NMR-analysis of monomers in restorative resins

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A study on the composition of the resin component of the several brands of composite resin has not been published so far. It was the purpose of the present work to fill out this gap in our knowledge of this important group of restorative materials by analyzing the monomers of the materials as delivered by the manufacturers. 24 brands of restorative resins were investigated by means of a Nuclear Magnetic Resonance spectrometer at 90 MHz. Spectra were taken of deuterated chloroform solutions of the organic part of the filling materials and compared with spectra of pure monomers that were conceivable constituents of the investigated brands. It was found that the BIS-GMA containing brands all contain at least one other monomer, most often TEDMA, in varying concentrations. The brands with MMA as main component in most cases also contain other monomers.

Key-words: Dental restoration; permanent; dental materials; resins; nuclear magnetic resonance-analysis

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It is well known that restorative resins have properties that depend on brand, i.e. composition. Acrylic resins for instance have lower compressive strength than materials on BIS-GMA basis (*Dennison & Craig*, 1972). Also within the group of materials based on BIS-GMA variations in properties have been demonstrated: *Dennison & Craig* (1972), and *Lee, Swartz & Smith* (1969) found statistically significant differences in mechanical and physical properties (e.g. compressive strength, and water absorption) between a number of investigated brands. *Asmussen & Jørgensen* (1972) showed that the width of gaps formed during polymerization between filling and cavity walls, and the time required for their closure by water absorption expansion, varied from brand to brand.

The properties of restorative resins depend upon a number of factors related to the organic phase and — in composite resins — to the inorganic phase and to the coupling between organic and inorganic phase. The amount by weight of inorganic phase of various composite brands has been determined by several investigators (*Dennison & Craig*, 1972; *Acharya & Greener*, 1972), but otherwise very little detailed information on the composition of resin filling materials can be found in the literature. The purpose of the present work was to analyse quantitatively the monomers in brands of restorative resins as delivered by the manufacturers. For the sake of completeness, two fissure sealants were included in the analysis.

MATERIALS AND METHODS

The brands listed in Table I were investigated. Proton magnetic resonance

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spectroscopy was chosen as analytical method. The apparatus used was a Bruker Spektrospin operating at 90 MHz. The spectrometer was made available by kind permission of Danish Natural Science Research Council and of Chemical Laboratory II, University of Copenhagen. The spectra were obtained with deuterated chloroform ($DC Cl_3$) as solvent and Tetra-Methyl-Silane as internal standard. A sample suitable for analysis of the monomers from the composite brands was obtained by dissolving the organic phase in $DC Cl_3$. After one day the filler particles had settled, and the resulting clear supernatant liquid was used in the spectrometer. The recorded spectra were integrated three times, and the relative intensities of the lines were obtained as the mean value of the integrations.

First a qualitative analysis was performed by comparing the spectra of the filling

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

Name	Batch No.	Manufacturer
Adaptic	3 C 010	Johnson & Johnson, New Jersey, USA
Addent 12	03 63 01 C	3M Company, Minnesota, USA
Addent XV	—	3M Company, Minnesota, USA
Blendant	catalyst: 230.77 universal: 32410483	Kerr Manufacturing Company, Michigan, USA
Compact	catalyst: 740121 universal: 740422	Svedia Dental Industri, Enköping, Sweden
Compocap	28 0374	Vivadent, Schaan, Liechtenstein
Compolite	catalyst: 72 1102 universal: 72 1116	William Getz Corporation, Illinois, USA
Concise	331317	3M Company, Minnesota, USA
Concise resin	32 361	3M Company, Minnesota, USA
Concise cap-c-rynge	31 76 1 G212	3M Company, Minnesota, USA
Cosmic	catalyst: PD 15 base: PD 12	Amalgamated Dental, London, England
DFR	581170	Surgident, Ltd., California, USA
Exact	47303	S. S. White, Pensylvania, USA
HL 72	HL 0034	Lee Pharmaceuticals, California, USA
Nuva Fil	73 102	L. D. Caulk Company, Toronto, Canada
Nuva Seal	72 157	L. D. Caulk Company, Toronto, Canada
Opotow	720420	Opotow Dental Mfg., New York, USA
Palakav	09	Kulzer & Co., Hamburg v.d.H., Germany
Palavit 55	1092	Kulzer & Co., Hamburg v.d.H., Germany
Polycap	21 07 72	Ivoclar, A.G., Schaan, Liechtenstein
Prestige	catalyst: HPR 0063 universal: HPR 0059	Lee Pharmaceuticals, California, USA
Sevriton Simplified	ML 1	De Trey Frères, S.A., Zurich, Switzerland
Smile	catalyst: 330.05 universal: 923125.73	Kerr Manufacturing Company, Michigan, USA
Swedon	105	Svedia Dental Industri, Enköping, Sweden
Texton	56 71 34	S.S. White Dental Mfg. Co. (G.B.) Ltd., Harrow, England
TD71	002 AD	Dental Fillings, Ltd., London, England

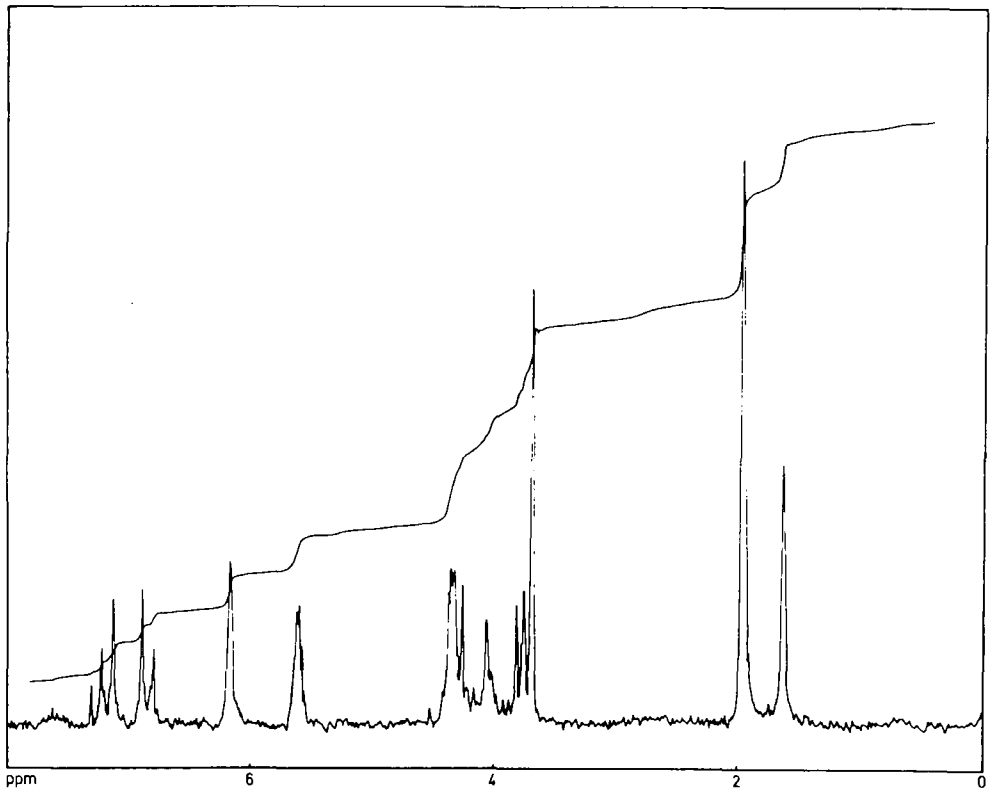


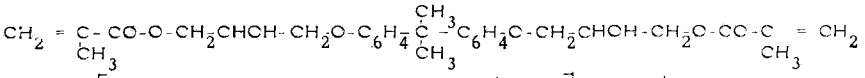
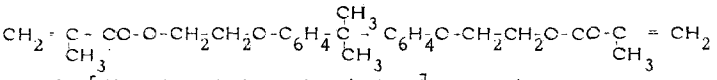
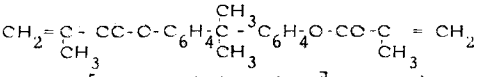
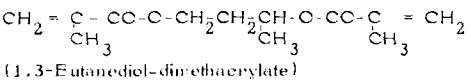
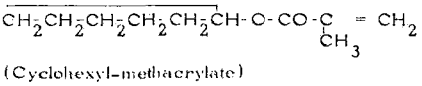
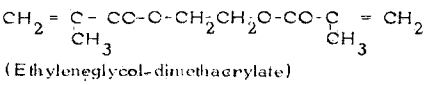
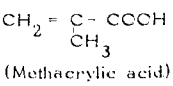
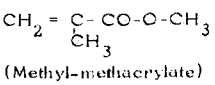
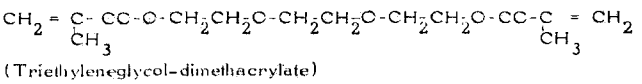
Fig. 1. NMR-spectrum of Prestige catalyst.

materials with those of a number of pure monomers that were conceivable constituents of the investigated brands.

Then, for each molecule identified as part of one or more of the brands the various protons were assigned to their respective lines by means of catalogued NMR-data, empirical rules, and relative intensities.

The contribution I_R of a given molecule R to the relative intensity of a given line is $I_R = k \cdot N_H^R \cdot N_R$ where k is a proportionality factor, N_H^R the number of protons per molecule R assigned to the line in question, and N_R is the number of molecules R per unit volume of sample. If several molecules contribute to the same line, the combined intensity is the sum of the individual intensities. For each spectrum of an investigated filling material in which every line could be assigned to protons in known monomers, a sufficient number of equations of the type above was set up to determine (apart from a constant factor) all the N_R values. The content of molecule R in the sample was then expressed in mole % by dividing $N_R \times 100$ by the total number of molecules per unit volume of sample. The analysis is estimated to give values that are correct within $\pm$ 3 mole %. As an example, consider the spectrum of Prestige Catalyst (Fig. 1) where all the lines could be assigned to either the BIS-GMA (B) or TEDMA (T) molecule (see Table 2). The lines at 1.63 ppm and 1.96 ppm were assigned to the bisphenolic methyl groups

Table II. *List of monomers identified in resin filling materials*

BIS-GMA:	 (2.2-Bis-[4(2-hydroxy-3-methacryloyloxy-propyloxy)-phenyl]-propane)
BIS-EMA:	 (2.2-Bis-[4(2-methacryloyloxy-ethoxy)-phenyl]-propane)
BIS-MA:	 (2.2-Bis-[4-methacryloyloxy-phenyl]-propane)
1.3 BUMA:	 (1.3-Butanediol-dimethacrylate)
CYHMA:	 (Cyclohexyl-methacrylate)
EDMA:	 (Ethyleneglycol-dimethacrylate)
MAA:	 (Methacrylic acid)
MMA:	 (Methyl-methacrylate)
TEDMA:	 (Triethyleneglycol-dimethacrylate)

($N_H^B = 6$) and to the acrylic methyl groups ($N_H^B = 6$, $N_H^T = 6$), respectively. The relative intensities of the two lines were measured by the average step height of the integration curves (only one is shown in Fig. 1) and found to be 2.3 mm and 5.8 mm, respectively. The above-mentioned equations then become $I_B = 2.3 = k \cdot 6 \cdot N_B$ and $I_B + I_T = 5.8 = k(6 \cdot N_B + 6 \cdot N_T)$, respectively. By solving $N_B = \frac{1}{k} \cdot 0.383$ and $N_T = \frac{1}{k} \cdot 0.583$, from which the B and T content can be calculated as 40 and 60 mole %, respectively. In the few cases where some of the observed lines could not be assigned to protons in known molecules only an incomplete qualitative analysis could be performed. The presence of an identified monomer will be indicated by a +.

Table III. *Results of analysis of monomers (mole %) in resin filling materials*

	BIS-GMA	BIS-EMA	BIS-MA	BUMA	CYHMA	EDMA	MAA	MMA	TEDMA
Adaptic cat	62		13						25
Adaptic uni	67		11						22
Addent 12 cat							82	18	
Addent 12 uni	74							26	
Addent XV		100							
Blendànt cat				41	59				
Blendànt uni	83			17					
Compact cat	81								19
Compact uni	86								14
Compocap		+							+
Compolite cat	82								18
Compolite uni	82								18
Concise cat	65								35
Concise uni	63								37
Concise resin cat	39								61
Concise resin uni	34								66
Concise cap-c-rynge	53								47
Cosmic cat	49								51
Cosmic base									+
DFR cat								100	
DFR liquid	34							66	
Exact cat	50					50			
Exact base	50					50			
HL 72	47								53
Nuva Fil									+
Nuva Seal	41							59	
Opotow	79								21
Palakav								79	21
Palavit 55								100	
Polycap								91	9
Prestige cat	40								60
Prestige uni	45								55
Sevriton Simplified						4	15	81	
Smile cat				36	64				
Smile uni	77			23					
Swedon						10		90	
Texton								100	
TD 71							28	72	

RESULTS

The results of the analyses are presented in Table II and Table III. In Table II are shown the monomers that were identified in the investigated filling materials. In Table III are shown the composiions of the investigated brands.

It appears that a majority of restorative resins belong to one of two groups, one group having BIS-GMA, the other group MMA as the principal constituent. Further, that the BIS-GMA containing brands in all cases contain at least one more monomer, most often TEDMA, and

that the »MMA-brands» in most cases also contain several monomers.

DISCUSSION

It has been shown that most of the different brands of restorative resins contain at least two monomers. In the BIS-GMA-containing brands a second monomer is necessary because BIS-GMA is too viscous to be used pure in a composite filling material (*Bowen et al.*, 1972). The additional monomers have a rather low viscosity and act as diluents, providing the organic phase with a suitable viscosity. In the two investigated fissure sealants the high content of diluting monomer results in the desired low viscosity of these materials. In the brands where MMA is the main constituent, additional monomers may serve as cross-linkers (EDMA, TEDMA). In the case of Sevriton and TD 71 the added MAA plays an essential role in the polymerization process. The catalysts, p-toluene sulfinic acid and an aliphatic mercaptan, respectively (*Morrant*, 1953; *McLean & Short*, 1969). are present as inactive salts and are converted by the MAA into the active acid forms.

To summarize, it has been demonstrated that the composition of the organic phase of the investigated restorative resins vary from brand to brand. It is probable that the information obtained from the above analyses will lead to a better understanding of the properties of the restorative materials.

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