A qualitative and quantitative analysis of tertiary amines in restorative resins

ERIK ASMUSSEN

The Royal Dental College, Copenhagen, Denmark

Asmussen, E. A qualitative and quantitative analysis of tertiary amines in restorative resins. *Acta Odontol. Scand.* 1980, 38, 95 - 99

Previous investigations have shown that the type and the quantity of tertiary amine influence the properties of restorative resins. It was the purpose of the present work to analyze qualitatively and quantitatively the amines in commercial restorative resins. The amines were extracted with hydrochloric acid from chloroform solutions of the monomers. For the qualitative analysis the acid amine solution was made alkaline, the amine extracted with methylenechloride and isolated. The method of analysis was NMR-spectroscopy. The quantitative determination was performed by means of UV-spectra of the acid amine solutions. Sixteen brands were investigated, and three species of amine were identified. The amount of amine varied between 0.3% and 4% by weight of the monomer. It is probable that the information obtained will lead to a better understanding of the nature of restorative resins.

Key-words: Dental materials; composition of restorative resins

Erik Asmussen, Department of Technology, Royal Dental College, Jagtvej 160, DK-2100 Copenhagen Ø, Denmark

Chemically activated restorative resins contain tertiary amines as part of the catalyst system. Previous investigations have shown that the type and the quantity of amine influence a number of properties of restorative resins (3, 4, 5, 6). Among these properties are setting time, compressive and tensile strength, and color stability. In order to obtain a better understanding of the role of the amine in proprietary restorative resins, the type and the quantity of amine have to be known. It was the purpose of the present work to analyze qualitatively and quantitatively the amines in commercial restorative resins.

MATERIALS AND METHODS

The amine-containing part of the brands listed in Table 1 was investigated. The methods of analysis were based on the alkaline nature of tertiary amines. By reaction with acid water, soluble ammoniumsalts are formed. As a consequence tertiary amines dissolved in chloroform can be extracted by shaking with hydrochloric acid. On the other hand, the dimethacrylate monomers of restorative resins are quite hydrophobic and can, therefore, be removed from aqueous solutions by shaking with chloroform.

Received for publication, November 12, 1979

Qualitative analysis.

10–15 g of paste were suspended/dissolved in 50 ml of chloroform. In cases involving the use of non-composite materials (brands B, C, F, H) or the capsulated products (brands E, O) 2–3 g of "monomer" were used. After sedimentation of any filler particles, 25 ml of the supernatant liquid was transferred to a 100 ml separating funnel and shaken with 25 ml 0.1 N hydrochloric acid. The chloroform phase was discarded, and the dissolved monomer was removed from the aqueous phase by two extractions with 25 ml chloroform. In the case of brand N and O only one extraction with chloroform was carried out, since the amine of these brands was unfavourably distributed between the chloroform and the aqueous phase. The solution of amine in hydrochloric acid was then made alkaline with 1 N aqueous solution of NaOH. The amine was thereby transformed to its non-ionized, less water soluble form. The amine was extracted with 25 ml methylenechloride and isolated after evaporation of the methylenechloride. NMR-spectra were obtained of the amines dissolved in deuterated chloroform. The apparatus used was a Bruker Spektrospin operating at 90 MHz. (The spectrometer was made available by the Danish Natural Science Research Council and Chemical Laboratory II, University of Copenhagen). The amines were identified by comparison with a number of spectra of available pure amines and with catalogued NMR-spectra. NMR-spectra of monomers in restorative resins have earlier been obtained (1). Hence it could be confirmed that the above mentioned two extractions reduced the content of monomer (as well as other possible compounds) to a level below detection. The monomer of brands N and O (BISPMA) (Bisphenole-A-di-propane-methacrylate) has extremely low affinity to water (Asmussen, unpublished results). It was found that this monomer was completely removed from the hydrochloric acid by only one extraction with chloroform.

Quantitative analysis

3 g of the composite pastes were accurately weighed and suspended/dissolved in 25.0 ml chloroform. With brands B, C, E, F, and H 300–600 mg, and with brand O 2 g of "monomer" accurately weighed were used. After sedimentation of any filler particles 15.0 ml of the supernatant liquid was transferred to a 100 ml separating funnel and shaken with 25.0 ml 0.1 N hydrochloric acid. The chloroform phase was discarded, and the aqueous phase was shaken twice (brands N and O only once) with 25.0 ml chloroform. UV-spectra of the dissolved tertiary ammonium-ions were obtained, and the absorption maximum near 260 nm was recorded. The apparatus used was a Beckman Spectrophotometer, model D.B. (The spectrometer was made available by kind permission of the Biochemical Department, Royal Dental College, Copenhagen).

In the qualitative analysis three types of amines were identified. DEPT and DEBA, but not DE34MA (Table 2) could be obtained from manufacturers of restorative resins. Calibration curves of the amines in 0.1 N hydrochloric acid were produced for DEPT and DEBA. The maximum absorption was plotted against amine content in mg per 25 ml 0.1 N HCl. A straight line through the origin was fitted to the points by means of the mean value of the absorbances per mg amine.

The distribution of DEPT and DEBA between chloroform and 0.1 N hydrochloric acid was determined by dissolving accurately weighed amounts of amine in 25.0 ml chloroform and shaking with 25.0 ml of the acid. The amine content of the acid was then obtained from the UV-spectrum by means of the above mentioned calibration curves. It was

Table 1. *List of brands used in the investigation*

Code	Name	Batch No.	Manufacturer
A	Adaptic	9A003	Johnson & Johnson New Jersey, USA
B	Adaptic Bonding Agent	6016 2755 FA	Johnson & Johnson New Jersey, USA
C	Adaptic Glaze	6009 2752 GB	Johnson & Johnson New Jersey, USA
D	Concise	8 C 3	3M Company Minnesota, USA
E	Concise Cap-C-Rynge	82891	3M Company Minnesota, USA
F	Concise Enamel Bond	7311 E1	3M Company Minnesota, USA
G	Cosmic	WL8 YA	Amalgamated Dental London, England
H	Delton	5001 2792 EA	Johnson & Johnson New Jersey, USA
I	Estic	41015	Kulzer & Co. Bad Homburg, W. Germany
K	Estic Microfill	AUG 79/28	Kulzer & Co. Bad Homburg, W. Germany
L	Isopast	140/377	Vivadent Schaan, Liechtenstein
M	Isopast Variant	121/078	Vivadent Schaan, Liechtenstein
N	Nimetic	E 311	Espe Seefeld, W. Germany
O	Nimeticap	C 300 N/1C	Espe Seefeld, W. Germany
P	Prestige	HPR 0123	Lee Pharmaceuticals California, USA
Q	Silar	9 A 2	3M Company Minnesota, USA

found that 97.3% of the DEPT and 33.7% of the DEBA present in the chloroform were transferred to the hydrochloric acid.

The filler content of the conventional composites was determined by weighing the pastes before and after burn-out at 600°C. The microfilled products contain prepolymerized, filled particles in a filled monomer. With these materials the filler content was determined as follows: 1 g of paste, accurately weighed, was suspended/dissolved in 25 ml chloroform. The mixture was filtrated through filter-paper, which retained the prepolymerized particles from the filtrate. The filter and its contents were washed twice with 10 ml chloroform, and allowed to dry. The contents of the filter were determined by weighing. The filtrate and the two washings were collected in a porcelain crucible; its content of microparticles was determined by weighing before and after burn-out at 600°C. The total content of filler particles in the paste was then found by addition. For each brand three determinations of the filler content were carried out. With the conventional composites the standard deviation of the determinations was 0.2 percent by weight; with the microfilled brands this figure was 10 times higher.

Based on the above measurements, the DEPT and the DEBA content in weight percent of the monomer was calculated. In the case of the composite materials the procedure was as follows: The monomer content of the 3 g of paste was first calculated. Assuming a monomer density of 1.11 g/cm^3 (2) the total volume of 25.0 ml $CHCl_3$ + dissolved monomer was estimated. From the UV-spectrum and by means of the calibration curves and the coefficients of distribution the amine content in 15.0 ml chloroform solution was determined. The total amine content in the 25.0 ml $CH\,Cl_3$ + monomer solution was then calculated. The amine content was expressed in percent by weight of the paste and of the monomer. Since DE34MA could not be obtained, the determination of this compound is only semi-quantitative. The following assumptions were made: 1) The amine is transferred 100% from the chloroform to the hydrochloric acid solution. From the structural formulae (Table 2) it is clear that this figure must be a little too high. 2) The molar extinction coefficient is the same as the one measured for DEPT. This coefficient was measured for a number of other available amines. It was found to deviate up to 30% from the mean value. Assumption 2) may thus be somewhat in error. For each brand two amine determinations were carried out. On the basis of the precision of the calibration and of the amine distribution between the chloroform and the hydrochloric acid, the calculated content of DEPT and DEBA was estimated to be accurate at the $P = 95\%$ level within ± 5% of the mean value of the two determinations. This estimation was verified from a number of amine determinations on BISGMA-TEDMA mixtures to which known amounts of amine were added. As explained above, the quantitative analysis of DE 34 MA is encumbered with a larger, unknown inaccuracy.

RESULTS

The results are presented in Table 2. It appears that three species of tertiary amine were identified. DEPT and DEBA were identified by a comparison with the NMR-spectra of the pure compounds. As mentioned above DE34MA could not be obtained in pure condition; the quantitative analysis of this amine was based on a comparison with spectra of available tertiary amines, relative intensities, and catalogued NMR-data. The amine content given is the mean of the two determinations. In all cases the two determinations deviated less than 3% of the mean value from each other.

DISCUSSION

The present study has shown that restorative resins differ as regards type and quantity of tertiary amine. It is probable that the information obtained from the above analyses will lead to a better understanding of the properties of the restorative materials.

Table 2. *Type and quantity of tertiary amine contained in restorative resins*

Code	Type of amine*	Quantity of amine	
		% w/w of paste	% w/w of monomer
A	DEPT	0.41	1.8
B	DEPT	–	3.2
C	DE34MA	–	2.6
D	DEPT	0.55	2.4
E	DEPT	–	0.56
F	DEPT	–	2.7
G	DEPT	0.34	1.6
H	DE34MA	–	2.9
I	DEPT	0.11	0.46
K	DEPT	0.49	1.6
L	DEPT	0.17	0.41
M	DEPT	0.57	1.8
N	DEBA	0.20	0.91
O	DEBA	–	0.30
P	DEPT	0.51	2.4
Q	DEPT	1.0	3.9

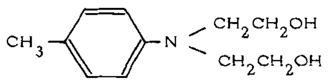
*) DEPT: N, N-diethanol-p-toluidine
DEBA: N, N-diethanol-3,5-di-tert-butyl-aniline
DE 34 MA: N, N-diethanol – 3,4-dimethyl-aniline

REFERENCES

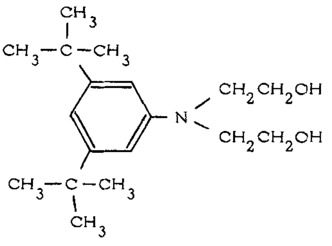
1. Asmussen E. NMR-analysis of monomers in restorative resins. Acta Odontol. Scand. 1975, 33, 129 – 134
2. Asmussen, E. Penetration of restorative resins into acid etched enamel. I. Acta Odontol. Scand. 1977, 35, 175 – 182
3. Bowen, R. L. & Argentar, H. Diminishing discoloration in methacrylate accelerator systems. J. Am. Dent. Assoc. 1967, 75, 918 – 923
4. Bowen, R. L. & Argentar, H. Amine accelerators for methacrylate resin systems. J. Dent. Res. 1971, 50, 923 – 928
5. Brauer, G. M., Davenport, R. M. & Hansen, W. C. Accelerating effect of amines on polymerization of methyl methacrylate. Modern Plastics 1956, 34, 153 – 168, 256
6. Dulik, Dianne M. Evaluation of commercial and newly-synthesized amine accelerators for dental composites. J. Dent. Res. 1979, 58, 1308 – 1316

Table 2 (cont.)

DEPT:



DEBA:



DE34MA: