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Investigation of modified phenolic hardeners and curing of an epoxy resin by TG–*FT*i.r.

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A TG–*FT*i.r. system is used to analyse the evolved gases during the decomposition of 2,6-dimethylol-*p*-cresol (DMPC) and the hexahydrophthalic acid anhydride modified product (HHPA–DMPC). The remaining solid sample is identified by diffuse reflection *FT*i.r. In accordance with the results of both methods a reaction mechanism is obtained. Furthermore, the curing of diglycidylether of bisphenol A (DGEBA) with HHPA–DMPC or HHPA–phenolnovolac as hardener and N-methylimidazole as accelerator is followed by TG–*FT*i.r. It could be shown that the amount of water formed in the post-curing period is responsible for the appearance of the sample. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: TG–*FT*i.r.; novolac; epoxy resins)

INTRODUCTION

TG–*FT*i.r. is a combined technique for determining the sample weight change with respect to temperature and for identifying the single compounds[1]. When the evolved gases consist of various components the information is limited to the respective substance classes. It is useful to create a contourplot before analysing *FT*i.r. spectra, because vertical and horizontal cuts give information about the peaks formed at a definite reaction time. Furthermore, the cuts deliver the single spectrum at a definite time and the thermogram showing the increase or decrease of a peak during the whole measurement.

TG–*FT*i.r. has been known for about ten years and can also be used for the thermal analysis of polymers[2,3]. Therefore, in this study the method is used for determining the thermal stability of 2,6-dimethylol-*p*-cresol and analysing evolved gases. The results are compared with earlier experiments of condensation reactions[4]. Modified phenolic hardeners can be used for epoxy curing. We have recently reported[5] an investigation of reactivity ratios during the synthesis of anhydride modified phenolic compounds. Such a hardener (HHPA–DMPC) is determined in terms of weight loss characteristics and evolved gas products. The present study is investigating the cause of the bubble formation during curing by means of TG–*FT*i.r., which is important for technical application.

THERMAL STABILITY OF 2,6-DIMETHYLOL-*p*-CRESOL (DMPC)

In 1948 Zinke and Ziegler[4] investigated the thermal curing process of phenolalcohols up to 230°C. They determined the formation and structural changes of polyethers by treating the resins with HBr and analysing the bromine content of the saponification products. The values depend on the ether linkages formed and the still existing methylol groups. The incomplete saponification of hardly soluble resins is a frequent problem. The authors reported that during the curing of 2,6-dimethylol-*p*-tert-butylphenol up to 155°C only water was found. At about 185°C the formation of formaldehyde started. Furthermore, the decomposition of the primer formed ether linkages into phenolaldehyde was observed.

In this study, the thermal stability and the evolved gases of a similar compound (2,6-dimethylol-*p*-cresol) are investigated by TG–*FT*i.r. in a temperature range from 65°C to 520°C. Zinke and Ziegler observed the formation of the three reaction products mentioned above one after the other. Therefore, the qualitative and quantitative determination of the evolved gases should be uncomplicated.

This is demonstrated in the weight loss curve of DMPC (*Figure 1*) showing three ranges. However, the contourplot (*Figure 2*) shows the formation of four evolved products (regions A to D).

Contrary to the results of Zinke and Ziegler[4], the curing reaction of DMPC starts at a higher temperature (190°C) and water and formaldehyde are detected together. This means the reaction rate determining step

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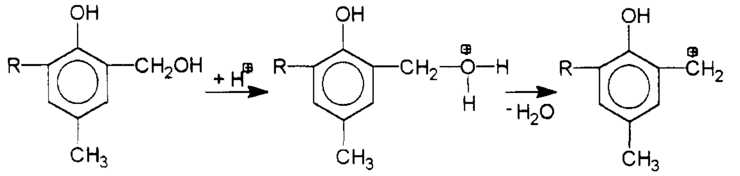
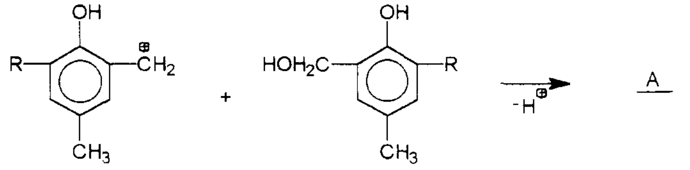
is the evolution of water. The resulting bonds between the phenolic parts are dimethylenether bridges:



(1)



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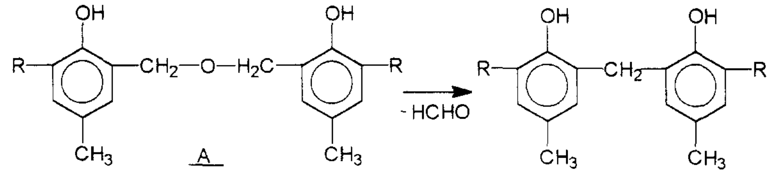

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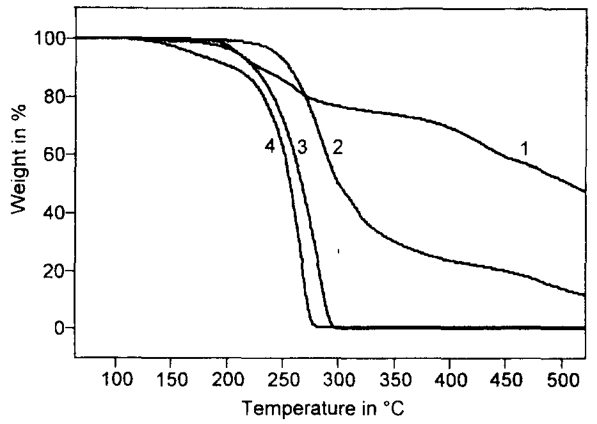


Figure 1 T.m.a. 7 curves (65°C to 520°C, heating rate 10 K min^{-1}). 1 = 2,6-dimethylol-*p*-cresol (DMPC); 2 = HHPA modified DMPC; 3 = HHPA modified benzylalcohol; 4 = HHPA modified *p*-cresol

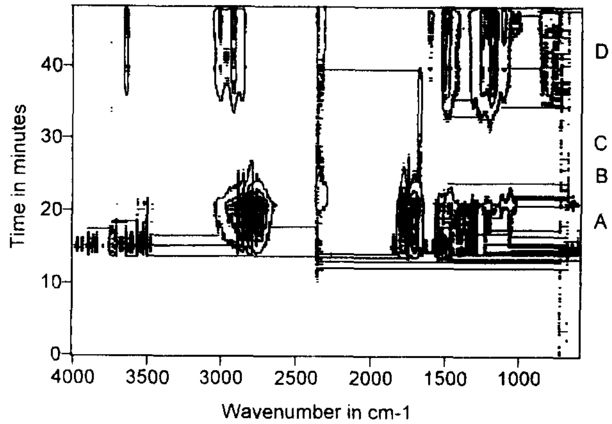
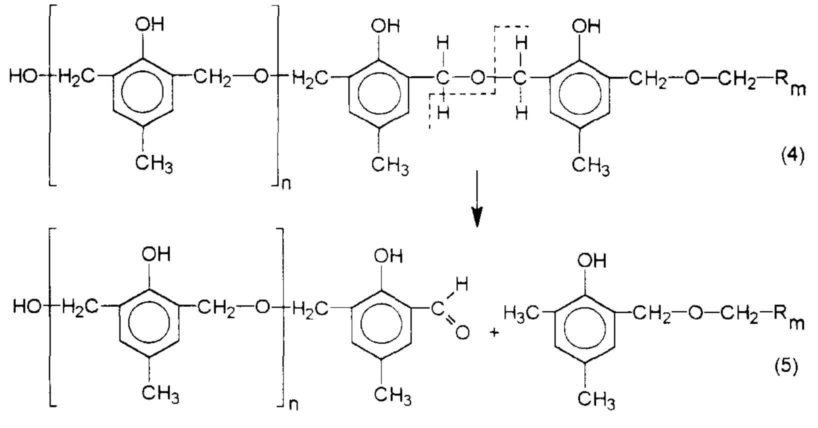


Figure 2 *FT*i.r. spectrum (contourplot) of evolved gases from 2,6-dimethylol-*p*-cresol (65°C to 520°C, heating rate 10 K min^{-1}, four scans per slice). (A) from 13 to 22 min, water and formaldehyde; (B) from 22 to 27 min, formaldehyde; (C) from 30 to 32 min, phenolaldehyde; (D) from 36 min, xylenol

Only at about 285°C the formation of formaldehyde prevails. Dimethylenether bridges are converted to methylene bridges [equation (3)]. The decomposition into phenolaldehyde proceeds in the following manner[4,6]:



(4)

(5)

Under the conditions chosen aldehyde is detectable for only 2 min (360–385°C). At higher temperatures (> 425°C) xylenol can be detected. Though there is a fluent evolution of the different gases, it is possible to

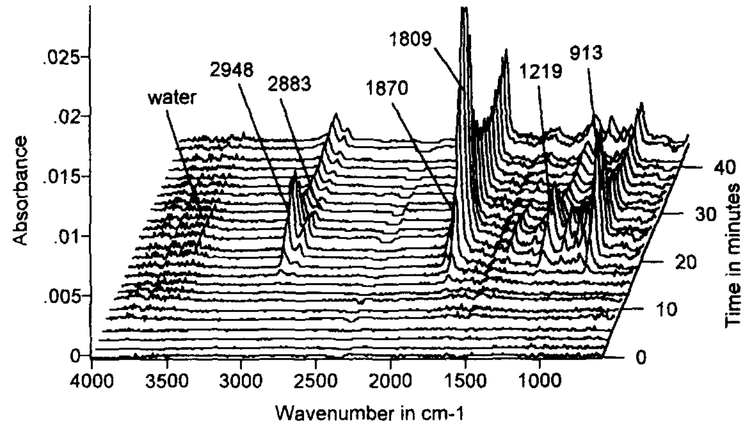


Figure 3 3D–*FT*i.r. spectrum of evolved gases from HHPA modified 2,6-dimethylol-*p*-cresol (65°C to 520°C, heating rate $10\,K\,min^{-1}$, four scans per slice)

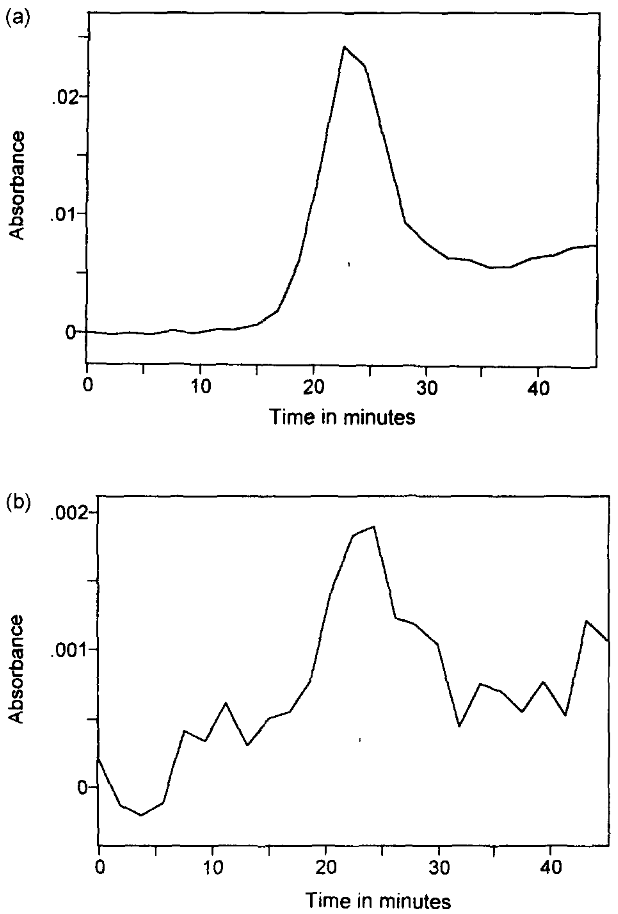


Figure 4 Gas release profiles from HHPA modified 2,6-dimethylol-*p*-cresol (65°C to 520°C, heating rate $10\,K\,min^{-1}$, four scans per slice). (a) $1809\,cm^{-1}$ (anhydride, $\nu_{as(C=O)}$); (b) $3650\,cm^{-1}$ (water, ν_{OH})

Table 1 Amount of evolved gases during the curing of 2,6-dimethylol-*p*-cresol determined by means of TGA 7 (from 65°C to 520°C at a heating rate of $10\,K\,min^{-1}$, in nitrogen)

	Evolved gas	Temperature range in °C	Weight loss in % within the temperature range
Region A	Water, formaldehyde	190–285	20.9
Region B	Formaldehyde	285–330	3.3
Region C	Phenolaldehyde	360–385	2.0
Region D	Xylenol	> 425	17.3

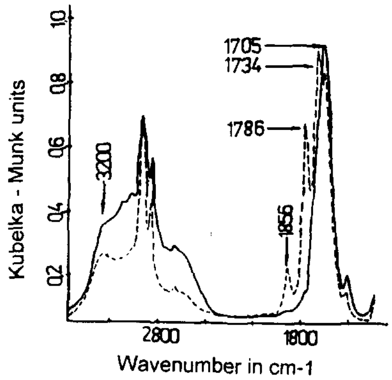


Figure 5 Diffuse reflection in Fourier-transform i.r. spectrum from HHPA modified 2,6-dimethylol-*p*-cresol: —— before thermal treatment, - - - - after thermal treatment (75 min at 200°C in an oven)

quantify their amounts (*Table 1*). Knop[6] reported that the content of aromatic aldehydes in cured resols amounts up to 2%. The result of our study confirms this observation.

THERMAL STABILITY OF HEXAHYDROPHTHALIC ACID ANHYDRIDE MODIFIED 2,6-DIMETHYLOL-*p*-CRESOL (HHPA–DMPC)

In the present study, HHPA-modified 2,6-dimethylol-*p*-cresol is analysed by TG–*FT*i.r. to investigate the decomposition of half-acid esters. The gas evolution starts at 188°C. *FT*i.r. spectra of the evolved gases are presented in *Figure 3*. The *FT*i.r. spectra and the thermograms (*Figures 4a* and *b*) demonstrate that hexahydrophthalic acid anhydride and water are formed. During thermal treatment of HHPA–DMPC (from 65 to 520°C at a heating rate of $10\,K\,min^{-1}$ in nitrogen) 88.35% evolved gases are formed.

The solid product of the thermal treatment of HHPA–DMPC (75 min in an oven at 200°C) is investigated by the diffuse reflection *FT*i.r. (*Figure 5*). The ν_{OH}-peak at $3200\,cm^{-1}$ is smaller compared to the spectrum of untreated HHPA–DMPC. The absorption of the symmetric and asymmetric carbonyl region of the anhydride increases ($\nu_{sy(C=O)} = 1856\,cm^{-1}$, $\nu_{as(C=O)} = 1786\,cm^{-1}$, $\nu_{(C-O)} = 905\,cm^{-1}$) after thermal treatment.

In accordance with the results of the evolved gas analysis and the solid residue it is possible to determine the reaction mechanism. The splitting of half-acid ester [equation (6)] effects an increase of the content of hydroxyl groups and anhydride.

$$\text{half-acid ester} \rightleftharpoons \text{anhydride} + \text{alcohol} \qquad (6)$$

$$\text{half-acid ester} + \text{alcohol} \rightleftharpoons \text{diester} + H_2O \qquad (7)$$

A phenolester linkage is likely to be less stable than an aliphatic ester linkage. This is illustrated in *Figure 1* showing the TGA 7 curves of two model compounds for HHPA–DMPC (i.e. HHPA–*p*-cresol, HHPA–benzylalcohol.

The formation of a diester [equation (7)] is inferred from the decrease of the content of hydroxyl groups in the spectrum of the diffuse reflection *FT*i.r. and the water found in the gas stream. This is confirmed by a decrease of the content of acid groups (1705 cm^{-1}). The thermograms (*Figures 4a* and *b*) at 1809 cm^{-1} (HHPA) and 3650 cm^{-1} (water) demonstrate that HHPA and water are evolved together. This means the diester evolution takes place instantaneously after the alcohol has been split. Higher temperatures result in a further increase of water formation because diester is formed more easily at temperatures > 200°C.

INVESTIGATION OF THE CURING OF AN EPOXY RESIN

Epoxy resins are duromer polymers with excellent electrical, thermal and mechanical properties applied as coatings, adhesives and insulation materials for electrical equipment. Due to their brilliant toughness epoxy resins are also used for matrix materials for reinforced fibre compounds. Technically most important resins are prepared by the polyaddition of low molecular epoxies with bisphenol A in the melt (advancement resins) or by polycondensation of bisphenol A, epichlorohydrine and sodium hydroxide (taffy resins). These prepolymers contain at least two epoxy groups in one molecule. The resins may be cured by means of hardeners (bi and polyfunctional amines, acids, phenols, acid anhydrides). The cheaper phenolic resins are often applied as hardeners. For better curing of the resin-hardener mixture accelerators (amines, imidazoles) are used. They determine the temperature and time of curing, the build-up of the network and finally the resulting properties.

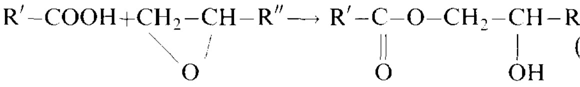
Kocks[7] gave a detailed report on the reasons of bubble formation, which, especially in coatings, cause difficulties. There are bubbles with and without liquid caused by inner stress and osmotic events (diffusion, permeation). These undesirable bubbles consisting of volatile products can occur during curing, too.

In this study, diglycidylether of bisphenol A is cured with HHPA-modified DMPC or HHPA-modified phenolnovolac and accelerated with N-methylimidazole (NMI).

Bubble formation cannot be avoided in mixture A. During the curing of the epoxy resin with modified technical phenolnovolac (mixture B) this phenomenon is not observed. Therefore both cases are investigated by TG–*FT*i.r. (equivalent molecular ratios):

mixture A: HHPA–DMPC/DGEBA/NMI = 1/1.5/0.05
mixture B: HHPA–novolac/DGEBA/NMI = 1/0.5/0.05

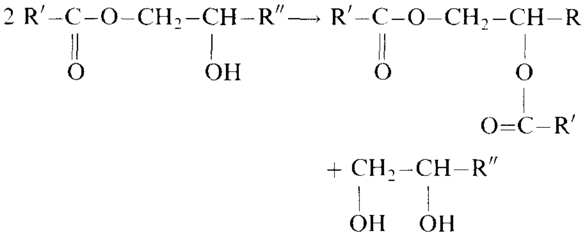
The reaction between epoxy and acid groups determines the network structure. Various laboratories[8–11] have investigated the possible reactions in epoxy–acid systems. Independent of the molecular ratio the main reaction is the formation of a hydroxyester [equation (8)].



$$R'\text{–COOH} + \underbrace{CH_2\text{–}CH}_{O}\text{–}R'' \longrightarrow R'\text{–}\underset{\underset{O}{\|}}{C}\text{–O–}CH_2\text{–}\underset{\underset{OH}{|}}{CH}\text{–}R'' \qquad (8)$$

With an excess of epoxy or acid further reactions (etherification or esterification) with the formed functional groups may occur.

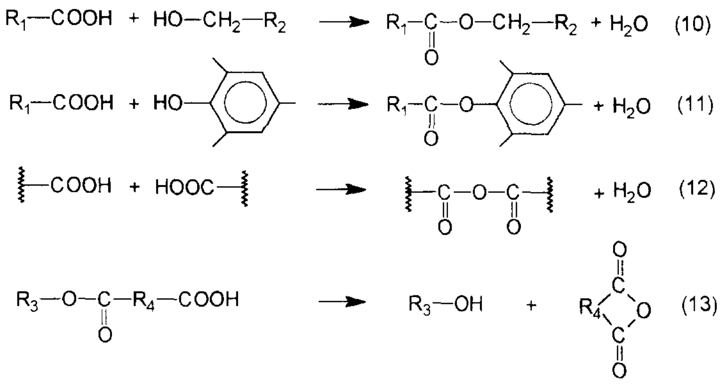
Matejka *et al.*[10] described the disproportionation of half-acid ester into diester and glycol [equation (9)].



$$2\,R'\text{–}\underset{\underset{O}{\|}}{C}\text{–O–}CH_2\text{–}\underset{\underset{OH}{|}}{CH}\text{–}R'' \longrightarrow R'\text{–}\underset{\underset{O}{\|}}{C}\text{–O–}CH_2\text{–}\underset{\underset{O=C\text{–}R'}{\underset{|}{\underset{O}{|}}}}{CH}\text{–}R'' + \underset{\underset{OH}{|}}{CH_2}\text{–}\underset{\underset{OH}{|}}{CH}\text{–}R'' \qquad (9)$$

Scheme 1 displays possible reactions during the curing delivering volatile products. Franzke[12] investigated an anhydride cured epoxy resin by *FT*i.r. and proved that a very small amount of anhydride segments was formed by an intermolecular condensation reaction [equation (12)]. Nevertheless, these segments are further reactive centres for curing.

Curing and post-curing of mixtures A and B are



Scheme 1 Possible reactions during curing of diglycidylether of bisphenol A with acid anhydride modified phenols delivering volatile products

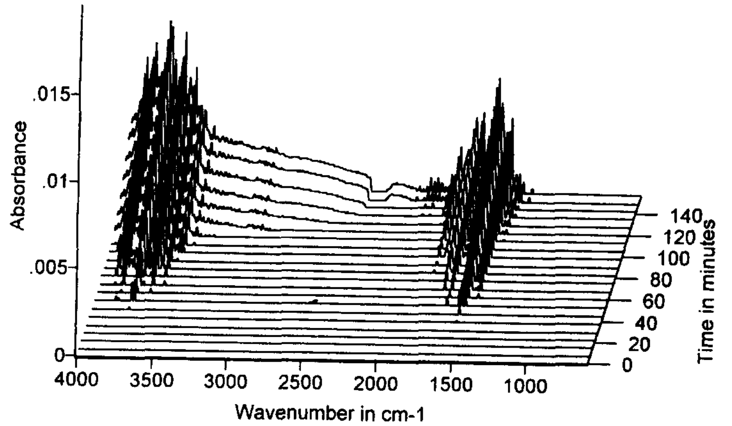


Figure 6 3D–*FT*i.r. spectrum from the curing reaction (60 min at 120°C, at a heating rate of $10\,K\,min^{-1}$ up to 180°C to stay there for 90 min, four scans per slice) of mixture A (HHPA–DMPC/DGEBA/NMI = 1/1.5/0.05)

investigated by TG–*FT*i.r. to find the cause of bubble formation. The temperature regime is adapted to the curing in a glass vessel. The observation by TG–*FT*i.r. shows that the decomposition of HHPA–DMPC into 2,6-dimethylol-*p*-cresol and anhydride starts at temperatures > 188°C. Therefore, the evolution of CO_2 by anhydride decomposition is negligible.

The *FT*i.r. spectrum of mixture A (*Figure 6*), only shows an evolution of water. It is interesting that no evolved gas can be detected during curing (120°C). This is due to the selectivity of the epoxy–acid reaction. After 60 min the system is heated to the post-curing temperature (180°C). Instantaneously, water is observed in the gas stream. Conversions delivering volatile products do not take place at lower temperatures. Though the whole weight loss [prevalent water after equations (10)–(12)] is only about 4% the sample is not bubble free.

At the beginning of the curing of mixture B small amounts of residual anhydride (esterification is an equilibrium reaction) are observed in the gas stream of TG–*FT*i.r. But the main content of the gas is water evolved in post-curing. The whole amount of the decomposition products is only 1% and thus the sample looks macroscopically bubble free.

Another cause for bubble formation is the stirring of the resin–hardener mixture to get a homogeneous sample. Due to the high viscosity of such melts air which is stirred into the mixture cannot be removed even by applying a vacuum.

CONCLUSIONS

The investigation of the thermal stability of 2,6-dimethylol-*p*-cresol shows that four evolved gases (water, formaldehyde, phenolaldehyde, xylenol) are formed. Contrary to the results of Zinke and Ziegler[4], water and formaldehyde (20.9% weight loss) are registered together. During the curing of a phenolalcohol the corresponding phenoldialdehyde is formed. There is no evidence—neither from the colourimetric[4] nor from the *FT*i.r.-spectroscopic methods—that monoaldehyde is formed as well. The amount of evolved phenolaldehyde (2%) is in accordance with ref. 6. It is possible to detect xylenol with our temperature programme up to 520°C (literature: up to 230°C). The half-acid ester HHPA–DMPC decomposes into anhydride and DMPC at > 188°C. The alcohol formed reacts with still existing half-acid ester to diester. It is proved that water is responsible for the bubble formation during the curing of an epoxy resin with anhydride modified phenols. The water has been evolved at the post-curing temperature (180°C) only. The evolved gases amounting to about 4% are responsible for bubble content of the sample.

EXPERIMENTAL

Starting materials

2,6-Dimethylol-*p*-cresol has been prepared as described in ref. 13. The synthesis of HHPA–DMPC is carried out in a melting process[5]. Stoichiometric amounts of hexahydrophthalic acid anhydride (HHPA) and DMPC are intensively mixed at 110°C. Other half-acid esters (HHPA–phenolnovolac, HHPA–benzylalcohol, HHPA–*p*-cresol) are prepared using the same procedure. Diglycidylether of bisphenol A (DGEBA) is recrystallized from an acetone–methanol mixture (20/80, v/v). N-methylimidazole is an Aldrich Chemical Co. Ltd. product (+99% redistilled). Before curing the resin, hardener and accelerator are mixed by means of a laboratory roller.

Instruments

A Perkin–Elmer TGA 7 is used to follow the sample weight change at a heating rate of $10\,K\,min^{-1}$ with a gas flow rate of $80\,ml\,min^{-1}$ in nitrogen. The sample (28–40 mg) is heated from 65°C to 520°C. A Perkin–Elmer System 2000 *FT*i.r. coupled with the TGA 7 instrument by a connecting heated gas line (its temperature being about 250°C) monitors the evolved gases with four scans per slice. A thermocouple controller maintains the gas cell temperature at about 250°C to prevent condensation.

The curing of the epoxy resin is carried out for 60 min at 120°C. The post-curing temperature (180°C) is reached by heating at a rate of $10\,K\,min^{-1}$ and is then held for 90 min.

A *FT*i.r. spectrometer 205 from Nicolet is used for the diffuse reflection in Fourier-transform measurement (nickel–diamond sample holder, 128 scans, resolution $4\,cm^{-1}$). For a maximum benefit from the high information content of the TG–*FT*i.r.-files the following data processing techniques are applied: (a) optimization of the time difference between the extractions of the single spectra for the construction of the multi-files, (b) extraction of thermograms and spectra from the multi-files,

(c) co-adding of *FT*i.r.-spectra in specified regions of wavenumbers for increasing the signal-to-noise ratio.

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