Journal of Thermal Analysis and Calorimetry, Vol. 76 (2004) 295–306

TIME–TEMPERATURE–TRANSFORMATION ANALYSIS OF AN ALKYD-AMINO RESIN SYSTEM

V. Vargha[*] *and Gy. Kiss*

Budapest University of Technology and Economics, Department of Plastics and Rubber Technology, 1111 Budapest, Műegyetem rkp. 3. H/1, Hungary

(Received July 15, 2003; in revised form October 1, 2003)

Abstract

The curing of a thermoreactive alkyd–melamine–formaldehyde resin system was investigated by rheologycal, TG and TMA-analysis, in order to construct the time–temperature–transformation diagram. The points of the gelation curve were determined by measuring the increase in viscosity during isothermal curing at different temperatures. A power-function could be fitted to the gelation curve, which is suitable to estimate gelation at any curing conditions, as well as to establish storage conditions. The reaction in the resin matrix was followed by monitoring the loss of mass during isothermal curing at different temperatures. The final section of the resulted iso-curing temperature (iso-T_{cure}) diagrams could be fitted with logarithmic functions, which may be used for estimating the conditions needed to a given, desirable mass loss, i.e. conversion. The steepness of the curves increases with temperature suggesting the forthcoming of degradation during cure with increasing temperature. From these data the iso-mass loss curves of the TTT-diagram were constructed. For determining the iso-T_{g} curves of the TTT-diagram isothermal curing was carried out in a drying oven at different temperatures, followed by TMA measurements. The iso-T_{cure} diagrams served to determine $T_{\mathrm{g}\infty}$, and to construct the iso-T_{g} curves of the TTT diagram. Vitrification curve is far beyond conditions of storage, curing and degradation, meaning that the resin matrix is in rubbery physical state before, during and after the cure. Curing conditions resulting degradation can also be estimated from the TTT-diagram.

Keywords: alkyd resins, amino–formaldehyde resins, isothermal TG, time–temperature–transformation analysis, TMA, TTT-diagram

Introduction

Time–temperature–transformation (TTT) analysis is a practical tool for evaluating the cure of thermosetting systems [1, 2]. Although alkyd-amino resins have their due place among the matrix resins used in the lacquer and paint industry [3], construction of TTT diagram for these is not a practice. Thermoreactive systems based on alkyd-amino–aldehyde resins are used in many fields of application, such as protective

---

[*] Author for correspondence: E-mail: vargha@muatex.mua.bme.hu

1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

coatings of metal surfaces under mechanical, and chemical exposure, or as adhesives. They can be formulated as solvent-borne, water-based or powder systems, if finely powdered melamine–formaldehyde resins are used as cross-linkers [4, 5]. These resin systems cure rapidly and are ideal for factory-applied industrial coatings that must meet demanding production schedules. The manufacture and use of protective surface coatings is a highly developed technology; consequently, the knowledge of curing schedule is essential.

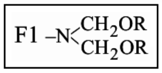
Goal of this work was the study of the curing behaviour of a selected thermoreactive alkyd–melamine–formaldehyde resin system and the construction and evaluation of the TTT diagram characteristic to this system. The process of curing was monitored on solventless matrix resin composition by rheologycal measurements, thermogravimetric and TMA analysis.

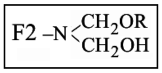
Curing reactions of an alkyd-amino resin

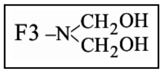
Short-oil alkyds prepared with 38–45% phthalic anhydride are suitable for application with amino aldehyde resins. The high hydroxyl functionality ensures good compatibility and serves reactive sites for heteropolycondensation resulting in the formation of three-dimensional network. For curing at room temperature acid catalysts are used.

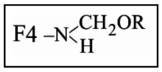
The two main reactions during the cure of alkyd-amino resins, heteropolycondensation and homopolycondensation take place simultaneously. Curing conditions should be selected to favour heteropolycondensation.

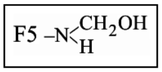
Amino-aldehyde resins differ from one another in the type of functional groups, degree of polymerisation and the type of alcohol used for etherification. The following functionalities can be distinguished:

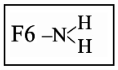

F1 $-\mathrm{N}\!<\!\begin{array}{l}\mathrm{CH_2OR}\\ \mathrm{CH_2OR}\end{array}$

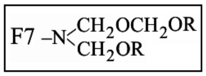

F2 $-\mathrm{N}\!<\!\begin{array}{l}\mathrm{CH_2OR}\\ \mathrm{CH_2OH}\end{array}$


F3 $-\mathrm{N}\!<\!\begin{array}{l}\mathrm{CH_2OH}\\ \mathrm{CH_2OH}\end{array}$


F4 $-\mathrm{N}\!<\!\begin{array}{l}\mathrm{CH_2OR}\\ \mathrm{H}\end{array}$


F5 $-\mathrm{N}\!<\!\begin{array}{l}\mathrm{CH_2OH}\\ \mathrm{H}\end{array}$


F6 $-\mathrm{N}\!<\!\begin{array}{l}\mathrm{H}\\ \mathrm{H}\end{array}$


F7 $-\mathrm{N}\!<\!\begin{array}{l}\mathrm{CH_2OCH_2OR}\\ \mathrm{CH_2OR}\end{array}$

Amino-aldehyde resins contain at least 4 moles of formaldehyde per mole urea or melamine, 2 moles of which react with the alcohol present to form ether. Types F3, F5 and F6 are susceptible to homopolycondensation, while types F1, F2, and F4 to heteropolycondensation.

During heteropolycondensation with hydroxyl functional alkyd resins transetherification takes place. Hexa-methoxy-methyl-melamine (HMMM) e.g. is one of the most frequently used curing agent for hydroxyl functional resins. Reactions during the cure of an amino-aldehyde resin synthesized in the presence of methanol may be summarized in the following [6].

$$\mathrm{{>}N{-}CH_2OH \rightleftharpoons {>}NH{+}HCOH} \tag{1}$$

$$\mathrm{{>}N{-}CH_2OH{+}HN{<} \rightarrow {>}N{-}CH_2{-}N{<}{+}H_2O} \tag{2}$$

$$\mathrm{{>}N{-}CH_2OH{+}R{-}OH \rightarrow {>}N{-}CH_2{-}OR{+}H_2O} \tag{3}$$

$$\mathrm{{>}N{-}CH_2OCH_3{+}R{-}OH \rightarrow {>}N{-}CH_2{-}OR{+}CH_3OH} \tag{4}$$

$$\mathrm{2{>}N{-}CH_2OCH_3{+}H_2O \rightarrow {>}N{-}CH_2{-}N{<}{+}HCOH{+}2CH_3OH} \tag{5}$$

$$\mathrm{{>}N{-}CH_2OCH_3{+}HN{<} \rightarrow {>}N{-}CH_2{-}N{<}{+}CH_3OH} \tag{6}$$

$$\mathrm{2{>}N{-}CH_2OCH_3 \rightleftharpoons {>}N{-}CH_2{-}N{<}{+}CH_3O{-}CH_2{-}OCH_3} \tag{7}$$

$$\mathrm{2{>}N{-}CH_2OH \rightleftharpoons {>}N{-}CH_2{-}O{-}CH_2{-}N{<}{+}H_2O} \tag{8}$$

$$\mathrm{{>}N{-}CH_2OCH_3{+}HO{-}CH_2{-}N{<} \rightleftharpoons {>}N{-}CH_2{-}O{-}CH_2{-}N{<}{+}CH_3OH} \tag{9}$$

$$\mathrm{{>}N{-}CH_2OCH_3{+}HOH \rightleftharpoons {>}N{-}CH_2{-}OH{+}CH_3OH} \tag{10}$$

The presence of free methylol groups results in the formation of formaldehyde whether in equilibrium reaction (1) or via splitting of methylene ether bridges (3, 8, 9). Reactions 2, 5, 6, 7, 8 and 9 result in homopolycondensation, while reactions 3 and 4 result in heteropolycondensation. The above reactions take place simultaneously, and the type of reaction depends on functionality, curing conditions, catalyst and moisture content of the matrix resin.

Any kind of reactions happen during the cure, low molecular mass materials evolve. Amino-aldehyde resins may also be synthesized in the presence of different alcohols, other than methanol, in order to improve resin properties. In this case the corresponding alcohol will evolve during transetherification. All this means that curing can be followed by monitoring the evolution of low molecular mass materials, which is in correlation with the conversion of curing. The most suitable technique for this is thermogravimetric analysis.

Experimental

Materials

Melamin–formaldehide resin (MF resin)

MF resin is one component of the resin matrix resulted as a condensation product of phthalic anhydride, maleic anhydride, isobutanol, melamine and paraformaldehyde. It is used in the form of a 60% solution in isobutanol with the following characteristics:

Viscosity (Flowing cup No 4 at 20°C)/s	150–250
Non-volatile content (120°C; 1 h)/%	58–62
Acid content/mg KOH g^{-1}	<4
Methylol group content/%	<8.0
White spirit tolerance/mL g^{-1}	<10.0
Density (20°C)/g cm^{-3}	1.020–1.024
Storage stability	12 months
Flash point/°C	28

Alkid resins

Two kinds of alkyd resins were used, Alkyd MT containing tall oil fatty acid, and Alkyd DC containing epoxydized synthetic fatty acid modifier for increasing adhesion.

Alkyd MT

The alkyd resin is synthesized by the reaction of tall oil fatty acid, phthalic anhydride, maleic anhydride, ethylene glycol, epoxydized soya bean oil, α-ethyl hexanoic acid and dimeric acid. After the reaction the resin melt is dissolved in xylene and isobutanol, and used as a 55% solution.

Viscosity (Flowing cup No 6 20°C)/s	100–150
Non-volatile content (120°C; 2 h)/%	53–57
Acid content/mg KOH g^{-1}	<10
Density (20°C)/g cm^{-3}	1.000–1.020
Iodine colour number/mg I_2 (100 mL)$^{-1}$	<10
Flash point (closed cup)/°C	25

Alkyd DC

The alkyd resin is synthesized by the reaction of phthalic anhydride, maleic anhydride, and diethylene glycol. Synthetic monobasic acid glycidyl ester is used as modifying agent. The resin melt is dissolved in isobutanol/xylene mixture, a 60% solution is used.

Viscosity (Flowing cup No 4 20°C)/s	30–60
Non-volatile content (120°C; 2 h)/%	58–62
Acid content/mg KOH g^{-1}	<15
Density (20°C)/g cm^{-3}	0.980–1.075
Flash point (closed cup)/°C	26

Preparing the resin matrix for the experiments

The above resin solutions were weighed in the following ratio:

MF resin	2.55 g
Alkyd MT	13.1 g
Alkyd DC	1.5 g

After homogenization at room temperature films of 60 μm wet thickness were applied on glass plate, and the solvent was removed by freeze drying. The solventless films were used for isothermal curing experiments by rheometry, and TG analysis. For TMA measurements the films were isothermally cured in a drying oven at five constant temperatures, namely at 100, 120, 130, 140 and 160°C for different times, i.e. for 10, 20, 25, 30, 35, 45 and 60 min.

Methods

Rotational viscometry

For determining the gelation curve on the TTT diagram isothermal curing of the films was made at five different temperatures, namely at 66, 75, 84, 95 and 110°C and the viscosity change was followed by using a Brabender Rheotron rotational cone and plate viscometer. The rate could be varied in two ranges of 0–1000 min^{-1} and of 0–10 min^{-1}. The radius of the applied cone was 10.01 mm, the cone angle 2.86^{o}. The torque applied on the cone is determined by the change of length of the measuring spring. The equipment was applied with three different springs, namely A, B and C. The deflection was detected by the way of induction.

Thermogravimetry

For thermogravimetric analysis a Mettler TA4000 TG50 was used. Measurements were carried out in flowing air on 8 mg samples. For dynamic measurements the heating rate was 5°C min^{-1}.

Thermomechanical analysis (TMA)

TMA measurements were carried out with a Mettler TA4000 TMA40 with a rate of 10°C min^{-1}, by using 0.1 N load.

Discussion of results

Rheological measurements

The process of curing could be monitored by viscometry in the temperature range of 60–110°C. The change of apparent viscosity during isothermal cure at 66, 75, 84, 95 and 110°C is shown by Fig. 1. Apparent viscosity at the beginning of curing is highest at 66°C, does not change during the first 10 min of curing, and after a transient it has a steep increase during the last curing section. By the increase of the curing temperature

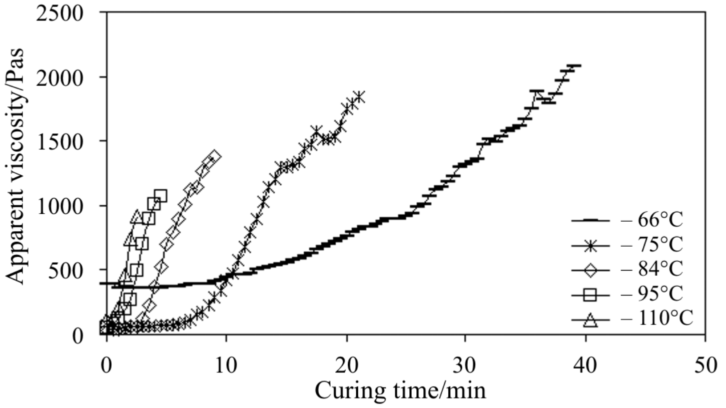


Fig. 1 The change of apparent viscosity during isothermal cure of the alkyd-amino resin matrix

the beginning stage of curing – during which there is no change in viscosity – is shorter, and the increase of viscosity follows a steeper curve during the last stage of cure. The time of gelation at each temperature of curing was determined as the abscissa of the intersection of the lines fitted to the beginning and to the final section of the curing time–viscosity diagram. The data of the gelation curve are given in Table 1 and are represented in Fig. 5.

Table 1 Data of the gelation curve of the alkyd-amino resin matrix

Curing temperature, T_{cure}/°C	Time of gelation, t_{gel}/min
66	18.28
75	8.9
84	2.9
95	1.7
110	0.8

The gelation curve is part of the TTT diagram (Fig. 8), and could be fitted with the following power function with R^2=0.9819:

$$T_{cure}=103.68t_{cure}^{-0.157}$$

By using the above function gelation can be estimated for any selected time or temperature of cure. It is especially advantageous for establishing storage conditions.

Thermogravimetric analysis

Before isothermal curing a dynamic thermogravimetric run was carried out in flowing air from 35 to 750°C (Fig. 2). The curing reactions accompanied by the evolution of low molecular mass materials take place in two distinct steps, one ranging from 50 to 154°C with 7.7% mass loss, the other from 154 to 232°C. The total loss of mass after the second stage of curing at 232°C is 15.2%. Thermooxidative decomposition starts at 240°C, takes place in more stages and ends at 640°C with no residual mass.

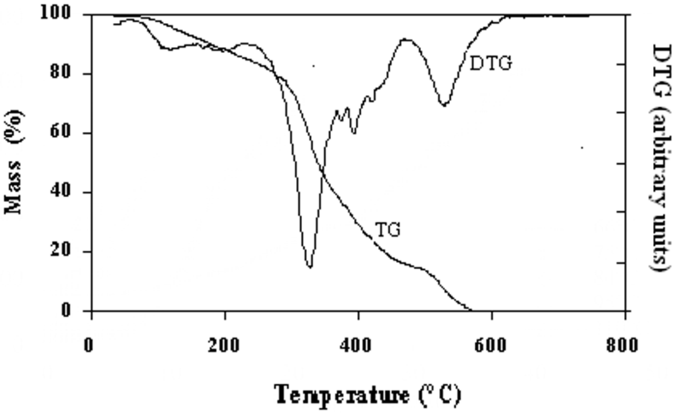


Fig. 2 TG and DTG curves of the alkyd-amino resin matrix from 35 to 750°C in flowing air

Since the process of curing involves the evolution of low molecular mass materials, it was monitored by carrying out isothermal thermogravimetric runs at five different temperatures, i.e. at 100, 120, 130, 140 and 160°C. The iso-T_{cure} diagrams, namely the change of mass loss in % *m*/*m* with the time of curing are reperesented by Fig. 3.

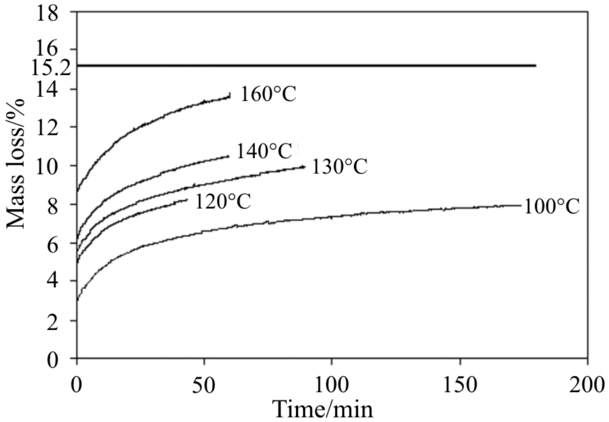


Fig. 3 Iso-T_{cure} diagram of the alkyd-amino resin system

In the temperature range of studies, i.e. between 100–160°C during 180 min curing time thermooxidative decomposition did not take place. This was supported by the fact that the loss of mass did not reach 15.2% corresponding to the maximum mass loss before thermooxidative decomposition started, as it was found by dynamic TG measurement.

The beginning section of the curing time–mass loss curves could be fitted with functions of 2nd order as given in Table 2.

Table 2 Functions of 2nd order fitted to the beginning sections of the iso-T_{cure} diagrams of the alkyd-amino resin system

Equation of the fitted curve, Δm/% in function of t_{cure}/min	R^2	Temperature/°C
$\Delta m=-0.0030\ t_{cure}^2+0.1780\ t_{cure}+3.1693$	0.9929	100
$\Delta m=-0.0048\ t_{cure}^2+0.2045\ t_{cure}+5.0260$	0.9955	120
$\Delta m=-0.0105\ t_{cure}^2+0.2674\ t_{cure}+5.5042$	0.9988	130
$\Delta m=-0.0127\ t_{cure}^2+0.3103\ t_{cure}+6.1959$	0.9975	140
$\Delta m=-0.0082\ t_{cure}^2+0.2768\ t_{cure}+8.6038$	0.9979	160

From the equations of Table 2 it is evident that volatile evolution, i.e. cross-linking reaction happened during heating up to the temperature of experiments. This volatile formation is highest, 8.6% at 160°C curing temperature. The steepness of the curves also increases with temperature showing the higher efficiency of curing at higher temperature.

The final section of the curing time–mass loss curves could be fitted with logarithmic functions as shown in Table 3. With increasing curing temperature the steepness of the curves increases referring to the change in the mechanism of curing at higher temperature.

Table 3 Functions fitted to the final sections of the iso-T_{cure} diagrams of the alkyd-amino resin system and the calculated times to reach maximum mass loss before thermooxidative decomposition

Equation of the fitted curve, Δm/% in function of t_{cure}/min	R^2	Curing temperature/°C	Calculated time to reach 15.2% mass loss	
			min	h
$\Delta m=1.1434\ln(t_{cure})+2.0781$	0.9984	100	96374	1606
$\Delta m=1.2308\ln(t_{cure})+3.5569$	0.9917	120	12833	214
$\Delta m=1.4328\ln(t_{cure})+3.4355$	0.9974	130	3680	61
$\Delta m=1.5580\ln(t_{cure})+4.1226$	0.9985	140	1224	20.4
$\Delta m=1.7747\ln(t_{cure})+6.3231$	0.9947	160	148.7	2.5

From the equations of the fitted functions the time needed to reach a given mass loss at a curing temperature, up to the maximum loss of mass before thermooxidative decomposition, can be estimated. The calculated time values for attaining the mass loss of 15.2% at the curing temperatures studied are also given in Table 3.

The effect of curing temperature on the conversion are well demonstrated by the iso-curing time (iso-t_{cure}) diagrams constructed from these same experimental data (Fig. 4).

The iso-t_{cure} diagrams can be fitted with exponential functions corresponding to the equations given in Table 4.

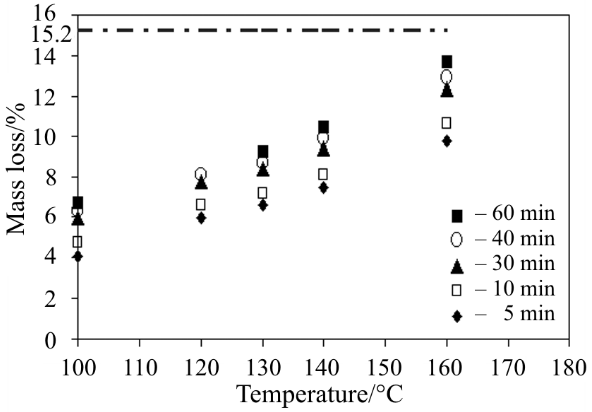


Fig. 4 Iso-t_{cure} diagram of the alkyd-amino resin system

Table 4 Functions fitted to the iso-t_{cure} diagrams of the alkyd-amino resin system and the calculated temperatures to reach maximum mass loss before thermooxidative decomposition

Equation of the fitted curve, Δm/% in function of T_{cure}/°C	R^2	Curing time/ min	Calc. temp. to reach 15.2% mass loss/°C
$\Delta m=1.0259e^{0.0142\,T_{cure}}$	0.9868	5	189.8
$\Delta m=1.2953e^{0.0132\,T_{cure}}$	0.9913	10	186.6
$\Delta m=1.8020e^{0.0119\,T_{cure}}$	0.9955	30	179.2
$\Delta m=1.9423e^{0.0117\,T_{cure}}$	0.9942	40	175.8
$\Delta m=2.0704e^{0.0117\,T_{cure}}$	0.9958	60	170.4

With the help of the functions in Table 4 the temperature can be calculated for a preselected curing time, which is needed to reach a preferred mass loss, i.e. conversion. The TTT diagram gives information on the possibility of the selected schedule for curing. In the knowledge of the TTT diagram of the investigated system (Fig. 8) the calculated temperatures needed to reach maximum mass loss (15.2%) with the selected curing times will definitely result in degradation simultaneously with curing.

The above data enable the construction of the iso-mass loss curves of the TTT diagram (Fig. 5).

Although many simultaneous reactions take place during isothermal treatment involving homopolycondensation, heteropolycondensation and even degradation, in the range of the TTT diagram, where chemical degradation does not occur, the iso-mass loss curves may be considered to correspond to the iso-conversion diagrams. The iso-mass loss curves belonging to m higher than 7.7% represent elevated curing reactions during which low molecular mass reaction components form corresponding to the second step detected by the dynamic TG run. Curing conditions selected for the experiments did not result in a mass loss higher than 10%.

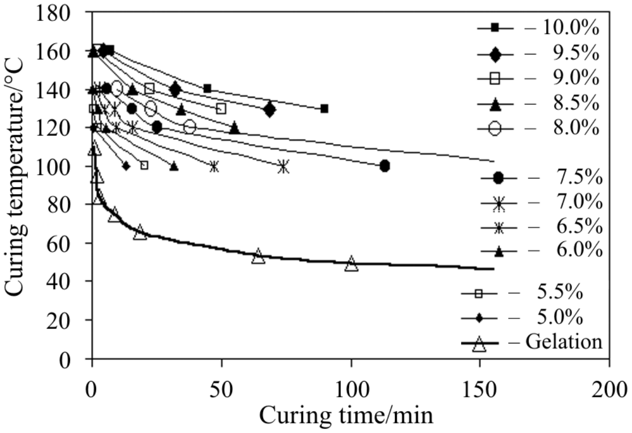


Fig. 5 Iso-mass loss curves and the gelation curve of the alkyd-amino resin system

Thermomechanical analysis

After curing schedule at 100, 120, 130, 140 and 160°C for different times the glass transition temperature of the cured matrix was determined by TMA measurements. The resulted iso-curing temperature (iso-T_{cure}) diagrams are represented by Fig. 6.

Thermal treatment at 100, 120 and 130°C resulted in a continuous increase in T_g, which relates a progress of cure. At 140°C a T_g maximum of 29.5°C is reached at 25 min, further thermal treatment resulted in a decrease in T_g. Thermal treatment for 10 min at 160°C resulted this maximum, further curing time causes drastic decrease in T_g, which may be a result of degradation. The maximum T_g value of 29.5°C corresponds to $T_{g\infty}$. The data of TMA analysis enable the construction of the curves representing the curing time–curing temperature values, which result the same T_g. These are the iso-T_g curves, which are part of the TTT diagram (Fig. 7).

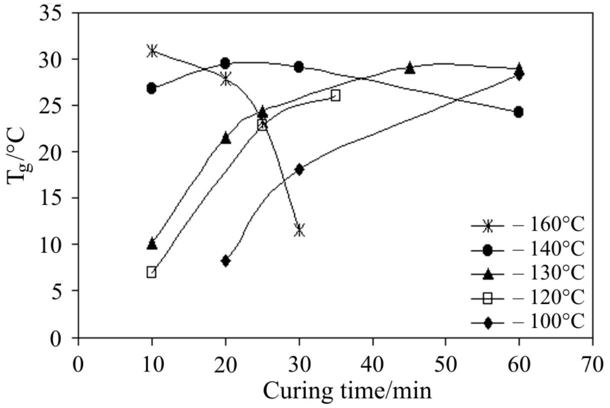


Fig. 6 Iso-T_{cure} diagrams of the alkyd-amino resin system by determining the glass transition temperature

The iso-T_g curves up to $T_{g\infty}$ represent the proceeding of the conversion. Most favourable is to select curing conditions, by which $T_{g\infty}$ can be approached or attained. Above the $T_{g\infty}$ curve degradation takes place under any curing conditions.

The TTT diagram

The TTT diagram of the investigated alkyd-amino resin system includes the gelation curve, the iso-mass loss curves and the iso-T_g curves (Fig. 8). Curing takes place above the gelation curve, although conditions should be selected below the $T_{g\infty}$ line, in order to avoid degradation. Both T_{g0} and T_{ggel} are lower than 0°C, and $T_{g\infty}$ is 29.5°C. This means that the resin matrix is in its rubbery physical state before curing, during the curing process and in the cured state. The gelation curve enables the estimation of the conditions for storage. The iso-T_g curves serve as a guide for properly selecting curing conditions for attaining a highly cured state without degradation.

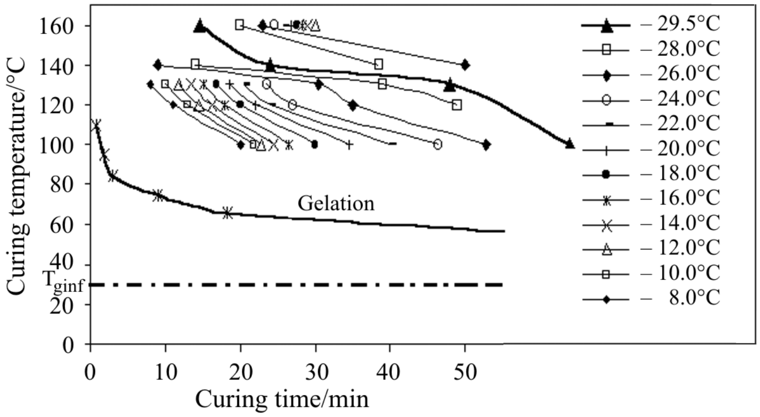


Fig. 7 Iso-T_g curves of the alkyd-amino resin system

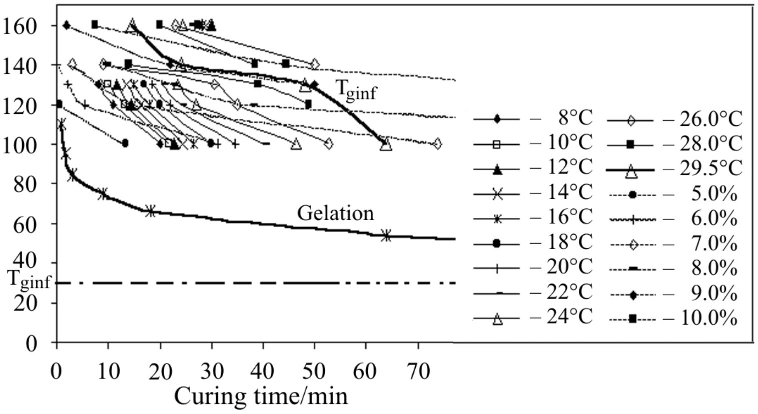


Fig. 8 TTT diagram of the alkyd-amino resin system

Conclusion

Rheological measurements served to determine the gelation curve of the TTT diagram, which could be fitted with a power function for the investigated alkyd-amino resin system. With the help of the equation, conditions for gelation, as well as proper storage conditions can be estimated.

Isothermal thermogravimetric measurements directly supplied the iso-T_{cure} diagrams, from which the iso-t_{cure} and iso-mass loss curves were constructed. The iso-mass loss curves of the TTT diagram correspond to the iso-conversional lines in the region where there is no thermooxidative degradation.

The iso-T_g curves of the TTT diagram were constructed from the iso-curing temperature (iso-T_{cure}) diagrams attained by measuring the glass transition temperature after isothermal cure at different temperatures. The proceeding of curing can be followed by the iso-T_g curves on the TTT diagram. The latest one corresponds to the $T_{g\infty}$ curve, beyond which curing is accompanied with degradation. The iso-T_g curves help to select properly the conditions for curing.

* * *

The authors express their thanks to OTKA T025589 for financial support and to Judit Szauer for TMA measurements.

References

1 L. Núńez, L. Fraga, M. R. Núńez, M. Villanueva and B. Rial, J. Therm. Anal. Cal., 70 (2002) 9.
2 J. J. Suńol, J. Therm. Anal. Cal., 72 (2003) 25.
3 K. D. Weiss, Progress in Polymer Science, 22 (1997) 203.
4 I. H. Updegraff, Alkyd Resins, Encyclopedia of Polymer Science and Engineering, 2$^{\text{nd}}$ Edition, Wiley, Chichester Vol. 1, 1998 p. 752.
5 H. J. Lanson, Amino Resins, Encyclopedia of Polymer Science and Engineering, 2$^{\text{nd}}$ Edition, Wiley, Chichester Vol. 1, p. 644.
6 W. J. Blank, J. Coating Techn., 54 (1982).