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PREPARATION, CHARACTERIZATION AND APPLICATION OF ALIPHATIC POLYAMINES

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ABSTRACT

Aliphatic polyamines (APA) were obtained by heating diethylenetriamine (DETA) with different amounts of water. The characteristics APA refraction index and amine number were evaluated by standard methods. From thermogravimetric analyses the activation energy ($E_{act.}$) and order (n) of the thermal decomposition reaction and thermal index of APA were calculated and then compared with the same data for DETA and triethylenetetramine. The IR spectra of the resulting APA and the most suitable absorbances for quantitative IR analyses were determined. The optimal quantities of the resulting APA for crosslinking of a Bisphenol A based epoxy resin were determined.

Keywords: aliphatic polyamines, hardeners of epoxy resins.

INTRODUCTION

The aliphatic polyamines are excellent hardeners of epoxy resins, but their toxicity is the reason for many investigations.

The decreasing of the toxicity of APA was done by different methods. For example, by modification of APA with phenol and formaldehyde, non toxic absorbents of carbon oxide were obtained [1]. By mixing of primary or secondary amines with inorganic carriers: silica, clay, talc, mica, kaoline, $CaCO_3$ and aluminas, hardeners for epoxy resins were obtained [2]. A metal amine solution was prepared from a metal compound, ethanolamine, polyethylenimine, ammonia and vinyl based polymers: poly(vinyl alcohol), poly(acryl amide), poly(N-vinyl pyrrolidone), poly(N-isopropyl acryl amide)[3]. From dithiasols and amines and their compounds with dimerised or trimerised fatty acids hardeners were obtained [4].

The reaction between compounds with cyclic carbonate functional groups and amine groups is described in [5]. Hardeners for epoxy resins, obtained by an interaction of amines with different compounds were described in [6].

It is well known that the toxicity of amines is connected with their low boiling temperatures. The increasing of the molecular mass APA is another way to increase their boiling temperatures. One technology to obtain APA is the reaction of ethylene oxide with ammonia. The aim of this study is to prepare APA by heating of DETA with water and the characterization of the resulting compounds as well.

EXPERIMENTAL

The triethylenetetramine(TETA) used for syntheses is a product of Merck (BRD). DETA is technical grade, produced by The Dow Chemical Company, (US).

The samples of DETA and amounts of 10, 15, 20 and 25 % distilled water were placed in a reactor, supplied with a condenser, a stirrer and a thermometer. The mixtures were heated at 100°C for 16 h. During this time samples were taken and their amine numbers were determined with standard methods [7]. The values of the refractive index of APA were obtained with an Abbe refractometer at 20°C. Thermogravimetric (TG) and differential thermal analyses (DTA), with rate of heating 5°C per min were made on an OD 102 MOM, Hungary derivatograph. The IR spectra were obtained with Specord 71 IR, Karl Zeiss, (BRD) in thin layer between KBr plates and also with Spectrum GX FT-IR, Perkin Elmer (USA) in thin layer on the KBr monocrystal surface. From the amine number of the resulting APA the quantity of every APA for crosslinking of Bisphenol A based epoxy resin Epoxa AP 1, product of Lackprom, Bulgaria was calculated. After variation around of the calculated values the optimal quantity of the hardeners was determined.

RESULTS AND DISCUSSION

Usually technical grade polyamines contain some amount of water because of their hydrophilicity. This is the reason for the sometimes milky color of their mixtures with epoxy resins. The water content of APA changes their characteristics in the crosslinking of epoxy resins. A condensation is possible in the heating of mixtures of amine and water. During our condensation the molecular mass of APA increased and their amine number decreased. The row material for the investigation was DETA with viscosity, determined with a BZ-4 device - 24s, non-volatile component - 36.6 %, the density- 0.93 kg m^{-3}. The density of the DETA for synthesis of Merck at 20°C, assay > 98 % and water < 0.5 % is 0.949 – 0.952 kg m^{-3}. The density of ethylenediamine for synthesis of Merck at 20°C, assay > 98 % and water < 1 % is 0.896 – 0.898 kg m^{-3}. In this way the sample of DETA, applied in this investigation contains not only water, but also another impurities. The amine number, determined by the method, described in [7] was made on two samples and the average value was calculated. For the samples of DETA were obtained equal values of 24.27 – difference 0 %. During the heating of the mixtures of DETA with 10 % water were registered significant differences: 15 % for the sample heated for 6 h, 8.2 % - 13 h and again 0 % - for a 16 h heating. The differences in the values of the amine numbers were result of non-homogenity of some samples of the mixtures DETA-water, heated less than 16 h. This is the reason to determine this time of heating as optimal one. The same results were obtained with other mixtures DETA – water and in this way four amines: APA 10, APA 15, APA 20 and APA 25 were prepared. The values of amine numbers and the refractive index (n_d^{20}) are presented in Table 1.

Table 1. Values of the refractive index and amine numbers of the resulting APA.

APA	n_d^{20}*	$n_d^{20}{}_{teor.}$	Amine number
APA 10	1.4742	1.4704	21.5
APA 15	1.4810	1.4631	14.74
APA 20	1.4800	1.4554	36.80
APA 25	1.4770	1.4478	25.54
DETA	1.4860	1.4826-1.4846	24.07

The value of n_d^{20} of water is 1.33299 [8]. From the content of the mixtures DETA and water the values of $n_d^{20}{}_{teor.}$ were calculated. The differences obtained between the measured values and $n_d^{20}{}_{teor}$ are because a condensation reaction takes place. The amine number decreased with increasing the amount of water.

The results from thermal analyses are given in Table 2. It is evident that there are differences in the values. With increasing of the quantity of water in the initial mixtures the $E_{act.}$ decreased maybe due to the presence of volatile components in these samples, which was evident from the values of the thermal index at low temperatures. On the other hand the thermal stability at high temperatures increased because of the formation of oligomers. The same results for thermal stability were obtained from industrial samples of DETA and TETA. These results and the data for the maximal rate of loss of mass (distillation) and the end temperatures of this process confirm the oligomerization of DETA during the heating with water.

Table 2. Thermal characteristics of APA.

APA	$E_{act.}$, [Kcal/mol]	n	100	150	200	250	300	350	400	450	500
APA10	2.636	0.28	7.79	36.06	74.59	80.73	82.78	86.06	89.34	91.8	99.99
APA15	1.741	0.06	8.89	32.71	69.66	83.92	85.34	88.18	90.32	93.30	98.85
APA20	0.58	~ 0	9.75	38.99	79.59	86.33	88.92	90.95	93.39	97.45	98.89
APA25	0.477	0.22	14.35	44.24	83.82	86.93	91.58	91.97	95.08	97.02	98.6
DETA	7.559	0.57	5.64	27.5	62.67	86.48	87.73	90.86	94.5	96.5	100
TETA	13.8	0.88	2.18	4.4	14.74	41.48	85.69	88.97	90.6	92.24	94.00

Two different techniques were applied for obtaining of IR spectra and determining the possibility of an interaction of APA with moisture in the air. When the samples are between KBr plates the possibility of this interaction is minimal in comparison with the second technique.

In order to evaluate the changes in the samples spectra were prepared using different periods of time for exposition of the thin films in open air and moisture of 75 %: 1, 5 and 10 min. In this way the hydrophilic APA absorbed the moisture. On the other hand we have a possibility for distillation of the low volatile compounds. From the IR spectra of the resulting APA obtained by Specord 71 IR, Karl Zeiss the values of the absorbances A for $-NH_2$ and –NH- groups and for absorbances for $-CH_2-$ group $A_{int.st.}$(internal standard) were calculated. The values of A' were obtained by the equation $A' = A/A_{int.st}$. The relationships between A' and the amine numbers (AN) of APA and DETA were made for every absorbances and the equation A'= a.AN + b, where a and b are coefficients. The values of a and b are given in Table 3. The most available absorbance for quantitative IR analyses of APA was with the minimal values of coefficients R and b and it is the absorbance for –NH- group at 3300 cm^{-1} and internal standard at 2916 cm^{-1}.

Table 3. Results for equation A'= a.AN + b.

№	-NH-, cm^{-1}	Internal Standard, cm^{-1}	a	b	R
1.	3330	2916	0.03	0.07	0.95
2.		1487	0.32	0.21	0.87
3.		814	0.48	0.4	0.74
4.	1600	2916	0.04	0.019	0.82
5.		1487	0.13	0.05	0.81
6.		814	0.19	0.12	0.65
7.	1200	2916	-0.003	0.01	0.99
8.		1487	0.01	0.05	0.92
9.		814	0.05	0.07	0.87

R - correlation coefficient; a - intercept value; b - slope value.

The values of the shift of the peaks in the obtained spectra determined from theoretical absorbancies are given in Table 4.

It is well known, that the values of shifts are connected with impurities and with hydrogen bonds formation. The biggest values of the shifts were registered in the spectrum of DETA. This result confirms the data for the difference between the experimental n_d^{20} and the value, given in the literature (Table 1). It is interesting, that the values of the shifts for most of the APA sample's absorbances are smaller in the spectra, made with Spectrum GX FT-IR than those made with Specord 71. Probably it is because of the distinction in the accuracy for these two apparatuses. The values of the shift, calculated from the spectra, made with Spectrum GX FT-IR increase with the time of exposition of the samples. The change of the values of the shift during the time of exposition confirms the idea for materials exchange between air and

Table 4. Values of the shifts, cm^{-1}.

№	A, cm^{-1}	DETA	APA_{10}	APA_{15}	APA_{20}	APA_{25}
1	3366	-56	-13.7	-15	-50	-16
2	3279	+7	+0.3	+41	+1	+15
3	2929	+49	+11	+29	-	+1
4	1698	-18	-42.5	-28	-40	-103
5	1456	+7	+10.2	+24	+30	+22
6	1385	+24	-10	-	+5	-
7	1364	+6	-	-	-	-
8	1303	+33	+14	+25	+17	+2
9	1130	+15	-12.5	-2	-5	-20

Table 5. Dependence of the degree of crosslinking of the epoxy compositions from the hardener quantity.

№	APA	Quantity hardener [%]	Degree of crosslinking [%]
1	APA10	9.5	97.62
2	APA10	10.0	97.02
3	APA10	10.5	97.12
4	APA15	11.0	96.26
5	APA15	11.5	94.55
6	APA15	12.0	95.22
7	APA20	12.5	95.18
8	APA20	13.0	96.86
9	APA20	13.5	95.86
10	APA25	14.0	97.97
11	APA25	14.5	96.90
12	APA25	15.0	96.49

thin layers of APA. It is necessary to decrease this possibility by changing the technique for sample preparation.

The data for application of resulting APA for hardening of epoxy resins are presented in Table 5.

It is evident, that all APA are excellent hardeners for Bisphenol A based epoxy resin because the degree of crosslinking is higher than 95 %. The influence of the hardener quantity is no so significant. This fact gives a possibility for dosage of the components with an accuracy of 1%.

CONCLUSIONS

By heating of mixtures DETA – water APA were obtained. After their characterization with thermal and IR analyses the condensation of DETA was confirmed. The most convenient absorbances for quantitative IR spectroscopy were determined. The resulting APA are excellent hardeners for Bisphenol A based epoxy resins.

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