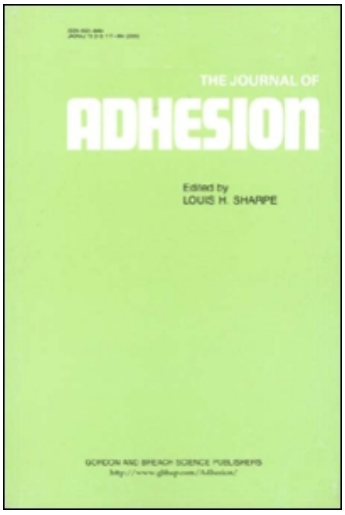

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The aim of this work was to characterize quantitatively the contribution of different failure modes during shear bond strength (SBS) measurements and to correlate both those sets of results. Four experimental dental adhesive systems were used to join dental composite with cobalt–based alloy plate. The samples were subjected to SBS measurements according to International Organization for Standardization (ISO) procedure and resulting fractures were examined by optical microscopy, including computer-aided processing of the images, to yield quantitative contributions of adhesive and cohesive failures. Identification of particular failure modes as well as quantitative determination of respective contributions appeared to be possible. The data were processed by statistical methods including Shapiro-Wilk and Mann-Whitney U tests. The results of fractographic analysis were found to correlate with SBS values. Contribution of adhesive failures appeared to determine the strength of adhesive bonds. A new dental adhesive system based on PM2EDM monomer exhibited a very good performance in respect to the metal alloy.

Keywords: Dental adhesive; Fracture surface; Optical microscopy; Restorative dentistry; SBS

1. INTRODUCTION

Modern adhesive dentistry employs a variety of defined chemical compounds featured both by their ability to be polymerized by use of

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visible light and/or redox initiating system as well as by some affinity to hard tooth tissue and/or metal surface [1,2]. The former requires a presence of a carbon-carbon double bond in a molecule, usually in a form of methacrylate group, whereas the latter is provided by various hydrophilic functional groups, like carboxylic, phosphate, hydroxyl, anhydride, amine, and others [1,3]. Compounds having properties as above were termed initially as surface active comonomers [4], coupling agents [5], and finally as adhesive monomers [1,3]. Structures of some of well-known compounds of that type are given in Fig. 1.

The dental adhesive systems comprise adhesive monomers in various formulations which historically yielded a series of generations in adhesive dentistry [1]. The most typical ones involve either a solution of an adhesive monomer in a volatile solvent (a primer—applied to a tooth surface prior to a bonding resin) or a bonding resin with an adhesive monomer dissolved therein [3]. The performance of adhesive systems is evaluated mainly in clinical trials [6] though some standardized procedures are employed as well, especially for commercial materials. Those comprise evaluation of selected physicochemical properties [7] and mechanical strength of an adhesive joint in respect to dentin [8] and a metal substrate [9]. So far, the influence of chemical structure of an adhesive monomer on performance of a dental adhesive formulation has not been widely discussed.

Previously we have reported the synthesis of isomeric bis(methacryloyloxyoligoethylenoxy) esters of 1,2,4,5-benzenetetracarboxylic acid

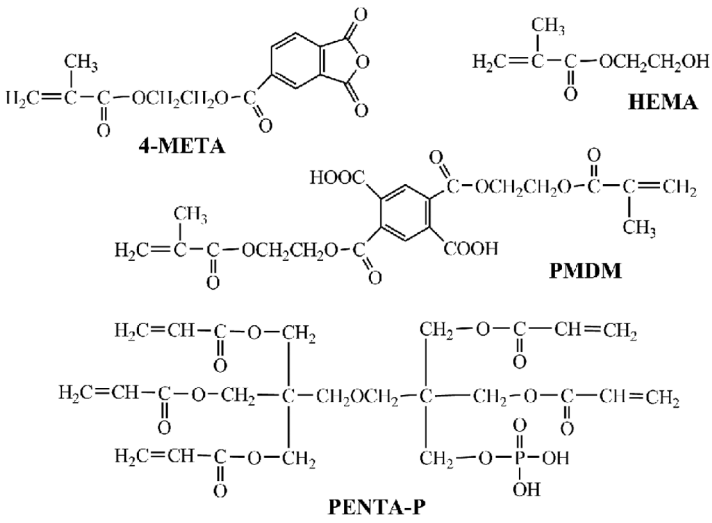

FIGURE 1 Chemical structures of some of the most well known dental adhesive monomers.

(PMnEDM) being homologs of the well-known PMDM monomer (structure of the latter is shown in Fig. 1) with increased distance between polymerizable methacrylate groups and hydrophilic carboxyl ones, the latter being responsible for adhesion to a tooth/metal substrate [10]. That was provided by use of monomethacrylates of di-, tri-, and tetraethylene glycols (oligoethylene glycol monomethacrylates, OEGMMA, n = 2, 3, and 4, respectively) instead of hydroxyethyl methacrylate (HEMA, n = 1) in the reaction with pyromellitic dianhydride (PMDA), as shown in Fig. 2. No data concerning the influence of a distance between the above functionalities on adhesive properties were reported so far. The new monomers resulting (PM2EDM, PM3EDM, and PM4EDM), as well as PMDM for comparison, were admixed with common dental monomers and other additives to yield four experimental light-cured adhesive resins. Those, when examined with respect to sensitivity to ambient light, curing time, depth of cure, and uncured film thickness, appeared to comply with ISO standardized requirements. Additionally, shear bond strength (SBS) of dental composite bonded to cobalt-based alloy substrate by use of the above adhesive resins was measured and the results appeared to be satisfactory except for the formulation containing PM4EDM.

The fracture surfaces resulting from SBS measurements were preliminarily examined by use of stereo-light microscopy (SLM) in

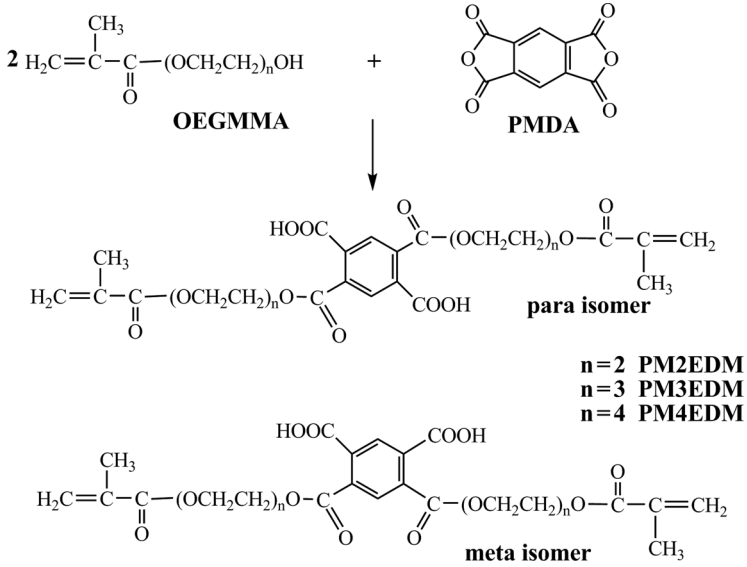

FIGURE 2 Reaction scheme for syntheses of PMnEDM monomers.

order to distinguish failure modes and to categorize them as adhesive, cohesive, and/or mixed. The aim of the present work was to determine quantitatively the contribution of particular failure modes based on SLM images and to relate the results to individual SBS values, which would be helpful in better understanding the reasons for success and for failure in an application of dental adhesive material.

2. MATERIALS AND METHODS

The details of the syntheses of PMnEDM monomers and structural assignments performed by nuclear magnetic resonance spectroscopy (NMR) have been given in a previous paper [10]. The resulting monomers (PMDM, PM2EDM, PM3EDM, and PM4EDM) were admixed with common dental monomers, *i.e.*, 2,2-bis[(2-hydroxy-3-methacryloyloxypropoxy)phenyl} propane (bis-GMA), urethane dimethacrylate (UDMA), and triethylene glycol dimethacrylate (TEGDMA), in 1:3:3:3 weight ratio, and a camphorquinone/N,N-dimethylaminoethyl methacrylate (CQ/DMAEMA) photoinitiating system was introduced into the mixture which was finally homogenized with silanized amorphous silica in 10:1 weight ratio to yield four experimental light-cured adhesive resins, coded as A, B, C, and D, respectively.

The adhesive resins were used to fix cylindrically shaped specimens (5 mm diameter, 2.5 mm high) made of dental composite (WMK-5, an experimental quartz-based light-cured material of a semi-hybrid type elaborated at the Silesian University of Technology, Gliwice, Poland) onto metal plates (square-shaped, *ca.* 10×20 mm, 2 mm thick) made of an experimental cobalt-based alloy (Institute of Non-Ferrous Metals, Gliwice, Poland). The surfaces were polished with AQUA® P1000C abrasive paper (FAS UNION, Bielsko-Biała, Poland). Five specimens were prepared for each adhesive (total 20) and SBS was measured with the aid of an Instron® 4505 machine (Instron Limited, High Wycombe, UK) equipped with Series IX software at 1 ± 0.3 mm/min cross-head speed. The procedure applied complies with the ISO recommendation [9].

Following the SBS test, fracture surfaces were examined by use of an optical microscope (Olympus SZ6045TR, Olympus Optical Co. Ltd. Tokyo, Japan) equipped with digital camera at 25× magnification. The adhesive and cohesive failures were identified visually; the latter could be differentiated as those occurring within the layer of the adhesive resin and within the composite. The images were processed by AutoCad® 13 software (PROCAD SA, Katowice, Poland). Uniform measurement areas were selected in the form of 5-mm diameter circles at the metallic side of the specimen's images. Areas of particular failure modes were marked manually directly onto a computer screen by a

single investigator to minimize subjective errors. The surfaces of particular failure modes were digitized to obtain percentage contributions.

The individual SBS values and the corresponding contributions of particular failure modes for each adhesive resin (A, B, C, and D) were subjected to statistical analysis. Normality of the distributions of continuous data regarding the measured parameters for each material was evaluated using the Shapiro-Wilk test. Since some of the distributions did not exhibit normality, the statistical hypotheses were verified using a non-parametric test and the data were characterized using descriptive statistics such as median, minimal, and maximal values.

The relation between the type of material used and SBS values as well as the relations between material used and the contributions of particular residues on the metal plate (adhesive resin, composite material, and total, *i.e.*, the sum of both the adhesive resin and composite material) were statistically evaluated by comparing every pair of trials using the Mann-Whitney U test, whereas the differences between the adhesive and composite residues for each material were statistically evaluated using the Wilcoxon signed-rank test. The question of whether there is a relation between two parameters was answered by use of Spearman's rank correlation parameter (r_s) and with a statistical evaluation of significance [11].

All the tests were carried out at a significance level $\alpha = 0.05$ with use of Statistica 6.0 software (SUM, Katowice, Poland).

3. RESULTS AND DISCUSSION

Analysis of failure mode in dental adhesive systems plays a crucial role in the evaluation of performance of commercial materials and in improvement of the application procedure [12,13]. Surface treatment, depending on technique applied, usually enhances adhesion and, therefore, the most objective comparison of different materials can be obtained in a standardized way, such as according to ISO recommendations [9]. Following the latter, we have used uniformly polished metal plates to compare the performance of the four experimental adhesives mentioned above.

Microscopic examination of fracture surfaces resulting from SBS measurements, both at the metal alloy plate and the composite specimen, revealed the possibility of identification of particular failure modes. Thus, when a clear metallic surface of a plate was observed as well as a smooth area at the corresponding place on the composite side of a specimen, the failure could be categorized as an adhesive one. Residues of cured adhesive resin at a metal surface resulted from cohesive failures either within an adhesive layer or at the

adhesive/composite interface; we could not distinguish between these modes at this stage. Therefore, those were categorized as cohesive ones within the adhesive resin. Sometimes a cohesive failure within the composite took place which was distinctly visible on both sides of a fractured specimen. Exemplary images are given in Fig. 3.

Since particular failure modes could be distinguished visually in SLM images, we attempted to estimate them quantitatively by use of appropriate computer software. Exemplary computer-processed images are given in Fig. 4.

Statistical data on SBS values and corresponding percentage contributions of the adhesive resin and/or composite residues at metal surfaces for the four experimental adhesive formulations are collected in Tables 1 and 2. Total residue means a sum of adhesive resin and composite material residues on the metal plate.

The lowest average of SBS (median = 4.9) was observed for the D adhesive and the highest one (median = 10.6) for B; the difference between them appeared to be statistically significant ($p = 0.0090$). Comparatively high SBS for A (median = 10.1) did not differ statistically from B ($p = 0.9168$) and differed from D ($p = 0.0472$). The SBS value for C (median = 5.2) was an intermediate one and did not differ statistically in respect to other materials. After fracture, the highest residue of adhesive resin (median = 13.7%) was found for B and the lowest one (median = 0%) for C; the difference was statistically significant ($p = 0.0283$). It should be noted that, when using C, in 60% (3/5)

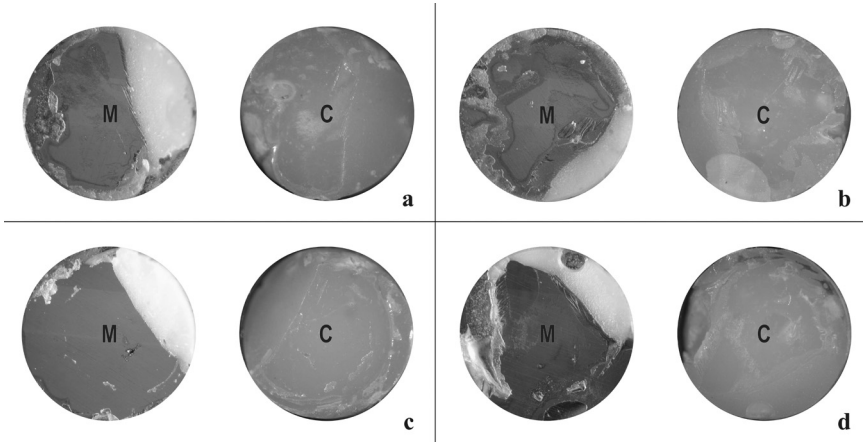

FIGURE 3 Exemplary SLM images of fractured surfaces after SBS measurement; metal side (M) and composite side (C) in a mirror arrangement; a, b, c, d—four representative specimens.

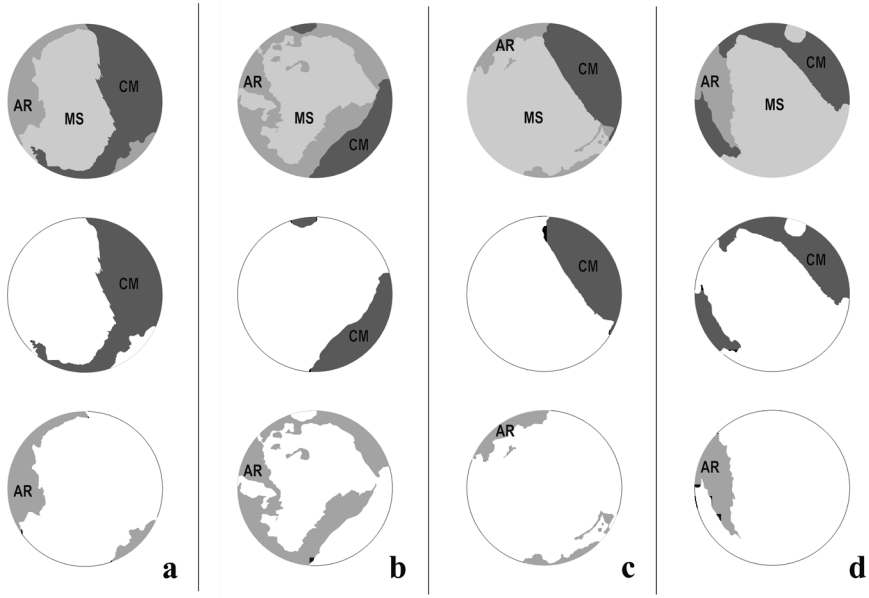

FIGURE 4 Computer-processed images corresponding to the specimens presented in Fig. 3; MS—metal surface, AR—adhesive resin, CM—composite material.

of the cases failure revealed no residue of adhesive resin. The amount of residue of composite material was similar for each of the tested materials and there were no statistically significant differences between them. In the evaluation of total residue (both adhesive resin and composite material) the highest median (34.3%) was found for B and this result was significantly different ($p = 0.0472$) in respect to

TABLE 1 Descriptive Statistics: Median [minimal value/maximal value] for SBS and Residue Contributions

	The material			
The parameter	A	B	C	D
SBS [MPa]	10.1 [4.6/19.1]	10.6 [8.7/12.9]	5.2 [3.1/11.5]	4.9 [1.5/7.8]
Adhesive resin residue [%]	1.3 [0/20.2]	13.7 [9.2/35.8]	0 [0/11.5]	10.7 [0/19.5]
Composite residue [%]	19.8 [0/36.6]	17.9 [15.8/34.9]	15.0 [0/26.4]	15.3 [0/24.6]
Total residue [%]	21.1 [0/53.4]	34.3 [28.0/52.3]	17.8 [0/36.3]	23.5 [15.3/36.5]

TABLE 2 Mann-Whitney U Test Probabilities (p) for Pairs of the Materials Compared

	Pair of the materials compared					
The parameter	A/B	A/C	A/D	B/C	B/D	C/D
SBS	0.9168	0.1745	0.0472	0.1172	0.0090	0.1745
Adhesive resin residue	0.2507	0.4647	0.7540	0.0283	0.3472	0.1437
Composite residue	0.9168	0.7540	0.7540	0.3472	0.2506	0.8345
Total residue	0.4647	0.7540	0.9168	0.0472	0.0472	0.4647

both for C (median = 17.8%) and D (median = 23.5%). Results for A are intermediate (median = 21.1%) but seem to be not very reliable because of high variability—values range between 0 and 53.4%. It might be noted also that B was characterized by the highest median results of SBS, adhesive resin residue, and total residue (both adhesive resin and composite material). The evaluation of the relation between SBS and amount of residue (regardless of the material, for all of the 20 results) have shown that there is a positive, statistically significant correlation ($r_s = 0.4473$, $p = 0.0480$) in the case of total residue and a correlation close to statistical significance ($r_s = 0.4181$, $p = 0.0666$) for composite material residue. The correlation between adhesive residue and composite material residue (regardless of the material) was also close to statistical significance ($r_s = 0.4272$, $p = 0.0603$). When taking into account the type of material, the only statistically significant correlations were a positive correlation between SBS and adhesive residue ($r_s = 0.8944$, $p = 0.0405$) for C and also a positive one between the adhesive resin residue and composite material residue ($r_s = 0.8947$, $p = 0.0403$) for A. The difference between contributions of adhesive resin residue and composite material residue was statistically significant for none of the materials (A: $p = 0.1088$; B: $p = 0.5002$; C: $p = 0.0679$; D: $p = 0.5002$), though for C the result was close to statistical significance.

From the statistical considerations above it is evident that performance of an adhesive resin depends mainly on the contribution of adhesive failures, *i.e.*, those at a substrate/resin interface, at least when bonding to a metal and/or metals alloy is concerned. Higher contribution of resin residues at the metal surface corresponds to higher shear bond strength. Since SBS values did not depend on the contribution of composite residues, mechanical strength of an adhesive joint is influenced mainly by the properties of the adhesive resin. Thus, in the series of formulations investigated, the chemical structure of the adhesive monomers from the PMnEDM series contained therein seems to be

essential. The best SBS results obtained for PM2EDM indicate that this particular monomer could be successfully applied in dental practice.

4. CONCLUSIONS

Examination of fractured surfaces in adhesive bonds by optical microscopy can be a useful method in characterization of performance of dental adhesive systems, especially in respect to metal substrates. The results of the quantitative determination of the contribution of particular failure modes correlated with shear bond strength; adhesive mode of failure appeared to be essential for the latter. The new compound having the PM2EDM structure seems to be a promising monomer to be applied in dental adhesive systems.

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