathematical models, which describe the change in conversion and viscosity are of paramount interest. The determination of the cure behaviour of VE resins [5–8] and VE/urethane interpenetrating networks [9–12] was object of numerous studies. In these works differential scanning calorimetry (DSC), fourier transform infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA) and viscosity measurements were used to monitor the crosslinking reactions. Surprisingly no detailed work was devoted to the cure kinetics of VEUH resins. Studies on VE/urethane resins with interpenetrating network formation can hardly be adopted to VEUH as the former systems undergo phase separation in contrast to VEUH.

Therefore, the aim of this study was to analyse the curing of a VEUH by DSC under isothermal and dynamic conditions. A further aim of this work was to derive empirical models, which describe the change of conversion during curing of the VEUH resin accordingly.

2. Experimental

2.1. Materials

The VEUH resin contained an bisphenol-A based, in styrene diluted VE of bismethacryloxy type (Daron® XP 45-A-2) and a (NPI; Daron® XP 40-B-1). Both are products of DSM-BASF Resins BV. In NPI the radical initiator benzoylperoxide (BPO) was dissolved. The reactants were used as received. The recipe was as follows:

100 parts VE (Daron® XP 45-A-2, styrene content: 30 wt%, ratio of the double bonds VE/styrene = 1 : 1.2)
38 parts NPI (Daron® XP 40-B-1, NCO functionality: 2.7)

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1.5 parts BPO (dibenzoylperoxide, Lucidol® CH 50L of Akzo Nobel, peroxide content: 50 wt%).

The styrene content, the double bound ratio of VE/styrene and the functionality of NPI was validated by nuclear magnetic resonance spectroscopy (^{1}H NMR). Apart to study the combined reactions in VEUH, viz. radical polymerisation + polyurethane formation, attempt was made to assess the radical polymerisation separately. The related recipe (VE/BPO) did not contain NPI. In this formulation the BPO was dissolved directly in VE. Additionally to the above mentioned two resin formulations a third one containing neat VE (nVE) diluted in xylene, and NPI was also involved in this study. This formulation served to study the polyurethane reaction separately. The non-commercial neat VE was also supplied by DSM-BASF and was identical with the VE diluted in styrene as proved by ^{1}H NMR. The xylene content was 30 wt%. The recipe of this third reactive resin nVE/Xyl/NPI was as follows: 70 parts nVE, 30 parts xylene, 38 parts NPI (Daron® XP 40-B-1).

2.2. Experimental techniques

2.2.1. DSC analysis

The measurement of the exothermal heat flow during the curing reaction was measured using a Mettler Toledo DSC821^e DSC and high pressure pans with fluororubber o-sealings to avoid evaporation of styrene or xylene during the experiment. Nitrogen was used as flushing gas. The sample weight varied between 10 and 25 mg and was chosen to assure that the increase of the sample temperature above the set point due to the exothermic reaction was negligible. Isothermal measurements were done at different temperatures in the range from 80 to 120 °C. As soon as the isothermal experiment was completed, the residual heat of reaction was measured in a dynamic scan at a heating rate of 10 °C min^{-1}. Dynamic DSC experiments were conducted in the temperature range from −100 to 280 °C with heating rates varying from 1 to 15 °C min^{-1}.

Since resins with different recipes are studied, the amount of heat (Q) released during the curing reactions had to be normalised

$$q = \frac{1}{m_{\mathrm{VE}}} Q \tag{1}$$

where m_{VE} is the mass of the vinylester (without styrene) in the sample.

When accessing curing kinetics of thermosetting resins with DSC, it is assumed, that the amount of heat (q) generated by the curing reaction is proportional to the degree of cure or conversion α [13]. Thus the measured heat flow ($\mathrm{d}q/\mathrm{d}t$) is proportional to the rate of conversion ($\mathrm{d}\alpha/\mathrm{d}t$) where q_{tot} is the total (normalised) amount of heat released during the experiment

$$\frac{\partial \alpha}{\partial t} = \frac{1}{q_{\mathrm{tot}}} \frac{\partial q}{\partial t} \tag{2}$$

Integrating Eq. (2) leads to

$$\alpha = \int_0^t \left(\frac{\partial \alpha}{\partial t} \right)_T \mathrm{d}t \tag{3a}$$

for the isothermal experiment and

$$\alpha = \int_0^t \left(\frac{\partial \alpha}{\partial t} \right)_\beta \mathrm{d}t \tag{3b}$$

in case of the dynamic measurement with a constant heating rate β.

q_{tot} can be derived from both isothermal and dynamic measurements, the are denoted $q_{\mathrm{tot,iso}}$ and $q_{\mathrm{tot,dyn}}$, respectively. Whereas $q_{\mathrm{tot,dyn}}$ is directly measured, $q_{\mathrm{tot,iso}}$ is the summation of the heat released during the isothermal (q_{iso}) and the residual heat measurement (q_{res}), thus $q_{\mathrm{tot,iso}} = q_{\mathrm{iso}} + q_{\mathrm{res}}$. The residual heats were measured in a subsequent scan with a heating rate of 10 °C min^{-1}. Having two reactions, polyaddition and radical polymerisation, the conversion defined above is an overall conversion. Glass transition temperatures (T_g) of the fully cured resins were measured by scans with a heating rate of 10 °C min^{-1}.

2.2.2. Fourier transform infrared spectroscopy

A Nicolet 510 FTIR spectrometer was used in transmission mode with a resolution of 4 cm^{-1} to obtain IR absorption spectra for the curing of the VEUH resin. A drop of resin was placed between two KBr pellets. This was cured in an air oven. Before and after curing a spectrum with an average of 50 scans in the range of 400–4000 cm^{-1} was recorded. The absorption peaks of C–H bounds of the aromatic rings of vinylester and styrene at 830 and 700 cm^{-1}, [8,14] respectively, were used as internal standards to control the possible evaporation of styrene.

3. Results and discussion

3.1. Phenomenological aspects

Fig. 1 shows the normalised total amounts of reaction heat of various isothermal and dynamic DSC measurements of the three resins VEUH, VE/BPO and nVE/Xyl/NPI. It is important to verify, that $q_{\mathrm{tot,iso}}$ and $q_{\mathrm{tot,dyn}}$ for each resin is nearly constant. Due to the vitrification, the point at which T_g of the partly cured resin equals the momentarily reaction temperature [13], q_{iso} increases with increasing temperature. Thus the residual heat q_{res} is decreasing with increasing temperature. Although there is theoretically no difference between $q_{\mathrm{tot,iso}}$ and $q_{\mathrm{tot,dyn}}$, Fig. 1 shows that the total amount of reaction heat derived from dynamic measurements is always higher then that derived from isothermal ones. This is because the conversion during the stabilisation of the DSC in the beginning of the isothermal measurement is not recorded and because it is difficult obtaining the correct value for the peak area of the residual heat. The residual heat is released when T_g is surpassed, thus one is having two

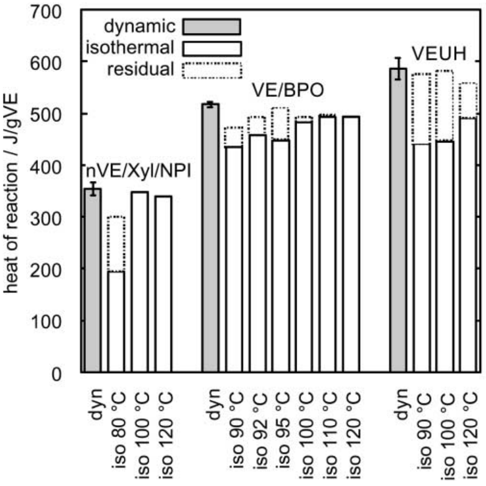

Fig. 1. Total heat of reaction normalised by the mass of VE (without styrene) of nVE/Xyl/NPI, VE/BPO and VEUH resins.

overlapping thermodynamic phenomenon when measuring the residual heat: the exothermic curing and the change in the heat capacity. In the following the $q_{\mathrm{tot,dyn}}$ value is used as total amount of heat in Eq. (2).

The comparison of the q_{tot} of the three resins VEUH, VE/BPO and nVE/Xyl/NPI gives an important conclusion to the reaction mechanism accessed by DSC. q_{tot} of VEUH is significantly smaller than the sum of the q_{tot} of VE/BPO and nVE/Xyl/NPI. The radical polymerisation dominates the reaction kinetic of the VEUH and the conversion rate of the polyaddition reaction of VEUH curing is reduced significantly compared to that of nVE/Xyl/NPI curing. This conclusion is supported by an FTIR measurement shown in Fig. 2. Fig. 2 shows the absorption spectrum of an VEUH sample before and after curing from 30 to 280 °C with a slope of 7.5 °C min^{-1}. The peaks at 945 cm^{-1} are assigned to the double bounds of styrene and those at 910 cm^{-1} to double bounds of the vinylester [14]. The peak at 2280 cm^{-1} is assigned to –NCO of the NPI. Whereas the double bounds are almost totally converted, the –NCO groups are still quantitatively detectable. After postcuring the sample at 200 °C for 3 h the –NCO groups are nearly totally converted as shown by the vanished peak at 2280 cm^{-1}. This finding is contrary to the curing behaviour of unsaturated polyester (UP) polyurethane hybrid resins, where the UP is terminated with hydroxyl groups [15]. In this case the two reactions are clearly time separated (two peaks in a DSC measurement) and the first peak is related to the polyaddition reaction. Since the kinetics of the polyaddition reaction taking place in the curing of the nVE/Xyl/NPI resin are changing significantly compared to those taking place in the curing of the VEUH resin, the nVE/Xyl/NPI resin is not able to serve as a substitute in order to analyse the polyaddition reaction separated from the radical polymerisation.

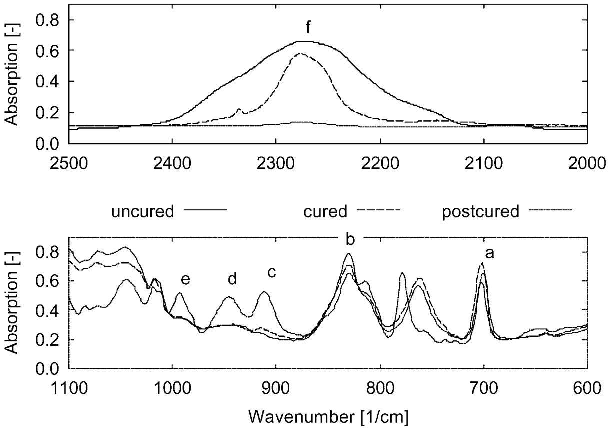

Fig. 2. FTIR absorption spectra of: uncured resins (solid line), cured VEUH resins under dynamic conditions with a heating rate of 7.5 °C min^{-1} (dashed line) and the resin postcured at 200 °C for 2 h (dotted line). Designation: (a) aromatic C–H bounds of styrene, (b) aromatic C–H bounds of VE, (c) double bounds of VE, (d) double bounds of Sty, (e) isocyanate of NPI.

In Fig. 3 the conversion rate against temperature of dynamic DSC measurements of the VEUH and VE/BPO resins at various heating rates are presented. The curve of the curing of VE/BPO resin at 15 °C min^{-1} heating rate has a minimum at 167 °C. The second maximum is significantly

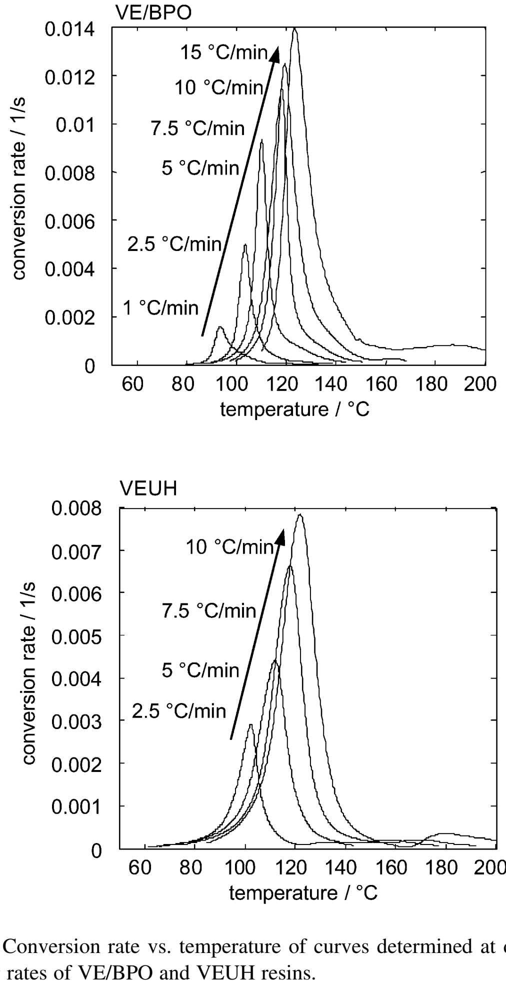

Fig. 3. Conversion rate vs. temperature of curves determined at different heating rates of VE/BPO and VEUH resins.

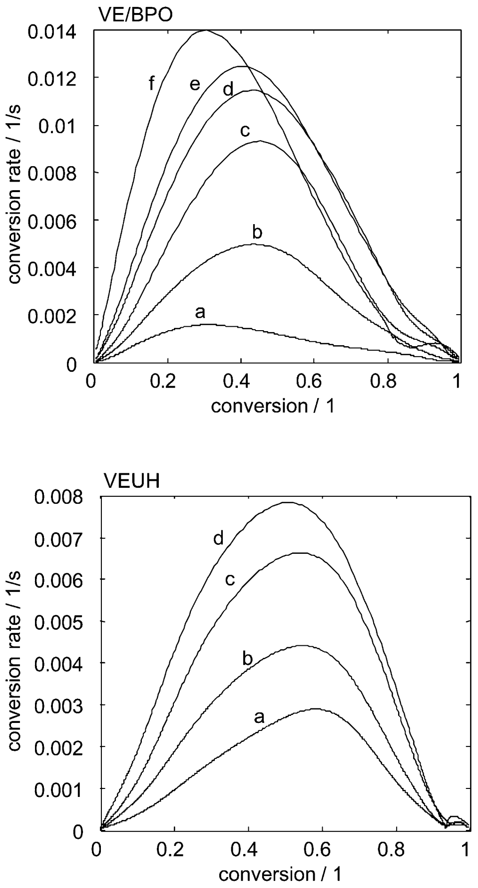

Fig. 4. Conversion rate vs. conversion of curves determined at different heating rates for the VE/BPO and VEUH resins. Designation: VE/BPO: (a) 1 °C min^{-1}, (b) 2.5 °C min^{-1}, (c) 5 °C min^{-1}, (d) 7.5 °C min^{-1}, (e) 10 °C min^{-1}, (f) 15 °C min^{-1}; VEUH: (a) 2.5 °C min^{-1}, (b) 5 °C min^{-1}, (c) 7.5 °C min^{-1}, (d) 10 °C min^{-1}.

lower. Such a second peak appears in experiments with heating rates above 7.5 °C min^{-1}. With a heating rate of 10 °C min^{-1} this minimum occurs at 157 °C. During the curing reaction of VE/BPO resin the T_g is increasing as a function of conversion from $T_g = -56$ °C at a conversion of 0 to $T_{g\infty} = 152$ °C at a conversion of 1 measured with DSC. Since the degree of cure is almost 1 when reaching the minima it is obvious that the reaction temperature is crossing T_g at these points. The dynamic measurements of the VEUH resin presented in Fig. 3 display similar minima. Their appearance can thus also be traced to vitrification. The vitrification point of the VEUH resin is reached at lower heating rates than that of VE/BPO. Thus the T_g of VEUH resin increases faster with the degree of curing than that of VE/BPO resin. Note that the $T_{g\infty}$ of fully cured VEUH resin is 220 °C measured by dynamic mechanical thermal analysis [4]. Since the development of the T_g with the degree of conversion is different when curing VEUH or VE/BPO resins, it is obvious, that, although the radical polymerisation is dominating the curing of VEUH accessed with DSC measurements, the polyaddition reaction is going on simultaneously.

3.2. Model for dynamic curing

In Fig. 4 curves of conversion rate vs. conversion of the dynamic curing of VEUH and VE/BPO are plotted. Various types of empirical kinetic equations were applied by other authors for the radical polymerisation of thermosetting resins [13,16]. In this study Kamal and Sourour's kinetic [17]

$$\left(\frac{\partial\alpha}{\partial t}\right)_T = k(T)\alpha^m(1-\alpha)^n \tag{4}$$

with the only temperature dependant rate constant k and the constants m and n developed for isothermal reactions is applied for the dynamic curing of VE/BPO and VEUH and describing the curves plotted in Fig. 4. Eq. (4) was rewritten by considering the heating rate β of the dynamic scans

$$\left(\frac{\partial\alpha}{\partial t}\right)_\beta = k(\beta)\alpha^m(1-\alpha)^n \tag{5}$$

Eq. (5) implies that the conversion α_{max} related to the maximum rate of conversion max($\mathrm{d}\alpha/\mathrm{d}t$) is constant

$$m = \frac{\alpha_{\text{max}}}{1-\alpha_{\text{max}}}n \tag{6}$$

and that the rate constant k is proportional to max($\mathrm{d}\alpha/\mathrm{d}t$). Fig. 5 shows the conversion α_{max} vs. β of the curing of the VE/BPO and VEUH resins. It is obvious, that α_{max} is not constant but strongly depends on the heating rate β. The empirical equation

$$\alpha_{\text{max}}(\beta) = \exp(a\beta^{-1} + b\beta + c) \tag{7}$$

is able to describe this dependency as can be seen in Fig. 5. The constant parameters a, b and c are fitted using the non-linear least-squares Marquardt–Levenberg algorithm.

The dependency of the maximum rate of conversion on the heating rate can be described by the empirical equation

$$\left.\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right|_{\text{max}}(\beta) = d\ln(\beta) + e \tag{8}$$

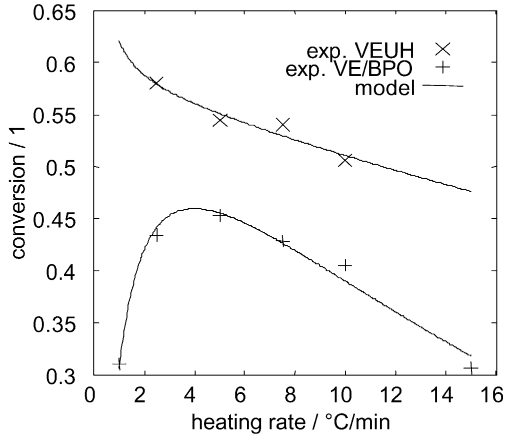

Fig. 5. Measured and calculated conversions at maximum conversion rate vs. heating rates of VE/BPO and VEUH resins.

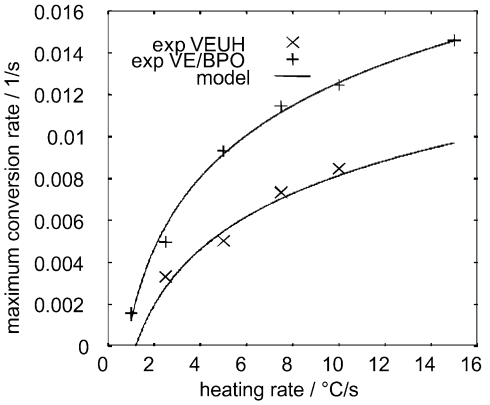

Fig. 6. Measured and calculated maximum conversion rate vs. heating rates of VE/BPO and VEUH resins.

The constant parameters d and e are fitted as shown in Fig. 6. Combining Eqs. (5)–(8) a model for the curing of the VE/BPO and VEUH resins is derived. The only remaining constant parameter n has to be adjusted to the experimental results (Fig. 3). For this fitting the same least-squares algorithm as mentioned previously is applied. The calculated constants are given in Table 1.

In Fig. 7 the correlation of the temperature ($T_{\max}$) at the point of the maximum conversion rate is plotted. Note that time and temperature are equivalent in case of a constant heating rate. Here the empirical equation

$$T_{\max} = f\ln(\beta) + g \tag{9}$$

gives a good fit with the experiments. In addition, Eq. (9) served as initial condition for solving the differential Eq. (5). In Fig. 8 the measured conversion vs. temperature curves and the calculated for the dynamic curing reaction of the VE/BPO and VEUH resin are given. During curing of the VEUH resin it is apparent that at the lowest heating rate the model is not matching the experiment exactly and that at conversion above 0.9 (where the diffusion control becomes significant) the model is also not exact. Nevertheless, the model proposed can describe the dynamic curing of both resins fairly and for the VEUH resin works extremely well.

Table 1
Calculated parameters for the models for the dynamic curing of VE/BPO and VEUH

	VE/BPO	VEUH
a (K s^{-1})	− 0.01114	− 0.002867
b (s K^{-1})	− 2.308	− 1.211
c	− 0.4657	− 0.4232
d (s^{-1})	0.004935	0.003847
e (s^{-1})	0.02142	0.01534
f (K^{-1})	10.91	14.04
g (K^{-1})	411.6	420.2
n	2.215	1.215

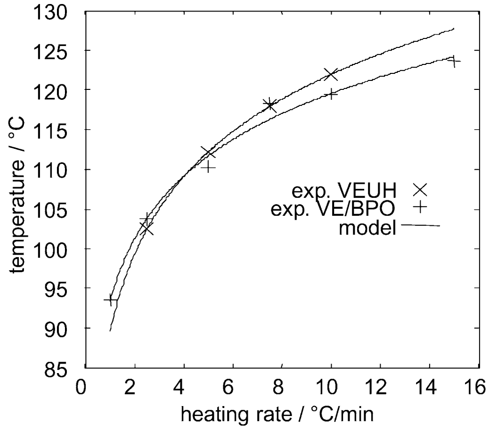

Fig. 7. Measured and calculated temperatures at maximum conversion rate vs. heating rate of VE/BPO and VEUH resins.

3.3. Model for isothermal curing

In Fig. 9 the conversion rate vs. conversion of the isothermal curing of VE/BPO and VEUH resins are plotted. Kinetic models proposed by other authors [13,16] for thermosetting resins cannot be adopted to describe our

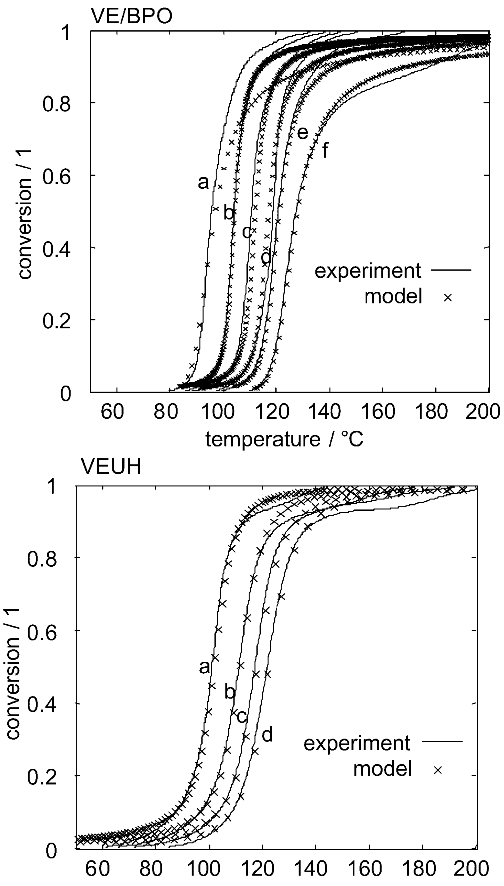

Fig. 8. Measured and calculated conversion vs. temperature curves at different heating rates for VE/BPO and VEUH resins for descriptions of Fig. 4.

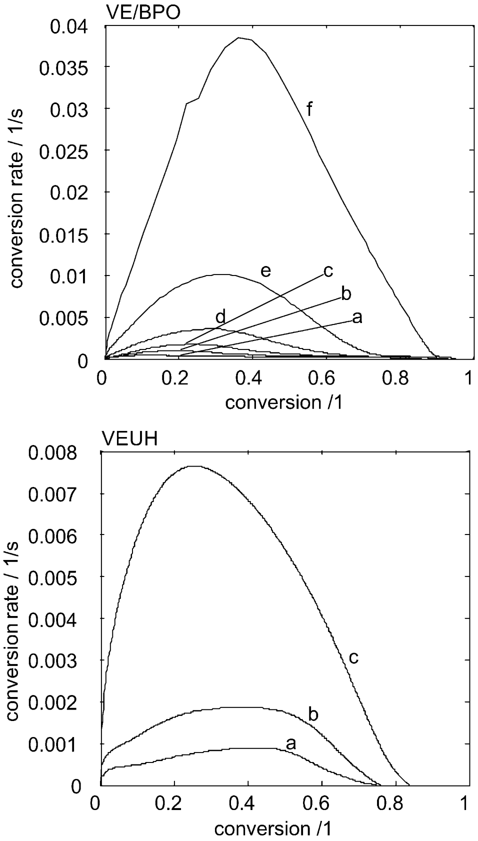

Fig. 9. Conversion rate vs. conversion in isothermal DSC scans for VE/BPO: (a) 90 °C, (b) 92 °C, (c) 95 °C, (d) 100 °C, (e) 110 °C, (f) 120 °C) and VEUH resins: (a) 90 °C, (b) 100 °C, (c) 120 °C).

experimental results. As a consequence the curing reaction of the VE/BPO and VEUH resins, the for dynamic DSC conditions applied model of Kamal and Sourour has to be modified.

For curing the VE/PBO resin the following empirical kinetic equation has been derived

$$\left(\frac{\partial \alpha}{\partial t}\right)_T = k(T)\alpha^{1.38}[0.01(\alpha_{\mathrm{vitri}}(T) - \alpha)^{0.60} + (\alpha_{\mathrm{vitri}}(T) - \alpha)^{n(T)}] \qquad (10)$$

with

$$k(T) = 1.78 \times 10\ \mathrm{s}^{-1} \exp\left(-\frac{9605\ \mathrm{K}}{T}\right) \qquad (11)$$

$$n(T) = \frac{15,379\ \mathrm{K}}{T} - 36.95 \qquad (12)$$

$$\alpha_{\mathrm{vitri}}(T) = \frac{-0.72\ \mathrm{K}}{T - 358.02\ \mathrm{K}} + 0.98 \qquad (13)$$

The function k describes the temperature dependence of the rate constant via an Arrhenius-type function and α_{vitri} means the maximum possible isothermal conversion of the resin at a given temperature. The initial values for solving Eq. (10) are calculated by

$$\begin{pmatrix} t \\ \alpha \end{pmatrix}_{\max}(T) = \begin{pmatrix} 8.51 \times 10^{-15}\ \mathrm{s} \exp(14,038\ \mathrm{K}/T) \\ -1.68\ \mathrm{K}/(T - 357.14\ \mathrm{K}) + 0.38 \end{pmatrix} \qquad (14)$$

The conversion and time, calculated by Eq. (14) correspond to that stage, where the conversion rate is maximal.

Fig. 10 shows the measured and modelled conversion vs. time curves. In the beginning of the curing reaction of the VE/BPO resin the model fits with the experiment very good. But with increasing conversion and thus by progressing diffusion control of the reaction, the model becomes less predictive. The difficulties in describing the diffusion control of the reaction are also indicated by the complexity of the third factor in Eq. (10), which is controlling the kinetics at conversion values near α_{vitri}. Note that the model for the dynamic curing of VE/BPO is also lacking of a suitable description of the curing at high conversions where the diffusion becomes a controlling parameter.

For the curing kinetic of the VEUH resin the following model was applied:

$$\left(\frac{\partial \alpha}{\partial t}\right)_T = [k_1(T)\alpha^{3.11} + k_2(T)\alpha^{0.59}](\alpha_{\mathrm{vitri}}(T) - \alpha)^{1.69} \qquad (15)$$

with

$$k_1(T) = 10.23\ \mathrm{s}^{-1} \exp\left(-\frac{1868\ \mathrm{K}}{T}\right) \qquad (16)$$

$$k_2(T) = 1.45 \times 10\ \mathrm{s}^{-1} \exp\left(-\frac{10,467\ \mathrm{K}}{T}\right) \qquad (17)$$

$$\alpha_{\mathrm{vitri}}(T) = 3.07 \times 10^{-3}\ \mathrm{K}^{-1}T + 0.47 \qquad (18)$$

The functions k_1 and k_2 describe the temperature dependence of the rate constants as Arrhenius-type equations and α_{vitri} the maximum possible isothermal conversion of the resin.

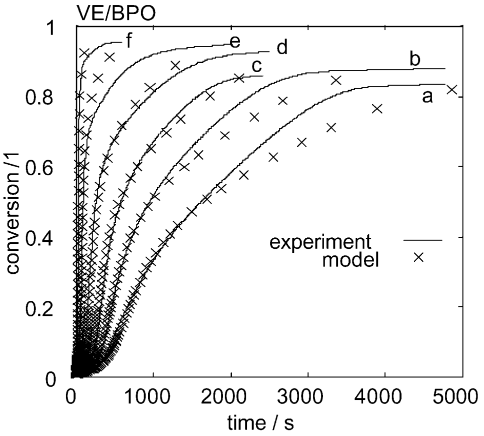

Fig. 10. Measured and calculated conversion rate vs. conversion in isothermal DSC scans for VE/BPO: (a) 90 °C, (b) 92 °C, (c) 95 °C, (d) 100 °C, (e) 110 °C, (f) 120 °C.

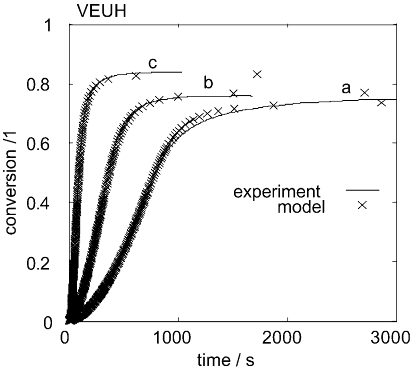

Fig. 11. Measured and calculated conversion rate vs. conversion in isothermal DSC scans for VEUH: (a) 90 °C, (b) 100 °C, (c) 120 °C.

For solving the differential equation (15), again the characteristic point of the maximum of the conversion rate was utilised. The temperature dependence of conversion and time of this point can be described by

$$\begin{pmatrix} t \\ \alpha \end{pmatrix}_{\max} (T) = \begin{pmatrix} s\,\exp(12,525\ \mathrm{K}^{-1}/T) - 27.92 \\ \exp(2561\ \mathrm{K}^{-1}/T - 7.88) \end{pmatrix} \tag{19}$$

Fig. 11 shows the measured and calculated conversion vs. time for the curing of the VEUH resin. The model matches the experimental data very well. Applying two kinetic constants in the model for the isothermal curing of the VEUH resin indicates, that two reactions are taking place but that reaction related to k_1 is dominating since $k_1 \gg k_2$. In contrast to the model for the curing of the VE/BPO resin in the case of the curing of VEUH the diffusion control at high conversions is of minor importance but still observable.

4. Conclusions

The reaction kinetics of the curing of a vinylester/urethane hybrid (VEUH) resin and VE resin were studied by DSC. Empirical models for the curing kinetics were developed for isothermal and dynamic temperature conditions. Despite the fact, that the curing of the VEUH is more complex since two reactions (viz. radical polymerisation + polyaddition reaction) take place during curing, the models provided for the VEUH curing are matching the experiments more exactly than those recommended for the VE, where only the radical polymerisation of styrene and VE is responsible for curing. Nevertheless, all models proposed describe the experiments fairly good. Furthermore, it was shown that the radical polymerisation dominates the curing reaction of VEUH resin as accessed by DSC measurements. On the other hand, the radical polymerisation is not separated by time from the polyaddition reaction and thus the VEUH curing can not be simplified for a peroxide initiated free radical crosslinking via styrene in VE.

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