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

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The curing behaviour of a thermosetting acrylic-amino-formaldehyde resin matrix has been investigated by rheological, thermogravimetric, and thermomechanical analysis. The time–temperature–transformation (TTT) diagram of the solventless resin matrix has been constructed. The gelation curve could be fitted with a power-function of $T_{\text{gel}}=118.14\cdot t_{\text{gel}}^{-0.1238}$. With the help of this function the conditions for gelation can be calculated, and storability of the matrix can be predicted. The onset temperature of thermooxydative decomposition is 220°C, and the maximum loss of mass belonging to this temperature was found to be 16.3%, corresponding to the ultimate conversion of curing. From iso-T_{cure} diagrams determined by isothermal thermogravimetric analysis, the iso-curing time (iso-t_{cure}) and iso-mass loss curves of the TTT diagram have been constructed. The iso-T_{cure} diagrams determined by TMA measurements, served the construction of the iso-t_{cure} and iso-glass transition temperature (iso-T_g) diagrams. The T_g of the fully cured system ($T_{g\infty}$) was found to be 30°C. The iso-T_g line of 30°C represents the ultimate conversion of the cured system, up to which no degradation takes place. This curve runs below the ultimate conversion determined by thermogravimetric measurements, meaning that above 160°C decomposition takes place simultaneously with curing reactions as supported by the increasing tangent of the straight lines fitted to the last section of thermogravimetric iso-T_{cure} diagrams. The T_g of the matrix before the cure (T_{g0}) is less than 0°C. This means that the system is in its rubbery physical state during the curing process.

Keywords: *amino-formaldehyde resin, thermogravimetric analysis, thermomechanical analysis, thermosetting acrylic resin, time–temperature–transformation analysis*

Introduction

Thermosetting acrylic polymers play an important role among matrix resins for coating applications. Their widespread use is due to their excellent mechanical performance, weatherability and chemical resistance. The properties may be taylored by varying the type and concentration of the monomer components and of the copolymer or comonomer used for cross-linking. In addition to their outstanding performance they retain their colour and excellent appearance during and after exposure.

Thermosetting acrylic-amino coatings are used for the protection of industrial equipment, motor cars, laboratory instruments, household appliances and articles made of metal. Their performance are in direct relation with the time and temperature of curing, therefore the exact knowledge of the time–temperature–transformation behaviour of these systems is essential. With the help of the time–temperature–transformation (TTT) diagram the processing parameters can be estimated, conditions of storability of the uncured system can be determined, so that preliminary gelation is avoided. The incline of the system to degradation during application can also be predicted. TTT analysis of thermosetting systems has been introduced by Gillham and co-workers [1–4]. The technic for revealing the time–temperature–transformation relation of curing systems has been continuously developed [5, 6].

Thermosetting acrylic polymers

Otto Rohm was the first who studied thermosetting acrylic resins and developed the first technology for their synthesis in 1927 [7]. Their use has been increased since the 1950s and they found their widest application as protective coatings. The development of thermosetting acrylics has been continued till today [8, 9].

Acrylic polymers will become thermosetting, if they contain functional monomeric units, such as methacrylic acid or hydroxyethyl acrylate. The functional groups on the polymer chain are capable of reacting with one another, or with a selected copolymer or comonomer resulting in a network structure. If low temperature curing is possible, mostly hydroxyl functional acrylics are used. For interior use carboxyl functional acrylic resins are cured with Bisphenol A epoxide. Table 1 shows the versatility of functional

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Table 1 Functional monomers used for thermosetting acrylic resins

Functionality	Functional monomer
Carboxyl	Acrylic acid (AA) Methacrylic acid (MAA) Itaconic acid (ITA)
Hydroxyl	Allylalcohol Monoallyl ethers of polyols 2-Hydroxyethyl acrylate (HEA) 2-Hydroxypropyl acrylate (HPA) 2-Hydroxyethyl methacrylate (HEMA) 2-Hydroxypropyl methacrylate (HPMA)
Epoxide	Glycidyl acrylate (GA) Glycidyl methacrylate (GMA) Allyl-glycidyl ether (AGE)
Amino	Dimethylaminoethyl methacrylate (DMAEMA) Vinylpyridine (VP) *t*-Butyl-aminoethyl methacrylate (BAEMA)
Amide	Acrylamide (Aam) Methacrylamide (MAAm) Maleiamide
Anhydride	Maleic anhydride (MA) Itaconic anhydride
Isocyanate	Vinyl isocyanate Allyl isocyanate

monomers used for synthesizing thermosetting acrylic resins [10].

Methyl-acrylamidoglycol methyl ether (MAGME) is a modern functional monomer carrying the polymerizable vinyl group and the methyl ether group capable for cross-linking with amines, or with alcohols in the presence of acidic catalysts at room temperature [8–9].

Non-functional monomers are used for influencing the properties and the glass transition range of the cured system. Alkyl acrylates, alkyl methacrylates, styrene, vinyl toluene and other unsaturated compounds may be used as non-functinal monomers for thermosetting acrylics. In case of alkyl acrylates and -methacrylates the increase in the length of the alkyl group results in a decrease in T_g, in hardness, and an increase in flexibility and in sensitivity of the film to organic solvents. Butyl- or higher alkyl acrylates, e.g. ensure excellent flexibility and resistance to water. Alkyl methacrylates, however, lend superior weatherability to the film than alkyl acrylates. The desired glass transition range may be set by the selected ratio of styrene and butyl acrylate. Styrene lends stiffness to the film and contributes to the reduction of the price of the coating.

Melamine-formaldehyde resins

Amino-formaldehyde resins are frequently used as curing agents in thermosetting systems [11, 12]. Melamine-formaldehyde resins are prepared by the reaction of melamine (2,4,6-triamino-1,3,5-sym-triazine) and formaldehyde, followed by etherification with alcohol [13, 14]. The formed ether groups due to the presence of the adjacent nitrogen atoms are inclined to nucleophilic substitution, therefore they may be used as curing agents. According to synthesis conditions, functionality and properties, melamine-formaldehyde resins may be divided into two groups represented by Table 2 [15].

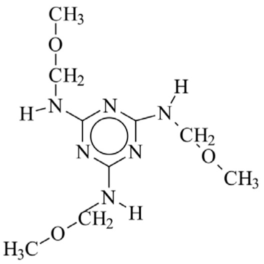
Melamine-formaldehyde resins in the cured state have excellent resistance to chemicals, therefore they may be advantageously used as curing agents in protective coatings exposed to chemicals or frequent cleaning with surface active agents (coating of motor cars, of domestic appliances etc.). In the beginning up to the years of 1950 the second class of melamine-formaldehyde resins were preferentially used with the average degree of polymerisation of 3. The etherifying alcohol was mostly *n*-butyl or *iso*-butyl alcohol. They were easy to prepare and were compatible with alkyd resins. The increasing demand for environmental protection required water-based or high solids resins. These requirements could be met by the use of melamine-formaldehyde resins belonging to the first class. The most important representatives of this class are the monomeric trimethoxymethyl melamine (TMMM), hexamethoxymethyl melamine (HMMM) and the newly developed tri(methoxymethyl) trimethyl melamine (TMMTMM) (Scheme 1).

Fully alkylated melamine-formaldehyde resins are most frequently used in the industry, since the elimination of formaldehyde can be avoided by their use (see the following section). Especially important is the hexa-methoxymethyl melamine. By the use of HMMM the hardness and chemical resistance of the coating is significantly increased.

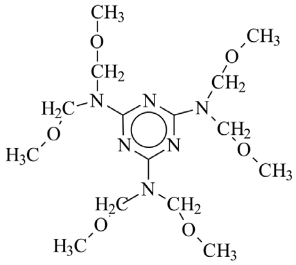
Table 2 Grouping of melamine-formaldehyde resins

Class	Preparation	Most frequent functional group	Properties
I	Excess of formaldehyde, excess of alcohol (ROH), strong acid catalyst	$–N(CH_2OR)_2$	High functionality, low molecular mass
II	Stoichiometric formaldehyde, excess of alcohol (ROH), mild acid catalyst	$–NHCH_2OR$	Low functionality, high molecular mass, incline to homo-polymerisation

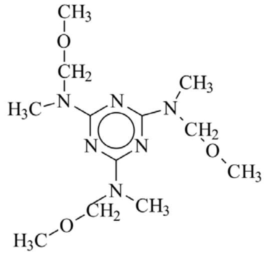
R= –CH3, n-C_4H_9, i-C_4H_9, 2-ethylhexyl



2,4,6-tri(methoxymethylamino)-1,3,5-triazine
Tri-methoxymethyl melamine (TMMM)



2,4,6-hexa(methoxymethylamino)-1,3,5-triazine
Hexa-methoxymethyl melamine (HMMM)

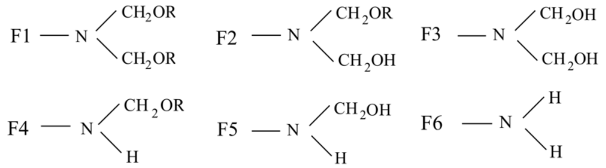


(2,4,6-trimethoxymethyl-2',4',6' -trimethyl)amino-1,3,5-triazine
Tri-methoxymethyl-trimethyl melamine (TMMTMM)

Scheme 1

Curing reactions with melamine-formaldehyde resins

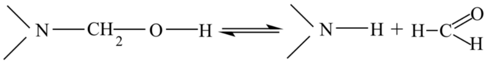
The type and degree of curing reactions are determined by the functional groups, reaction conditions including the moisture content of the film. The possible functional groups in melamine-formaldehyde resins are the following [15]:



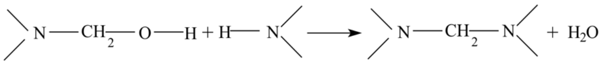
The reactions during the cure of thermoreactive systems containing melamine-formaldehyde resins may be divided into homopolymerisation and copolymerisation by the step-polymerisation mechanism.

Curing by homopolymerisation – 'self cross-linking'

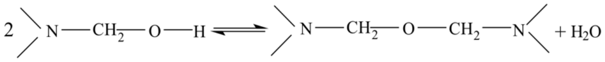
High temperature and high relative moisture content favour homopolymerisation of the melamine-formaldehyde resin. Partly alkylated (methylated) melamine-formaldehyde resins are susceptible to non-desired side-reaction, i.e. dehydroxymethylation involving formaldehyde emission [11, 15]:



Homopolymerisation of the MF resin results in methylen- and methylenether formation between the triazine rings enabling the formation of dimers, trimers and higher oligomers. The degree and kind of homopolymerisation reaction depend on reaction conditions, i.e. pH, temperature, molar ratio of the components, time of reaction and many other factors [11, 13–14]. The synthesis of MF resins in the presence of acidic catalyst and by using formaldehyde ratio less than stoichiometric, results mostly in the formation of methylene bridges via homopolymerisation:



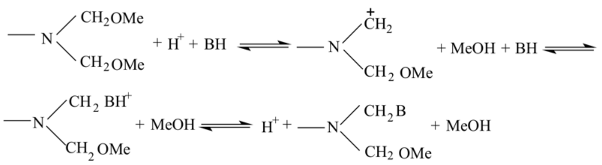
Methylene ether bridges may form by the reaction of methylol groups with each other, e.g. during acid catalysed etherification:



Formation of methylene ether bridges via homopolymerisation are non-desirable, because they are susceptible to scission accompanied by formaldehyde emission.

Curing by copolymerisation

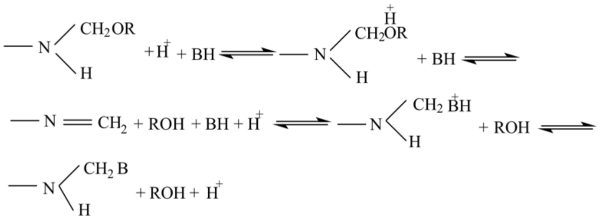
Under acidic conditions fully alkylated melamine-formaldehyde resins may react with copolymers with reactive groups containing mobile hydrogen, such as –OH, $-CONH_2$, –COOH, according to the following mechanism [16]:



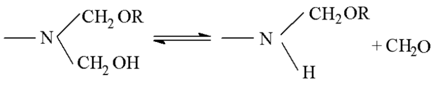
where BH represents the copolymer bearing the mobile hydrogen.

This mechanism requires strong acidic catalysts, such as *p*-toluene sulfonic acid. Saxon [17] investigated the mechanism of curing of fully alkylated melamine-formaldehyde resins with copolymers containing –COOH, –OH, and $–CONH_2$ groups. The rate of reaction was determined by the length of alkyl groups in the etherified melamine-formaldehyde resin. The highest rate of curing was detected, when HMMM was used, since methanol as a low volatile alcohol easily eliminated from the system. The effect of functionality of the copolymers depended on the acidity of the catalyst used. In the presence of acidic catalyst the order of reactivity was $–OH>–CONH_2>–COOH$, while in the absence of acidic catalyst it was $–COOH>–CONH_2>–OH$.

Partly alkylated melamine-formaldehyde resins cross-link according to a complex mechanism. Generally acidic catalysts are used for curing, and the following mechanism has been accepted [15]:



From the mechanism follows that even non-dissociating weak acids are also capable of catalyzing the reaction. Copolymers with low acidic functionality also catalyze the curing reaction without using external catalyst. Strong acids desactivate the triazine ring by protonation. Melamin-formaldehyde resins with mostly F2 functionality are susceptible to equilibrium reaction resulting in the formation of F4 functional groups [15]:



Partially alkylated melamine-formaldehyde resins emit more formaldehyde during the curing process, than fully alkylated MF resins. Due to more and more rigorous environmental requirements the use of fully alkylated, monomeric MF resins (e.g. HMMM) is preferred. For high solids coatings mainly fully methylated MF resins are used. The newly developed tri(methoxymethyl)trimethyl melamine (TMMTMM) is especially advantageous for high solids or solventless coatings. It ensures high cross-linking rate, and in the presence of diluted acid catalysts it cures at low temperatures, i.e. at 125°C.

Thermosetting systems based on acrylic- and melamine-formaldehyde resins

During the cure of thermosetting systems based on acrylic- and melamine-formaldehyde resins homo- and copolymerisation takes place simultaneously. Homo- or copolymerisation depends on the ratio of alkoxylated functional groups of the MF resin and of the functional groups of the copolymer capable to react with the former groups. If this ratio is stoichiometric, copolymerisation is favoured. If the alkoxy groups of MF resin are in excess, homopolymerisation of the MF resin occurs preferably. With the ratio of the functional groups, and with correctly selecting reaction conditions copolymerisation may be induced and the desired network structure may be attained. The cross-linking of acrylic- and melamine-formaldehyde resin systems has been studied by many researchers [18–23]. Zimmt [18] investigated the effect of the ratio of formaldehyde (degree of methylolation) of fully alkylated MF resins on the resistance to surface active agents in acrylic-based coatings. Partly methylolated MF resins were inferior to fully methylolated ones. Blank [19] studied the effect of the degree of alkylation of MF resins in acrylic-MF systems on the chemical resistance. Best results have been attained with fully alkylated MF resins. Kine [20] found relation between the loss of mass during the cure and the hardness of the resulted coating. With the increase of the mass loss hardness increased. He also studied the effect of the length of the alkyl group in etherified MF resins. Methanol-etherified MF resins resulted the greatest hardness of the acrylic-MF coating. Japanese researchers investigated the structure and functionality of the acrylic resin on the glass transition temperature, on the segment molecular mass between cross-links, and on the polymer-solvent interaction parameter [21–23]. Thermogravimetric analysis is a practical tool for studying the thermochemistry and mechanism of cross-linking in thermosetting systems [24].

Aim

The goal of this work is the evaluation of the curing behaviour of a carboxyl-functional acrylic resin with an etherified melamine-formaldehyde resin. For monitoring the cure of the system rheological, thermogravimetric and thermomechanical analysis are used. The results enable the construction of the time–temperature–transformation diagram.

Experimental

Materials

Thermosetting acrylic resin – acrylic resin

Terpolymer of styrene, butyl acrylate, hydroxyethyl acrylate and methacrylic acid. It is used in the form of a 48% solution in isobutanol/xylene with the following characteristics:

Viscosity (flowing cup No. 4 20°C)/s	130–180
Non-volatile content (120°C 2 h)/%	48
Acid content/mg KOH g^{-1}	40
Density (20°C)/g cm^{-3}	0.930–0.940
Iodine colour number/mg I_2 (100 mL)	1
Flash point (closed cup)/°C	24
Storage stability/month	6

Melamin-formaldehyde resin – MF resin

Melamin-formaldehyde resin is the reaction 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 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/month	12
Flash point/°C	28

Preparation of the resin matrix for TTT analysis

The above resin solutions were weighed in, in the following ratio:

Acrylic resin	21.08 g
MF resin	5.99 g

The solutions were homogenized, then applied onto 50×50×1 mm aluminium foils in wet thickness of 0.3 mm. The solvent had been 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 constant temperatures of 100, 120, 140, 160, 170, 180°C for different times, i.e. for 5, 10, 15, 20, 30 and 60 min. The glass transition temperature of the cured films was measured.

Methods for characterisation

Rotational viscometry

Rheological measurements took place with 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°. 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.

Results

Determining the gelation curve of the TTT diagram

In the beginning stage, up to gelation, curing can be monitored by the increase in viscosity with curing time at a given curing temperature. Isothermal curing was carried out in the cone and plate rotational viscometer at different temperatures, and the change of apparent viscosity was measured with time. The results are represented by Fig. 1.

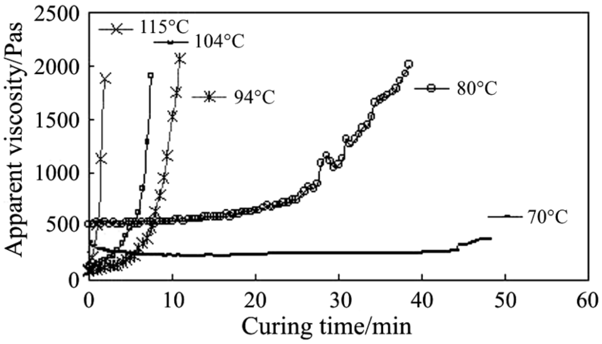


Fig. 1 The change of apparent viscosity of the acrylic-MF resin matrix with curing time at different curing temperatures

At curing temperature of 70°C the apparent viscosity started to change only after 40 min. At 80°C the viscosity slightly changes up to about 20 min, then it starts to increase steeply due to gelation. The time of gelation may be determined as the abscissa of the intercept of the straight lines fitted to the beginning and last section of the diagram. At 80°C the time of gelation was found to be 23 min. At curing temperatures above

80°C the time of gelation is much shorter due to the high rate of curing.

The curves of Fig. 1 are equal to the iso-curing temperature (iso-T_{cure}) diagrams measured by viscometry. They serve to determine the points of the gelation curve ($t_{\mathrm{gel}} - T_{\mathrm{cure}}$), which is the iso-conversion line of the TTT diagram representing the conversion in the gelled state (Table 3, Fig. 5).

Table 3 Points of the gelation curve of the acrylic-MF resin matrix determined from the iso-T_{cure} diagrams of Fig. 1

t_{gel}/min	T_{cure}/°C
0.8	115
5.8	104
7.5	94
23.0	80
44.0	70

A power function could be fitted to the gelation curve with the following equation (R^2=0.91):

$$T_{\mathrm{gel}} = 118.14 t_{\mathrm{gel}}^{-0.1238}$$

From the equation of the gelation curve lifetime (storage time) of the resin matrix at different ambient temperatures can be estimated.

Monitoring conversion by thermogravimetry

Curing reactions of acrylic-MF resins revealed that each type of reaction involves the elimination of low molecular, volatile materials. This means that the overall curing process may be followed by thermogravimetric analysis. In order to determine the starting temperature of thermooxidative decomposition, and the overall loss of mass involved by the curing process up to the onset of thermooxidative decomposition, dynamic thermogravimetric run has been carried out in flowing air, and the results analysed. The curve is shown by Fig. 2, the results are summarized in Table 4.

Curing reactions start at 80°C involving a steep decrease in mass, and proceed up to 220°C, determined as the onset and endset temperature of the derivative curve corresponding to the curing stage.

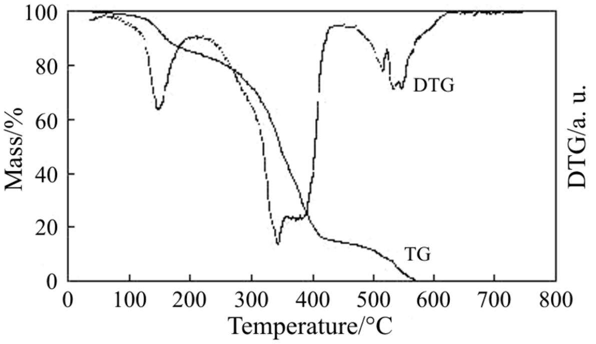


Fig. 2 Results of dynamic thermogravimetric analysis of the acrylic-MF resin matrix (5°C min^{-1}, flowing air)

Curing involves an overall mass loss of 16.3%. Thermooxidative decomposition starts at 264°C and proceeds in two steps. The main decomposition step takes place between 264 and 408°C, the second between 408 and 612°C, during the latter the burning of the residual carbon takes place.

Isothermal curing has been carried out in the thermogravimetric analyzer at different temperatures, and the change of mass was detected with time. Isothermal thermogravimetric measurements supply directly the iso-curing temperature (iso-T_{cure}) diagrams. The overall loss of mass of 16.3% involved in curing during dynamic thermogravimetric run is considered as final conversion to be attained, when drawing the iso-T_{cure} and constructing the iso-t_{cure} and iso-mass-loss diagrams. The results are shown in Figs 3–5.

The iso-T_{cure} diagrams practically show the change of overall conversion of curing with reaction time. At curing temperatures below 160°C high conversion cannot be attained during reasonable reaction time. Although the functions fitted to the final section of the curves enable the estimation of curing time at a curing temperature up to a given mass loss, i.e. conversion (Table 5). The tangent of the fitted straight line functions are almost equal at 100, 120, 140°C, it is higher at 160 and 170°C, and the highest at 180°C referring to different curing reactions at these high temperatures. The reason for the higher tangent at higher curing temperatures may also be due to the starting of simultaneous decomposition reactions during cure.

From the data of isothermal thermogravimetric analysis the iso-curing time (iso-t_{cure}) diagrams can

Table 4 Results of evaluation of the dynamic curve of acrylic-MF resin matrix

Thermal event	Temperature/°C	Mass/%	Mass loss/%
Onset of curing	40	100.0	0.0
Endset of curing	220	83.7	16.3
Onset of thermooxidative decomposition 1st stage	264	80.3	19.7
2nd stage of decomposition	408	15.1	84.9
Endset of thermooxidative decomposition	612	0.0	100.0

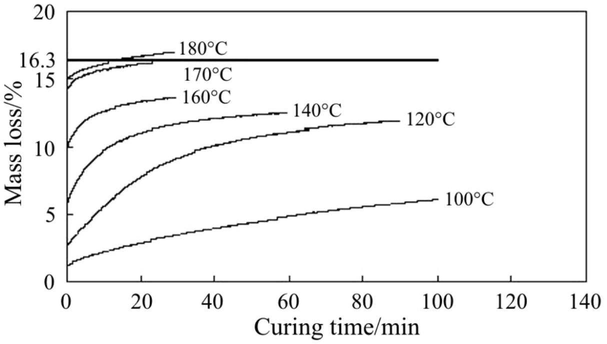


Fig. 3 Iso-curing temperature (iso-T_{cure}) diagrams of acrylic-MF resin matrix detected by isothermal thermogravimetric measurements

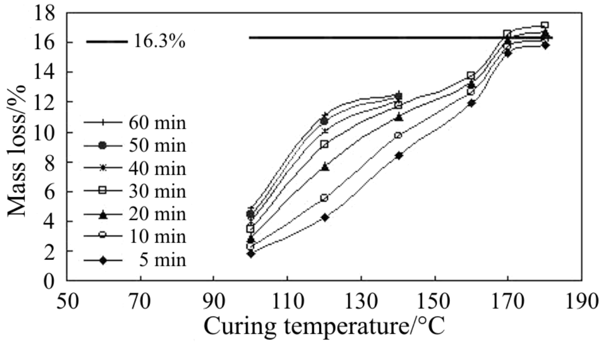


Fig. 4 Iso-curing time (iso-t_{cure}) diagrams of the acrylic-MF resin matrix calculated from thermogravimetric measurements

also be constructed (Fig. 4). The iso-t_{cure} diagrams show the effect of temperature on the conversion (mass loss) at different reaction times. At temperatures below 160°C the system is not susceptible to degradation, and time is a significant factor to conversion. At temperatures above 160°C the system is susceptible to degradation, and time does not have such a significant effect on the cure, than temperature. With the help of the iso-t_{cure} diagrams curing conditions up to the desired conversion can be selected. By choosing short curing times of 5 or 10 min, the maximum mass loss (conversion) can be approached at curing temperatures between 160–170°C without degradation.

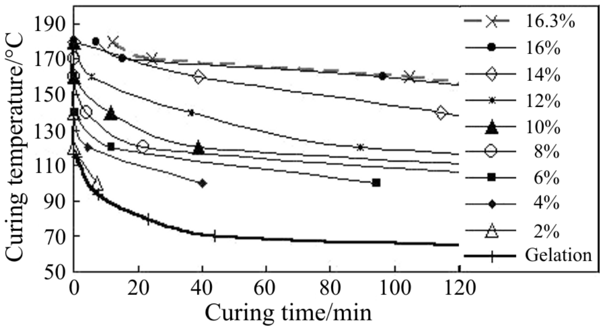


Fig. 5 Iso-mass loss diagrams and the gelation curve of the acrylic-MF resin matrix

The results of isothermal thermogravimetric analysis also enable the construction of the iso-mass loss curves, which already constitute part of the TTT diagram (Fig. 5).

The iso-mass loss curves correspond to the iso-conversional lines of the TTT diagram showing relation between curing time and curing temperature resulting in a given loss of mass during the curing process. The iso-mass loss curves enable selection of processing conditions, i.e. curing time and curing temperature. The curve belonging to mass loss of 16.3% represents the highest conversion of curing. Exceeding this value of mass loss degradation is unavoidable.

Monitoring the cure by the change of the glass transition temperature

The solventless resin matrix has been thermally treated in a drying oven at different temperatures for different curing times. The glass transition temperature of each cured matrix has been determined by TMA-analysis and the onset of glass transition has been accepted for each measurement. From the results the iso-t_{cure} diagrams have been constructed showing the change of glass transition temperature with the curing temperature at given curing time (Figs 6–7).

Table 5 Functions fitted to the final sections of the iso-T_{cure} diagrams of the acrylic-MF resin matrix and the calculated times to reach maximum mass loss before thermooxidative decomposition

Equation of the fitted curve; Δm/%, t_{cure}/min	R^2	Curing temperature/°C	Calculated time to reach 16.3% mass loss/min
$\Delta m=0.0277t_{cure}+3.3727$	0.9980	100	467
$\Delta m=0.0274t_{cure}+9.5282$	0.9866	120	247
$\Delta m=0.0255t_{cure}+11.079$	0.9784	140	205
$\Delta m=0.0347t_{cure}+12.647$	0.9769	160	105
$\Delta m=0.0348t_{cure}+15.453$	0.9683	170	24
$\Delta m=0.0473t_{cure}+15.706$	0.9767	180	12.5

Figures 6 and 7 show the monotonous increase in T_g with curing temperature up to a maximum. After reaching the maximum, the T_g decreases or increases due to degradation of the matrix resin at high temperature region. The maxima of T_g correspond to the highest degree of curing, i.e. T_{ginf} or $T_{g\infty}$, which is 30°C. From the results of TMA measurements the iso-T_g curves of the TTT diagram can be constructed (Fig. 8).

The iso-T_g curves of Fig. 8 represent the iso-conversion curves of the acrylic-amino-formaldehyde matrix resin determined indirectly by TMA measurements. The line corresponding to $T_{g\infty}$ is the border line up to which no degradation takes place during the curing process.

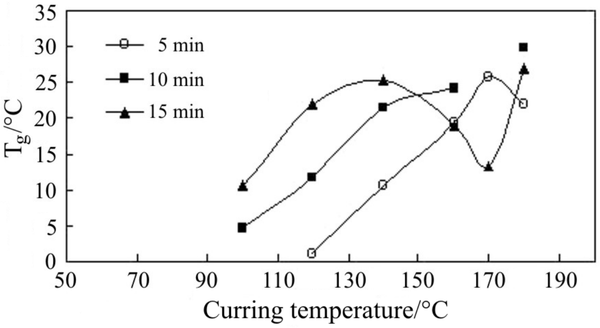


Fig. 6 The iso-t_{cure} diagrams of the acrylic-MF resin matrix determined by the glass transition temperature at 5, 10 and 15 min curing time

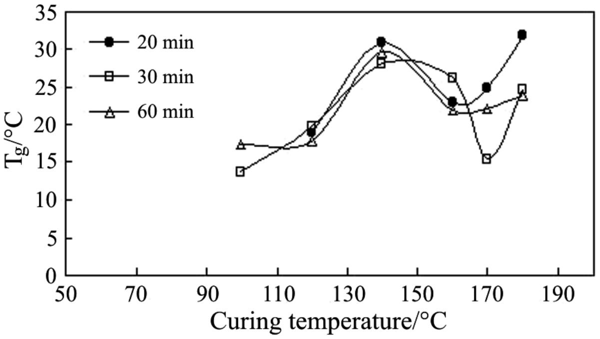


Fig. 7 The iso-t_{cure} diagrams of the acrylic-MF resin matrix determined by the glass transition temperature at 20, 30

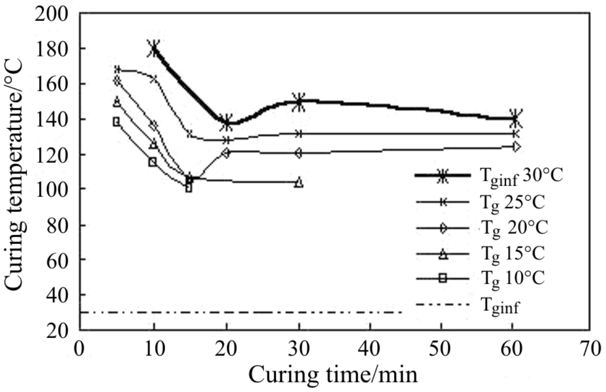


Fig. 8 Iso-T_g curves of the acrylic-MF resin matrix

Time–temperature–transformation (TTT) diagram

The TTT diagram of the investigated acrylic-amino-formaldehyde resin matrix is represented by Fig. 9. It shows the relation between curing time and curing temperature by the iso-conversional lines determined by different methods. The gelation curve corresponds to the conversion of the gelled system. Gelation can be attained at 80°C for 23 min or at 94°C for 7.5 min. With the help of the equation of the curve fitted to the gelation curve the time for gelation can be calculated at any temperature, so the lifetime of the uncured resin matrix before processing can be estimated.

The iso-mass loss curves determined by isothermal thermogravimetric measurements represent the iso-conversional lines of the overall curing process. The curves help to select processing conditions up to a desired mass loss, i.e. conversion. To maximum mass loss of 16.3% belongs the ultimate conversion before thermooxidative decomposition starts, as determined by dynamic thermogravimetric analysis. Curing conditions should be selected to approach, but not to exceed this mass loss. Ideal curing conditions for this, correspond to curing temperatures between 160–170°C for curing time within 20 min. Thermogravimetric measurements may be extended by GC-MS technic, in order to analyze the eliminating low molecular mass materials.

By inserting the iso-T_g curves (Fig. 8) into the TTT diagram, it becomes clear that the curve of $T_{g\infty}$ is below the line corresponding to the maximum mass loss found by dynamic thermogravimetric measurement before thermooxidative decomposition. This means that curing conditions should be selected so, that $T_{g\infty}$ should be approached, not the mass loss of 16.3%. This finding supports the suspicion that simultaneous degradation takes place with curing

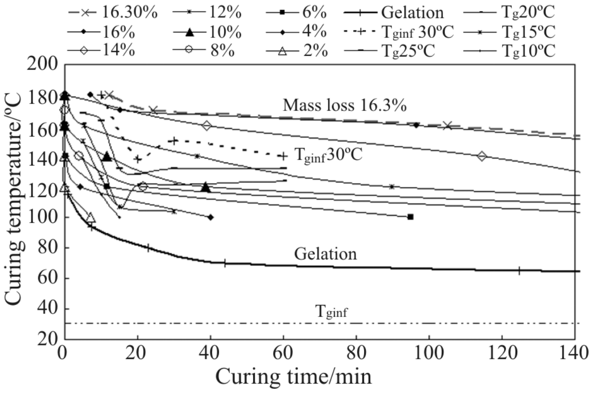


Fig. 9 Time–temperature–transformation diagram of the acrylic-melamine-formaldehyde resin matrix (T_{g0}<°C)

above 160°C, as found by the increasing tangent of the straight lines fitted to the last section of the iso-T_{cure} diagrams determined by isothermal thermogravimetric analysis. The TTT diagram also represents the physical state of the resin matrix before, during and after curing. Since the glass transition temperature of the resin matrix before curing was below 0°C (T_{g0}<0°C), and in fully cured state 30°C ($T_{g\infty}$=30°C), the material is in rubbery physical state under the conditions represented on the TTT diagram. The curing behaviour of a hydroxyl functional alkyd-resin may be compared to that of the carboxyl-functional acrylic resin after studying an earlier work of the authors [25].

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