Curing of bisphenol A-aniline based benzoxazine using phenolic, amino and mercapto accelerators

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Received 15 December 2014; accepted in revised form 8 February 2015

Abstract. The curing of bisphenol A-aniline based benzoxazine was studied applying different accelerators (4,4'-thiodiphenol, *o*-dianisidine, 2-mercaptobenzimidazole and 4-mercaptophenol) to initiate the catalytic ring-opening of benzoxazine. Possible pathways of benzoxazine ring-opening, polymerization and cross-linking without and with the addition of different accelerators are presented. The curing kinetics was investigated by model-free kinetic analysis of experimental data obtained by differential scanning calorimetry (DSC). The addition of different accelerators significantly reduced the onset temperature of curing in dynamic experiments. The effects of accelerators on the results of isothermal conversion prediction were studied and discussed in detail. Among the used accelerators, thiodiphenol showed the best accelerating efficiency and was consequently used in further studies, where its amount was varied. By low heating rate DSC analysis the catalytic ring-opening, thermally accelerated ring-opening and the diffusion-controlled steps were identified. The amount of added accelerator affected particularly the ring-opening and diffusion-controlled steps.

Keywords: thermosetting resins, benzoxazine, accelerators, curing mechanisms, deconvolution

1. Introduction

Recently, much attention has been given to the development of benzoxazine-based family of phenolic resins due to their adaptable mechanical and physical properties, which are often considerably better than those of traditional phenolic resins [1]. Benzoxazines are a class of heterocyclic compounds with typically one or two oxazine rings in their molecules. They are synthesized from a phenolic derivative, a primary amine and formaldehyde. Polybenzoxazines are formed by ring-opening polymerization of benzoxazine molecules. Properties of polybenzoxazines can be easily adjusted due to a high design flexibility of their molecular architecture, which opens great opportunities in further enhancement of benzoxazine resins properties. They have demonstrated various attractive properties such as good thermal, mechanical, chemical, electrical and physical prop-

erties, high char yields, high glass transition temperature (T_g), low water absorption, near-zero shrinkage, and low flammability. The important factor, which has great influence on their adoption, both in the academic and industrial communities, is also their relative cheapness. However, the disadvantages associated with polybenzoxazines, which need to be addressed, are their high curing temperature (i.e. polymerization and cross-linking temperature), brittleness and outgassing during the curing process [2–10].

The classical method for production of polybenzoxazines is polymerization of benzoxazine monomers at high temperature (usually at $T > 180^\circ\text{C}$) without the addition of an accelerator [1], which may be a catalyst, initiator, or co-monomer. However, the high temperature, which is required for the curing process, may in some cases lead to thermal degradation of

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the corresponding resin [11]. Lower curing temperature would therefore lead to a significant process and resulting material improvement. In order to respond to this issue, a considerable amount of different catalysts have been applied to promote ring-opening polymerization, including nucleophilic catalysts and Lewis acids [12–14]. Also the use of carboxylic acid groups as accelerators have been extensively studied and a significant decrease in the polymerization temperature has been observed [15–17]. Even though, the studied catalysts showed good catalytic activities, there is still much effort needed for further lowering of the polymerization temperature [18]. The important question, when using benzoxazines of different chemical structures in combination with different catalysts, is the effect of functional groups present in benzoxazine and catalyst molecules not only on the ring-opening but also on the polymerization and cross-linking reactions. Therefore, it is of great importance to understand the nature of the cured material and the effect certain functional group has on the curing process, i.e. on the ring-opening, polymerization and cross-linking mechanisms [1, 2, 12, 14, 19–29].

The terminology used for accelerators is varied and may sometimes cause confusion since the terms accelerator, catalyst, promoter, initiator, etc., are sometimes used loosely even though they can apply to very specific types of materials having distinctly different characteristics and functions. This study focuses on benzoxazine resin systems and the term accelerator is used to describe a variety of compounds used to increase the reaction rate, whatever the reaction mechanism. The term accelerator is applied instead of terms catalyst, initiator, and/or co-monomer, since the applied accelerators initiate ring-opening polymerization and co-react with benzoxazine to form polybenzoxazine. In the literature of curing reactions the term catalyst is often used, but by definition a catalyst lowers the activation energy of a chemical process without being a reactant.

In the present study, we have examined the accelerating efficiency of a number of different accelerators in the curing process of bisphenol A-aniline based benzoxazine (BOX). Possible pathways of benzoxazine ring-opening, polymerization and cross-linking without and with the addition of different accelerators are presented. The curing kinetics was investigated by model-free kinetic analysis of exper-

imental data obtained by differential scanning calorimetry (DSC). The basic assumption for the application of DSC technique for curing process following is that the rate of kinetics process is proportional to the measured heat flow [30–32]. Among tested accelerators, thiodiphenol showed the best effect on the curing process of benzoxazine in terms of conversion predictions obtained by isoconversional model-free approach. For that reason the effects of different amounts of thiodiphenol on the curing process of benzoxazine were studied in detail.

2. Experimental

2.1. Materials

For the kinetic studies, benzoxazine based on bisphenol A and aniline (BOX, 98%) was employed along with different polymerization accelerators. As accelerators 4,4'-thiodiphenol (TDP, 99%), *o*-dianisidine (DA, 97%), 2-mercaptobenzimidazole (MBI, 98%) and 4-mercaptophenol (MP, 90%) were used as received from Sigma-Aldrich Chemie GmbH, (Steinheim, Germany). Bisphenol A-aniline based benzoxazine (commercial name Araldite MT 35600) was kindly provided by Huntsman Advanced Materials (BVBA, Everberg, Belgium).

2.2. Sample preparation

Homogeneous mixtures of benzoxazine monomer and accelerators were prepared by dissolving them in 10 mL of dichloromethane by mixing with magnetic stirrer for 15 minutes. The solvent was then removed from samples by evaporation at room temperature for 12 hours and subsequent drying for 4 hours in vacuum oven at 60°C. For DSC experiments benzoxazine mixtures with 20 mol of accelerator (TDP, DA, MBI and MP) per 100 mol of benzoxazine (16.7 mol%) were prepared. The amounts of different accelerators in benzoxazine mixtures are given in mol% in order to provide comparable quantity between the mixtures. When the amount of accelerator on benzoxazine/thiodiphenol mixture curing was investigated, the prepared benzoxazine/thiodiphenol contained 1, 2, 5, 10, 20, 35 and 50 wt% to the weight of benzoxazine.

2.3. Differential scanning calorimetry (DSC)

The DSC measurements were performed on Mettler Toledo DSC1 instrument with intra-cooler using STAR software. In and Zn standards were used for the temperature calibration and for the determina-

tion of the instrument time constant. Samples of around 10 mg were weighed in standard 40 μL aluminum pans. DSC measurements were performed in nitrogen atmosphere with 30 mL/min nitrogen flow rate. For investigation of the effect of accelerator type on curing kinetics the samples were subjected to four different heating rates (5, 10, 15 and 20°C/min) in the temperature range from 20 to 350°C. To study the effect of different amounts of thiodiphenol on the curing process also a lower heating rate of 1°C/min was used.

3. Results and discussion

3.1. Curing reaction

Curing (polymerization and cross-linking) of benzoxazine is thermally accelerated cationic ring-opening polymerization, which may be carried out with or without using accelerators (Figure 1). Different accelerators, which lower benzoxazine curing temperature, may bear different functional groups capable of initiating or catalyzing the oxazine ring opening. This is why several mechanisms were proposed for benzoxazine curing [13, 14, 26, 33–35]. Regardless to the type of the accelerator used, the mechanism of the curing process involves several steps, which complicate the kinetics. The curing is always autocatalyzed as the newly produced hydroxyl groups in phenolic structure (compound III in Figure 1a) act as an additional initiator. Moreover, in the early stage of curing, the reaction medium is a liquid composed of benzoxazine, accelerator and just formed oligomers. As the reaction progresses, the average molecular weight, the viscosity and the glass transition temperature (T_g) of the resin increase. Therefore the molecular mobility, in turn, decreases, which affects the curing kinetics. The latter becomes diffusion rather than kinetically controlled [1, 36].

Figure 2 shows DSC thermograms of benzoxazine and its mixtures with 16.7 mol% of accelerators in the temperature range from 20 to 350°C using heating rate of 20°C/min. The addition of accelerator significantly reduced the onset temperature of curing process, which was detected as an exothermic signal. This exothermic peak for the accelerated benzoxazine was broader than that for the unaccelerated benzoxazine, implying presence of multiple reactions during the curing process with accelerators. The presumed reaction pathways occurring in the presence of accelerators are drawn in Figure 1b–1e.

Phenols, such as 4,4'-thiodiphenol and 4-mercaptophenol, can initiate oxazine ring opening and accelerate benzoxazine polymerization by the formation of an intermolecular hydrogen bond and subsequent reaction at the ortho position of the phenol or other benzoxazine molecule (Figure 1c). The other possible ring-opening mechanism is the initial protonation of benzoxazine, where protons behave as an actual catalyst. The protonation is followed by condensation reaction of the iminium species and the phenolate or other benzoxazine molecule to a phenolic structure (Figure 1b) [33]. The initiation by protonation or by intermolecular bond formation (hydrogen bond) can take place at either the nitrogen atom or the oxygen atom, but it was found, that in the case of protonation, the oxygen protonated species are reactive, whereas the nitrogen protonated species are stable [26] (Figure 1b).

On the other hand, imidazoles, such as 2-mercaptobenzimidazole, and aromatic amines, such as dianisidine, accelerate benzoxazine polymerization through the formation of an arylether structure (N,O-acetal-type linkage) [14, 34] (compound VI in Figure 1d). Formation of N,O acetal intermediate is present especially in the case of N-aryl-1,3-benzoxazines, before it rearranges to Mannich-type structure at higher temperatures. The arylether structure is thermally unstable and undergoes structural transformation to the phenolic-type with Mannich bridge ($-\text{CH}_2-\text{NR}-\text{CH}_2-$) at elevated temperature [1, 2].

Curing of benzoxazine with accelerators bearing thiol group is proposed to proceed according to Colbert reaction mechanism (Figure 1e) [37]. Initially the thiol proton protonates the nitrogen in oxazine ring. Then the sulfide attacks the adjacent methylene group located between the nitrogen and the oxygen. The thioether bond is created, which causes benzoxazine ring opening and phenolic hydroxyl group formation. The newly formed phenolic hydroxyl group of compound VII in Figure 1e is available for further reactions with benzoxazine.

3.2. Kinetic analysis

Kinetic analysis of non-isothermal resin-cured system is based on the rate equation and can be performed by the multiple heating rates [38, 39]. This method is attractive since the kinetic data can be obtained in short period of time. The rate of the curing process is considered to be a function of two variables, T and α (Equation (1)):

Figure 1. Possible pathways of benzoxazine polymerization and cross-linking, a) thermally accelerated ring-opening, b) ring-opening by protonation, c) ring-opening by hydrogen bond formation, d) polymerization through formation of an arylether structure (N,O-acetal-type linkage), e) Colbert reaction mechanism via two-step acid catalyzed nucleophilic addition

Figure 2. DSC thermograms of pure benzoxazine (BOX) and its mixtures with 16.7 mol% of selected accelerators in the temperature range from 20 to 350°C at a heating rate of 20°C/min

$$\frac{d\alpha}{dt} \equiv \beta \frac{d\alpha}{dT} = k(T)f(\alpha) \quad (1)$$

where $k(T)$ is a temperature-dependent reaction rate constant, $f(\alpha)$ is the reaction model, β is the heating rate in °C/min and $d\alpha/dt$ is the conversion rate in s^{-1} . Temperature dependence on rate constant is represented through the Arrhenius equation (Equation (2)):

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where A is the pre-exponential factor in s^{-1} , E_a is the apparent activation energy in J/mol, R is the ideal gas constant in $J \cdot mol^{-1} \cdot K^{-1}$, and T is the absolute temperature in K. Four kinetic methods widely used in order to study dynamic kinetics of thermosetting polymers are Kissinger (Equation (3)), Ozawa (Equation (4)), Friedman (Equation (5)), and Flynn-Wall-Ozawa (Equation (6)) methods [40–43]:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{Q_p A R}{E_a}\right) - \frac{E_a}{RT_p} \quad (3)$$

$$\ln\beta = \ln\left(\frac{AE_a}{R}\right) - \ln F(\alpha) - 5.331 - 1.052\left(\frac{E_a}{RT_p}\right) \quad (4)$$

$$\ln\frac{d\alpha}{dt} = \ln[Af(\alpha)] - \frac{E_a}{RT} \quad (5)$$

$$\ln\beta = \ln\left(\frac{AE_a}{R}\right) - \ln g(\alpha) - 5.331 - 1.052\left(\frac{E_a}{RT}\right) \quad (6)$$

where $F(\alpha)$ is a constant function, $g(\alpha)$ is the integral conversion function, T_p is the peak temperature and $Q_p = [df(\alpha)/d\alpha]_{\alpha=\alpha_p}$.

The results of calculated apparent activation energies by using the Kissinger and Ozawa methods (Table 1) showed that TDP was a superior accelerator in the studied system, since the activation energy was the lowest among the used accelerators. However, it has to be mentioned that calculated activation energies were only apparent, which is why pure BOX has lower activation energy than BOX/DA and BOX/MBI even though DA and MBI were labeled as accelerators. Such differences between the values with and without the accelerator can be expected, since the calculated value of E_a depends on how T_p value changes with heating rates for each of the studied systems. Therefore it is possible to obtain a higher E_a value for a system with lower T_p values. The peak temperatures of BOX/DA and BOX/MBI were lower than that of BOX, which may indicate that curing started at lower temperatures and DA and MBI really accelerate the curing process. Slightly higher activation energies may be observed by using Ozawa method in comparison to Kissinger method, though. Further on, the curing kinetic study was extended to isothermal conversion prediction using the method by Vyazovkin in order to complement the picture of kinetic studies.

3.3. Isothermal conversion prediction

In thermoset industry practice, it is of great importance to be able to predict the conversion of a material during the curing process. To predict the curing kinetics of a complex reaction system, such as benzoxazine/accelerator reaction systems, the use model-

Table 1. Apparent activation energies obtained from DSC experiments at various heating rates (β) for the BOX and BOX/accelerator formulations using Kissinger and Ozawa method

Accelerator	T_p [°C]				E_a [kJ/mol]	
	5°C/min	10°C/min	15°C/min	20°C/min	Kissinger	Ozawa
BOX	233	248	257	264	91,5	95,2
BOX/DA	218	227	232	238	137,9	139,0
BOX/MBI	210	223	231	238	92,7	96,0
BOX/MP	197	212	222	229	78,0	81,9
BOX/TDP	192	208	218	225	72,8	76,8

free isoconversional method developed by Vyazovkin [30–32] has been proposed. The isoconversional method enables simulation of the extent of reaction as a function of time in isothermal conditions using data obtained by dynamic experiments, without knowing the exact mechanism and individual reaction rate constants. Due to its proven great accuracy and wide applicability to any temperature program this approach has been widely used. In the applied isoconversional method the E_α value is determined as the value that minimizes the function (Equations (7) and (8)):

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha T_i(t_\alpha)]}{J[E_\alpha T_j(t_\alpha)]} = \min \quad (7)$$

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

where i and j denote different dynamic experiments, T is temperature in K, R is the ideal gas constant in J/(mol·K), E_α is apparent activation energy for a specific conversion α in J/mol, $\Delta\alpha$ is the small increment in α (usually around 0.02), t_α and $t_{\alpha+\Delta\alpha}$ are reaction times up to α or $\Delta\alpha$, respectively. In this study, the integral J given in the Equation (2) was evaluated numerically from the experimental data by using trapezoidal rule. Repetition of minimization procedure in Equation (1) for each α resulted in the E_α -dependence. After knowing the E_α vs. α relationship, the isoconversional method can be used to predict isothermal kinetic conversion as a function of reaction time for different temperature programs with the use of Equation (9):

$$t_\alpha = \frac{\int_0^{t_\alpha} \exp\left(-\frac{E_\alpha}{RT(t)}\right) dt}{\exp\left(-\frac{E_\alpha}{RT_0}\right)} \quad (9)$$

where t_α is the reaction time to a specific conversion α and T_0 is a fixed isothermal reaction temperature. t_α can be estimated by Equation (10) using results of dynamic experiment with a constant heating rate (β):

$$t_\alpha = \frac{\int_0^{T_\alpha} \exp\left(-\frac{E_\alpha}{RT}\right) dT}{\beta \exp\left(-\frac{E_\alpha}{RT_0}\right)} \quad (10)$$

Figure 3 compares conversion predictions for benzoxazine/accelerator mixtures with that of benzoxazine without accelerator at 140, 160, 180 and 200°C.

As expected, at 140°C (Figure 3a) significantly higher conversions were predicted for curing with accelerators, which promote the ring-opening reaction. According to predictions (Figure 3a), the conversion without accelerator would be just little over 5% after 180 minutes at 140°C. By increasing the temperature the predicted conversion after 180 min was significantly increased. The result is straightforward, since higher temperature increases ring-opening reaction rate and the rate of hydroxyl group formation. Newly formed hydroxyl groups further accelerate the curing of benzoxazine through initiation by protonation and/or intermolecular bond formation as depicted in Figures 1b and 1c, respectively. Due to the fact that the ring-opening reaction is exclusively thermally initiated in the absence of an accelerator, the most evident difference in the progress of the conversion with increasing temperature is noticeable in this case (Figure 3).

With increasing curing temperature also the predicted conversions increased for all benzoxazine/accelerator mixtures as expected (Figure 3). The higher the temperature, the smaller the differences between benzoxazine/accelerator mixtures. Thiodiphenol (TDP) showed the best performance among the tested accelerators at 140°C. Thus at higher temperatures both accelerators of phenol type showed similar efficiency. Interestingly, at higher curing times, the MP efficiency became even higher than that of TDP. Moreover, by a detailed inspection of conversion curves in Figures 3a and 3b it may be noticed that the MP efficiency was higher also at the very beginning of the curing process. The observations may be explained by the fact that MP contains two different functional groups, which accelerate benzoxazine curing, i.e. a phenol and a thiol group, while TDP contains only phenol groups. Thus, curing with TDP follows the mechanisms depicted in Figures 1b and 1c, while curing with MP follows the mechanism depicted Figure 1e as well. At lower curing times, the better MP accelerating efficiency may be attributed to the relatively fast reaction of thiol group with oxazine ring. Since –SH groups are consumed during the reaction their accelerating effect diminishes with time. At the same time, the newly formed –OH group (compound VII in Figure 1e) is sterically hindered, but still possesses an acceleration capability. As the concentration of phenol –OH groups was higher when TDP, instead of MP, was used, the curing with TDP (through mechanisms

Figure 3. Conversion versus time at 140 (a), 160 (b), 180 (c) and 200°C (d) for benzoxazine (BOX) and its mixtures with different accelerators based on model-free isoconversional method

depicted in Figures 1b and 1c) proceeded faster after –SH groups of MP were consumed. However, at higher curing times, the conversion of curing with MP became higher again, which may be attributed to the higher cross-linking density of molecules V formed in reaction with TDP (due to larger number of reactive ortho sites on phenol). As mentioned before, a higher cross-linking density leads to lower molecular mobility and the process becomes diffusion-controlled.

By comparing conversion evolutions of benzoxazine (BOX) with those of its mixtures, where curing through the formation of an aryether structure (DA and MBI) was accelerated, an interesting phenomenon may be observed, which may be explained by already discussed reaction mechanisms again. When the acceleration proceeds through the mechanism shown in Figure 1d, N,O-acetal type structure is formed, which is without any hydroxyl groups. Consequently, the concentration of hydroxyl groups may be higher if no DA or MBI are added. The higher the concentration of –OH groups, the higher the rate of autocatalyzed curing reaction. Thus, it is

possible that the thermally initiated benzoxazine curing becomes faster than curing through the formation of an aryether structure. Of course, this is unlikely at lower temperatures and reaction times. To our opinion, this effect is observable in Figures 3b and 3c, where BOX curves overcome BOX/DA curves and reach BOX/MBI curves. However, for simulations at 200°C, the conversion of BOX/DA and BOX/MBI is once again higher than that of BOX, presumably due to the fast transformation of molecule VI to the Mannich bridge structure III. The N,O-acetal structure is thermally unstable and after the breakdown of the molecule VI, hydroxyl groups are formed, which leads to the final molecule III and higher simulated conversions of BOX/DA and BOX/MBI than BOX (Figure 3d).

3.4. Curing behavior of benzoxazine using thioldiphenol as accelerator

The model-free kinetics analysis showed that thioldiphenol is the best choice among the tested accelerators. Acceleration with thioldiphenol is efficient and gives polybenzoxazine with enhanced cross-linked

Figure 4. DSC thermograms of benzoxazine with 16.7 mol% of thiodiphenol at different heating rates

structure. DSC thermograms of mixtures containing 16.7 mol% of thiodiphenol obtained at different heating rates are shown in Figure 4. The exothermal signal of curing comprised of several overlapped peaks (Figure 4). The overlapping was more evident when lower heating rates were applied. This clearly indicated that the reaction of benzoxazine with thiodiphenol had at least two curing stages, which is in accordance with the known mechanisms of benzoxazine curing with phenolic accelerators [12, 13, 33, 34]. The lower the heating rate, the more noticeable the boundary between the reactions stages. Nevertheless, the heating rate showed no effect on the total exothermic reaction heat estimated from the area under the overlapped peaks. The average total exothermic reaction heat was 370 J/g.

To investigate the curing stages further on, the effect of thiodiphenol amount on the curing was studied. Additional DSC experiments at fixed heating rate of 1°C/min were performed. At such a slow heating rate the effect of the accelerator on the progress of the curing was clearly observable. As it can be seen in Figure 5 the amount of thiodiphenol had the greatest impact on the initial stage of the reaction, which was the oxazine ring opening (formation of compound II in Figure 1a). The next process, related to the polymerization and cross-linking (formation of final cured compound III in Figure 1a), was not affected to the same degree.

DSC peaks fitting and deconvolution (Figure 5) was performed by the OriginPro program using the Pearson VII distribution, which gave best DSC peaks fitting and deconvolution results. In the case of benzoxazine without accelerator (Figure 5a) the two deconvoluted peaks may be associated with the thermally

accelerated ring-opening accompanied by autocatalytic reaction (Δ in Figure 5) and the diffusion-controlled step in curing reaction ($\square$ in Figure 5), respectively. The reaction of thermally accelerated ring-opening is shown in Figure 1a and results in formation of compound II. The autocatalytic reaction, which mechanism is the same as depicted in Figure 1c, involves the catalysis of ring-opening reaction by hydrogen bond formation between hydroxyl group of the compound II and other benzoxazine molecule. The diffusion-controlled step comprises same reactions but the mobility of molecules is hindered. Most likely, the sterical hindrance prevents the autocatalytic ring-opening reaction through hydrogen bond formation at this stage.

On the other hand, for mixtures with thiodiphenol, another peak ($\circ$ in Figure 5) emerged during the fitting process. Since the new peak emerged at the beginning of the curing process it was assigned to the accelerated oxazine ring opening (mechanisms presented in Figures 1b and 1c). With increasing the amount of the accelerator the peak shifted to lower temperatures and became even more noticeable. Note, the deconvoluted peak (marked as Δ), assigned to the autocatalytic reaction, associated to the benzoxazine hydroxyl groups, is still present in Figures 5b, 5c, and 5d. In the case of the highest amount of the accelerator (Figure 5d) the peak of the diffusion-controlled step disappeared, which may be explained by involvement of smaller accelerators molecules in the curing reactions. Based on this observation it may be deduced that the formation of compounds V (Figure 1c) is more favorable than the formation of compounds II and/or III. Furthermore, it is possible to conclude that the reaction of benzoxazine with thiodiphenol leads to products of lower cross-linking density.

4. Conclusions

The influence of phenolic, mercapto, amino and imidazole accelerators on the benzoxazine curing process was studied and discussed in detail. The model-free kinetics analysis of DSC data showed that thiodiphenol is the best choice among the tested accelerators. In order to investigate the curing of benzoxazine/thiodiphenol mixture in detail the accelerator amount was varied. By low heating rate DSC analysis exothermic signals of curing, composed of several overlapped peaks, were obtained. The peaks were sensibly associated to catalytic ring-opening,

Figure 5. DSC curing peaks (solid line) and peaks obtained by deconvolution (dashed lines) for benzoxazine (BOX) with different amount of thiodiphenol ((a) 0, (b) 5, (c) 20, (d) 50 wt%). Peak assignment: thermally accelerated ring-opening and autocatalytic reaction (Δ), diffusion-controlled step ($\square$), catalytic ring-opening ($\circ$).

thermally accelerated ring-opening and to the diffusion-controlled step. The amount of added accelerator affected particularly the ring-opening and diffusion-controlled steps. The kinetic regime in the diffusion-controlled step was dominated by cross-linking density of benzoxazine resin, which is also dependent on the accelerator amount and functionality.

Acknowledgements

The financial support of this work by the Slovenian Ministry of Higher Education, Science and Technology (Grant P2-0191) is gratefully acknowledged.

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