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REACTION OF PHENOL-FORMALDEHYDE NOVOLAC RESIN AND HEXAMETHYLENETETRAMINE IN OH – CONTAINING SOLVENTS AS MEDIUM

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ABSTRACT

The reaction between phenol-formaldehyde novolac resin and hexamethylenetetramine in the presence of p-tert-butyl phenol was carried out in the solution of OH - containing solvents at temperature of 80° C in order to obtain a slightly cross-linked olygomer still soluble in different solvents. The main goal of the work is to obtain a product, which could be used as a hardener for epoxy resins at lower temperatures then the normal ones for this reaction.

The proceeding of the carried out reaction was controlled by the pH – values of the mixture and its increasing viscosity as well. The final solution and the end yellow colored powder product, precipitated and washed by the water were analyzed by IR, ^{1}H NMR, DSC and GPC methods in order to suggest the probable structure at the precipitated powder. The IR and ^{1}H NMR spectra tend to presume the expected slight cross-linking of the still soluble phenol-formaldehyde novolac resin through the formation of benzoxazine rings promoted by the presence of p-tert-butyl phenol. The presence of tertiary N – atoms in the benzoxazine linkage could promote the cure of epoxy resins with the modified phenol-formaldehyde novolac resin.

Keywords: polyaromatics oligomers, synthesis, hexamethylenetetramine, low temperature cross-linking.

INTRODUCTION

The reaction of hexamethylenetetramine (HMTA) with phenol-formaldehyde novolac resin (PFNR) has been studied in different papers in the past [1-4]. The reason for the investigations made concerns with both the scientific interest to the model reactions between phenol and HMTA and the practical profit of the knowledge of the commercial novolac resin curing interactions with HMTA as well [5] . Of particular interest is the release of the gaseous products during the curing process and the way to minimize it at the technological operations [6] .

The curing mechanism of the PFNR with HMTA is described in details using different classic methods (IR spectroscopy, DTA, TG, ^{1}H NMR, ^{13}C NMR, GPC) measurements etc [5,7-9]. The different transient intermediates of this interaction in solid state were specified [7, 9]. The earliest appeared product of the model reaction between phenol and HMTA as designated by [3] has been found at 103°C to be benzoxazine. In another study [2] it was suggested that during the curing process at higher temperatures (up to 150°C) the reaction passes throughout benzylamine to form in a presence of excess of phenol a cross-linked structure with the evolution of ammonia. The further investigations have been shown among the variety of transient intermediates the prevalence of the benzoxazine ones [3,7] especially in the presence of free phenol. However in the recent literature the possible reaction of HMTA with a novolac phenol-formaldehyde resins in solvents as liquid media was not reported.

The aim of our work was to study the possibility to obtain a partially cross-linked product of commer-

cial PFNR with HMTA at a temperature lower than 103°C. The idea was to carry out a probable reaction in a presence of free p-tert-butyl phenol (PTB) using ethanol and a mixture of ethanol and 2-ethoxyethanol (ethylglycol) as well as a reaction medium. In both cases a reaction temperature was maintained on a level of ethanol boiling point temperature (max 82°C).

EXPERIMENTAL

Materials: Phenol-formaldehyde novolac resin - commercial product (novolac resin), Fikosota [Bulgaria], m. p 83-85°C, Ethanol, technical grade - commercial product, Shell Chemicals (UK), 2-ethoxyethanol, technical grade - commercial product, BP Chemicals (UK), hehamethylentetramine - commercial product, Neochim (Bulgaria), p-tert.butyl phenol - commercial product, Hóls (Germany), recristalized from ethanol.

Methods: Differential scanning colorimetry (DSC) – Perkin Elmer, DSC – 2C;

Infrared spectroscopy (IR) - Perkin Elmer, Specord 71 PM; ^{1}H NMR – Spectrometer,

Jeol JNM –PS-100; Viscosity measurements – Rheoviscometer Hϕpler;

Gel permeation chromatography (GPC) measurements were carried out with THF as a mobile phase at 40°C column temperature. The flow rate chosen was 1ml min^{-1}.

Differential scanning colorimetry (DSC) was performed at a heating rate of 20°C min^{-1} and sample weight of about 6–10 mg. Infrared spectra (IR) were recorded over a range 500 – 4000 cm^{-1} at a resolution of 4 cm $^{-1}$, using the thin film technique with KBr pellets. The ^{1}H NMR spectra were obtained at 25°C with d – DMSO as a solvent and as an internal standard.

After the PFNR, HMTA and PTB were solved in the chosen reaction media (ethanol or mixture of ethanol and 2-ethoxyethanol), the reaction was carried out in three-neck flask with reflux and permanent stirring and heating at a temperature of 80°C. The solid content of PFNR in the solvent was always 50 m.%. The quantity of HMTA and PTB were both equals of 7 m.% towards the weight of PFNR.

The product obtained after 3h reaction time was precipitated from water, several times washed and dried under vacuum at 40°C to give yellow colored powder. The molecular masses MM of the obtained products and their dispersity were determined by GPC methods. The propagating viscosity of reaction mixture was determined by Hϕpler Rheoviscometer. The gelatination times for different products (olygomers and mixtures) at different temperatures were also established.

RESULTS AND DISCUSSION

1 hour after the reaction temperature has been established (following the method described in the experimental part) the evident increase of the viscosity of reaction mixture was observed (Fig.1).

At the reaction time of 3 hours the propagating gel-formation started without syneresis phenomenon. When the reaction was carried out in 2-ethoxyethanol instead of ethanol the gel-formation started much earlier. When the reaction medium was the mixture of ethanol and 2-ethoxyethanol in ratio 4:1 and 3:1 mass parts as well the change of the viscosity was similar as it was in pure ethanol. The increased presence of 2-ethoxyethanol over the ratio 3:1 led again to earlier gel-formation and to insoluble product as well. The final

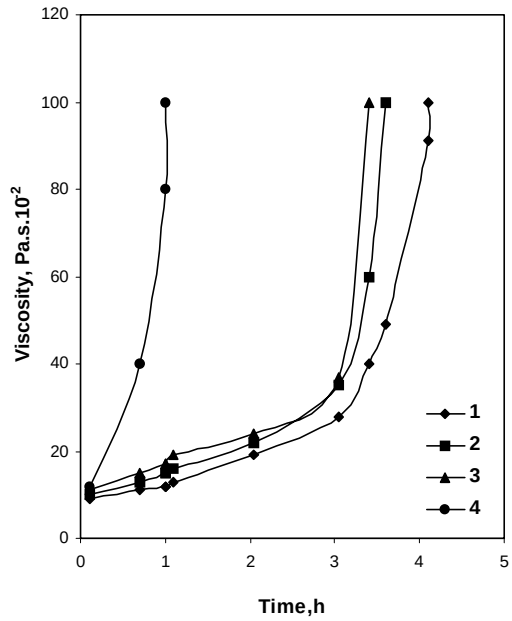


Fig. 1. Viscosity changes of the propagating reaction: 1– PFNR, HMTA and PTB in ethanol; 2- PFNR, HMTA and PTB in ethanol : 2-ethoxyethanol 4:1 in mass parts; 3- PFNR, HMTA and PTB in ethanol: 2-ethoxyethanol 3:1 in mass parts; 4- PFNR, HMTA and PTB in 2-ethoxyethanol.

state of reaction mixture showed pH=10,5 (at initial value 5,5) and strong odour of ammonia.

The increased viscosity during the reaction of PFNR with HMTA in the liquid media is the first obvious sign for the running interaction of the components of the reacting mixture assuming partial cross-linking. The final gel-formation suggests clearly the limited cross-linking of the olygomer molecules by the transient products on the base of HMTA. This suggestion was confirmed by the gel-formation observations (Fig.2) where the influence of different medium is obvious. The most rapid gel-formation occurred when the medium is solvent mixture with maximal content of 2-ethoxyethanol. This fact coincides with the most rapid gel-formation on the same reaction mixture at 80°C. All discussed in the literature mechanisms of the processes during the cure of novolac resin by HMTA [1-8] are considered to exist at a temperature at least over 103°C and usually over 130°C. Obviously it is not possible to adopt the same mechanism as it was suggest for the solid state reactions [3] (still not absolutely confirmed because the continuous investigations [9]) but some facts suppose to take into consideration similar transient steps. The observed increasing of the viscosity and the strong odour of amines or ammonia products could lead to the presumed appearance of HMTA derivatives. This can be attributed to the presence of OH groups from alcohol and alkoxyglycol and especially from the free phenol – PTB. According [3] this presence activates the

Table 1. Molecular masses and dispersity.

№	Product	MM [a] (Da)	n [b]
1.	PFNR of origin	491	3,18
2.	Reaction product from ethanol	1204	3,21
3.	Reaction product from mixture ethanol: 2-ethoxyethanol 4:1mass p.	686	4,78
4.	Reaction product from mixture ethanol: 2-ethoxyethanol 3:1mass p.	673	6,76

[a] *Molecular mass*

[b] *Dispersity*

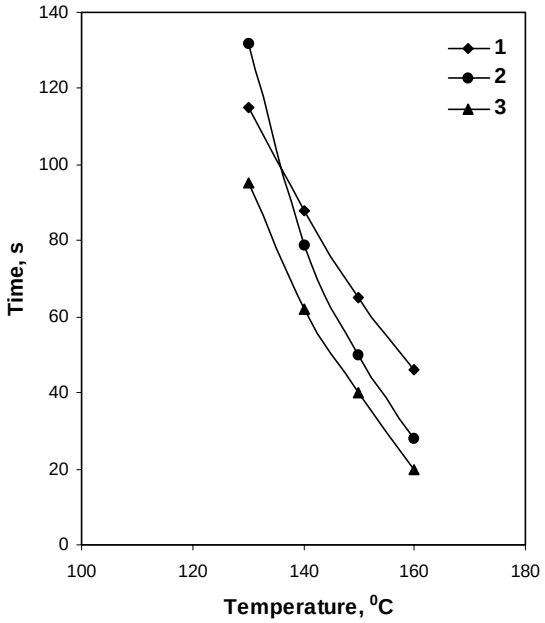


Fig. 2. Times of gelatination at different temperatures for different reactions mixtures:
1- PFNR, HMTA and PTB in ethanol; 2- PFNR, HMTA and PTB in ethanol: 2-ethoxyethanol 4:1 in mass p.; 3- PFNR, HMTA and PTB in ethanol: 2-ethoxyethanol 3:1 in mass parts.

active places in the phenol rings of the PFNR preferably at o-, but also at p–positions. To confirm it the DSC investigations were carried out for the physical mixtures of PFNR + HMTA and PFNR + HMTA + PTB as well with the same mass ratio as it was in the reacting mixture (Fig. 3). The energy of activation of the exothermic reaction with NH_3 – evolution, according to the approved in the literature [3] decomposition of HMTA (at 157,18°C and 158,84°C) is 406 kJ/mole and 188 kJ/mole, respectively. It is evidently that the presence of PTB will promote the easier running of the interaction with HMTA. The isolated by the water yellow colored powder products also show the calculated from DSC measurements energy of activation 179 kJ/mole and 154 kJ/mole, respectively, for the product from ethanol reaction medium and from the mixture ethanol/2-ethoxyethanol (3:1 in mass parts) as a reaction media as well. Meanwhile the temperature of the exothermic peak became lower (147,41°C and 150,27°C, accordingly). All these facts show that the reaction product obtained approaches easier to the cross-linked state than the physical mixture due to the already commenced cross-linking. The values of molecular masses and the dispersity of the different products obtained by GPC analyses (Table1) confirm this presumption.

The similar consideration is possible for the melting temperature intervals of the original PFNR and the reaction products with HMTA (Table 2).

The extents of cure at 140°C for 1h determined from the gel fractions by Soxhlet extraction (Table 2) also show the increased ability to cross-linking of the isolated from water reaction product. The original PFNR was cured for the uniformity also with the quantity of 7 mass % of HMTA. The big differences in the values of the extents of cure suggest that the cross-linking is propagated upon a different mechanism than already proposed for the interaction of PFNR and HMTA at the temperatures higher than 140-150°C.

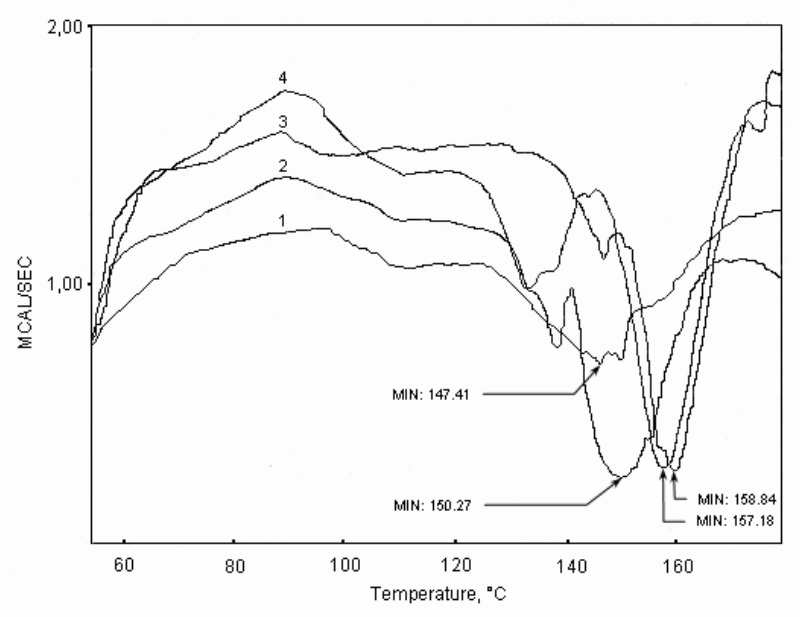


Fig. 3. DSC analysis: 1– Physical mixture of PFNR and HMTA; 2- Physical mixture of PFNR, HMTA and PTB; 3– Reaction powder product from ethanol; 4 – Reaction powder product from mixtures ethanol: 2-ethoxyethanol 4:1 in mass parts.

It is difficult to outline the most probable transient intermediates of the proceeded interaction in liquid media at 80°C (instead in a solid state) of PFNR, HMTA and PTB but the obtained IR and ^{1}H NMR spectra suggest some possibilities. The presence of traces of water in the intentionally not absolutely dried reaction components and the strong amine odour of the propagating reaction together with already mentioned pH value increase to 10,5 as well shows the probable appearance of the amino alcohols as $NH(CH_2OH)_2$ and $N(CH_2OH)_3$ coming from the HMTA hydrolysis. It is logical to presume that one part of them participates in the cross-linking process and retains linked to the isolated products as well providing them with mentioned strong amine odour. Following this presumption they could also promote and participate as well in the limited cross-linking and formation of end situated methylol groups as it is at the alkaline catalyst cross-linking of resol phenol formaldehyde resins with triethanolamine [3]. The above considers the increased reactivity of aryl ring by the presence of free PTB.

Table 2. Melting temperature intervals and extents of cure.

№	Product	MTI [a] (°C)	EC [b] (%)
1.	PFNR of origin	83 - 85	64
2.	Reaction product from ethanol	97 – 100	80
3.	Reaction product from mixture ethanol: 2-ethoxyethanol 4:1mass parts	102 – 104	85
4.	Reaction product from mixture ethanol: 2-ethoxyethanol 3:1mass parts	104 - 106	87

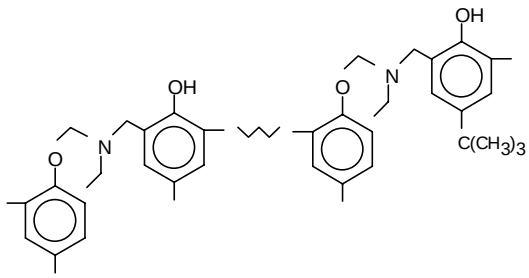
[a] *Melting temperature intervals*

[b] *Extent of cure*

The appearance of chemical shifts at 1,16 ppm (a) in ^{1}H NMR (Fig. 4) spectrum of powder product of reaction medium ethanol precipitated from water suggests the presence of PTB in the ends of olygomer chains sometimes may be inside the chains as well.

An additional confirmation of this suggestion is the fact that the mentioned ^{1}H NMR is missing the shift at 1,3 ppm (b) as a sign for free PTB. The shifts at 3,45 – 3,86 ppm (c) for the same product, valid for the CH_2 – bridges, do not confirm clear the type of linkage (o-o or o-p) but the both types could exist simultaneously. The characteristic shift at 4,5 ppm (d) for the benzoxazine rings is surprising. An additional prove for the existence of some structure in precipitated product was the content of bound N in quantity of 1,7 - 1,8 mass % corresponding to the quantity of N - atoms in the reaction mixture of origin.

Following this consideration on the benzoxazine rings one suggestion of linkage in the structure of the discussed product could be made:



The IR spectra of the product confirm the presence of - N-CH_2- units from bound HMTA by the band at 1030 cm^{-1} (A). The splitting of the bands at 1375 cm^{-1} (B) shows the presence of bound PTB. The peak at 1250 cm^{-1} (C) in the IR–spectrum (Fig. 5) of the final reaction solution shows the existence of units C-N coming from the presence of unreacted HMTA, but in the IR – spectrum of precipitated from water powder product the characteristic peak for HMTA at 1000 cm^{-1} does not exist. An additional information was obtained by the ^{1}H NMR spectra. They show except the already mentioned chemical shifts for the presence of H atoms from -$C(CH_3)_3$ groups of PTB units, also very clear shift at 4,5 ppm (d). It is responsible for -CH_2 bridges from benzoxazine ring reported on [1] because the free HMTA had to be removed during the washing process by the water. The shift at 5,7 ppm (e) could show the probable appearance of CH_2-OH groups.

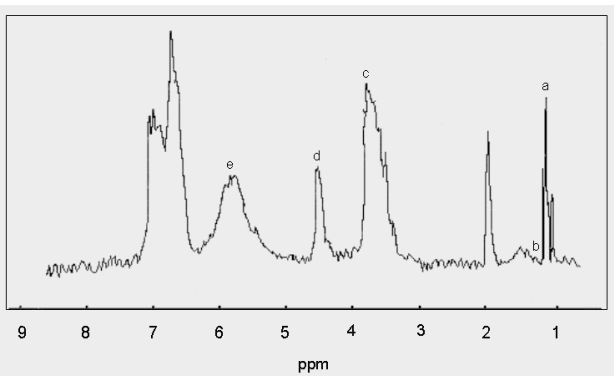


Fig. 4. H NMR spectra of reaction powder product from mixtures ethanol: 2-ethoxyethanol 4:1 in mass parts.

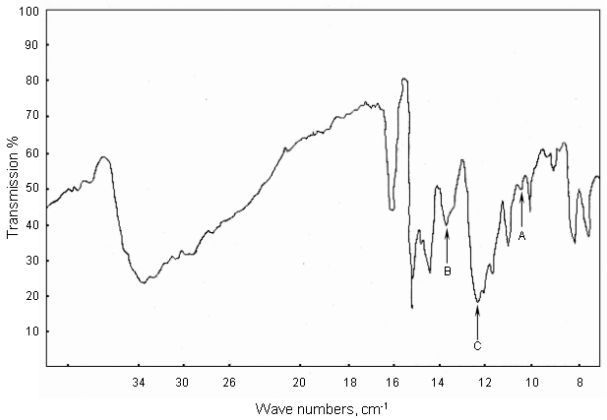


Fig. 5. IR spectra of the final reaction solution of the product of PFNR, HMTA and PTB in solvent mixture ethanol/2-ethoxyethanol 4:1 in mass parts.

CONCLUSIONS

The proposed structure of the new obtained product of the reaction between PFNR and HMTA in solution is realized at temperature of 80°C, which is much lower than the known one for the same reaction in solid state following the decomposition of HMTA. The linkage of the olygomer molecules by the benzoxazine structures leads to the product with tertiary N-atoms which could be used for the subsequent cross-linking of that product if used in the electronic production without the release of gaseous products. The presence of tertiary N–atoms could tend also to the use of this product as a hardener at low temperature of epoxy resins used in the electronics.

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