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Investigation of thiol-ene and thiol-ene-methacrylate based resins as dental restorative materials

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Abstract

Objectives—The objective of this work was to evaluate thiol-norbornene and thiol-enemethacrylate systems as the resin phase of dental restorative materials and demonstrate their superior performance as compared to dimethacrylate materials.

Methods—Polymerization kinetics and overall functional group conversions were determined by Fourier transform infrared spectroscopy (FTIR). Flexural strength and modulus were determined with a 3-point flexural test. Polymerization-induced shrinkage stress was measured with a tensometer.

Results—Thiol-ene polymer systems were demonstrated to exhibit advantageous properties for dental restorative materials in regards to rapid curing kinetics, high conversion, and low shrinkage and stress. However, both the thiol-norbornene and thiol-allyl ether systems studied here exhibit significant reductions in flexural strength and modulus relative to BisGMA/TEGDMA. By utilizing the thiol-ene component as the reactive diluent in dimethacrylate systems, high flexural modulus and strength are achieved while dramatically reducing the polymerization shrinkage stress. The methacrylate-thiol-allyl ether and methacrylate-thiol-norbornene systems both exhibited equivalent flexural modulus (2.1 ± 0.1 GPa) and slightly reduced flexural strength (95 ± 1 and 101 ± 3 MPa, respectively) relative to BisGMA/TEGDMA (flexural modulus; 2.2 + 0.1 GPa and flexural strength; 112 ± 3 MPa). Both the methacrylate-thiol-allyl ether and methacrylate-thiol-norbornene systems exhibited dramatic reductions in shrinkage stress (1.1 ± 0.1 and 1.1 ± 0.2 MPa, respectively) relative to BisGMA/TEGDMA (2.6 ± 0.2 MPa).

Significance—The improved polymerization kinetics and overall functional group conversion, coupled with reductions in shrinkage stress while maintaining equivalent flexural modulus, result in a superior overall dental restorative material as compared to traditional bulk dimethacrylate resins.

Introduction

Resin-based composites are currently utilized as an alternative to dental amalgams for repairing tooth defects. The resin component of these composites is composed primarily of either an

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Step 2

aromatic or urethane dimethacrylate, typically 2,2-bis[4-(2-hydroxy-3methacryloyloxypropoxy)phenyl]propane (BisGMA) or urethane dimethacrylate (UDMA). Due to the high viscosity of these materials, a diluent is added to increase conversion and manipulate the consistency of the composite paste. The most commonly utilized diluent is triethylene glycol dimethacrylate (TEGDMA). Arguably, the most significant drawback of polymer based materials is shrinkage and shrinkage stress that arise during polymerization [1-3]. Upon curing, composite systems undergo from 2 % to 4 % volumetric shrinkage, resulting in stresses that arise between the composite and the tooth of as much as 130 kg/ cm² [4]. Bonding between the composite and tooth is negatively impacted by these shrinkage stresses and can lead to marginal gaps through which saliva and bacteria can penetrate into the tooth structure, leading to marginal staining, if not secondary cavity formation [5,6].

In addition to undergoing polymerization shrinkage, most polymer composites exhibit relatively low double bond conversion upon curing. Multifunctional monomers used for dental restorations typically exhibit final double bond conversion of 50 to 75% [7-9]. Furthermore, researchers have found at least 6% residual monomer in BisGMA/TEGDMA resin systems after curing [10], which can be heightened by cyclization [11] or lower conversion. This unreacted monomer is extractable and may leach into the body where various fates are possible. Even though the dentin layer below a restoration has been found to reduce the amount of monomer that diffuses to the pulp space [12], concern still remains about both local and systemic sensitization and allergic reactions some patients exhibit to residual monomer [13, 14].

In this work, thiol-ene-based polymer systems are evaluated as alternatives to purely methacrylate based resins. Thiol-enes differ fundamentally from methacrylate systems in that they polymerize via radical-mediated step-growth reactions between multifunctional thiol and vinyl monomers rather than a chain-growth process [15,16]. Initiation occurs via typical photoinitiators, such as excitation of diaryl ketones followed by hydrogen abstraction (most commonly benzophenone) and by direct cleavage initiators such as dimethoxyphenyl acetophenone (DMPA) [15,17] or without any initiators at all [15,18]. Camphorquinone and an amine accelerator, as is commonly utilized in dental materials, can also be utilized to initiate polymerization. Radical termination occurs via bimolecular radical-radical recombinations [19,20].

In cases where the ene monomer is not homopolymerizable, the polymerization proceeds by a step-growth addition mechanism via sequential propagation of a thiyl radical through an ene functional group followed by chain transfer to the thiol, which regenerates the thiyl radical [15,16,18,21,22]. This successive propagation/chain transfer mechanism is the basis for the traditional thiol-ene step growth mechanism and is presented in the scheme below:

Addition $R \longrightarrow S \cdot + H_2 C \longrightarrow R^* \rightarrow R^* \xrightarrow{f_1} H_2 \cdot R^*$ Step 1 Chain Transfer $R \xrightarrow{f_1} R^* + R \xrightarrow{f_2} R^* + R \xrightarrow{f_3} R^* + R \xrightarrow{f_3} R^*$

An additional level of complexity is involved in the polymerization mechanism due to additional propagation steps that occur when a ternary thiol-ene (e.g., methacrylate-thiol-ene) polymerization is considered [18,23,24]. The propagation mechanism for these types of thiol-ene systems includes a carbon radical propagation step (step 3) in addition to the thiyl radical propagation and chain transfer steps (steps 1 and 2). A ternary system therefore exhibits a combination of both step-growth and chain-growth polymerization mechanisms, depending on the composition and the relative kinetics for each step in the reaction.



Step 3

The step growth mechanism of thiol-ene polymerizations leads to several unique polymerization properties that make them advantageous for use as dental restorative materials. Owing to the slower build up of molecular weight associated with the step-growth mechanism, the viscosity of the reacting media does not significantly increase until high conversion, enabling rapid polymerizations to a higher final conversion, which can dramatically reduce the amount of residual extractable monomer in the material. This outcome results in uniform consumption of low molecular weight species, and a more homogeneous, crosslinked polymer is formed. Thiol-ene polymerizations are not significantly inhibited by oxygen and therefore do not exhibit an uncured tacky layer at surfaces exposed to ambient conditions [15,18]. Most importantly for dental restorative materials, thiol-enes exhibit dramatically reduced volume shrinkage and shrinkage stress due to the step growth mechanism and the delayed gel point conversion [25,26]. As a result of the delayed gel point, much of the shrinkage occurs prior to gelation and this phenomenon dramatically reduces the shrinkage stress in the final polymer material [26].

When methacrylates are polymerized with thiol-enes, the methacrylate functional group has a strong homopolymerization tendency and results in a pseudo two-stage polymerization [23]. The first stage is dominated by methacrylate homopolymerization and chain transfer and the second stage is dominated by thiol-ene polymerization. Due to the hybrid nature of this polymerization, the thiol-ene component serves as a solvent and chain transfer agent for a significant portion of the methacrylate consumption and results in an overall delayed stress development.

There are a few drawbacks commonly associated with thiol-ene based systems, most notably odor and shelf stability. The thiol component is associated with a sulfur odor. The strength and offensiveness of the odor vary greatly depending on the molecular weight of the thiol compound and its concentration in the resin. For the thiol monomer evaluated in this study, the high molecular weight and low concentrations result in resins with minimal odor. After curing, the thiol-ene polymers exhibit no odor. Pure thiol-ene resins are also known to exhibit poor shelf stability, with shelf lives ranging from days to months [15,27]. The incorporation of an appropriate inhibitor system and acrylics into thiol-ene systems dramatically improves shelf stability [15].

Despite the many advantages of thiol-ene polymerizations, readily available thiol-ene materials do not currently achieve the mechanical properties necessary for dental restorative materials [26]. Polymerization kinetics and shrinkage stress of thiol-ene systems were significantly improved over the control resin BisGMA/TEGDMA (70/30 wt%). However, the achievable glass transition temperature, flexural strength, and flexural modulus were significantly less

than values for BisGMA/TEGDMA. Though not commercially available, norbornene monomers have been synthesized in an effort to achieve a wider selection of thiol-ene materials with improved mechanical properties [28]. These thiol-norbornene materials provided relatively high glass transition temperatures ranging from 41 to 94 °C [29]. Another approach to achieve high glass transition materials is to utilize thiol-yne systems [30] or thiol-methacrylate systems. In particular, it has been demonstrated that thiol-BisGMA systems exhibited glass transition temperatures greater than 70 °C [23]. However, the thiol-BisGMA systems systems exhibited extremely low conversion of thiol functional groups (25 - 30%).

Here, this study evaluates the properties of resins intended as polymer matrices for new dental composite restoratives. Thiol-norbornene systems are evaluated as well as the feasibility of utilizing thiol-enes as reactive diluent alternatives in place of TEGDMA. We hypothesize that utilizing a combination of thiol-ene and methacrylate polymerizations will synergistically combine the advantageous mechanical properties of dimethacrylate resins with the improved kinetics, overall conversion, and reduced shrinkage stress of thiol-ene systems. More specifically, polymerization kinetics, overall functional group conversion, volume shrinkage, shrinkage stress, flexural modulus, and flexural strength were evaluated for thiol-norbornene and methacrylate-thiol-ene systems and compared to a control resin composed of conventional resins. The experimental procedures were designed to eliminate other considerations, including differences associated with the initiation rate. As such, an ultraviolet initiating system was chosen that utilizes a cleavage initiator. The initiation rate for cleavage initiating systems is far less affected by monomer composition/chemistry than the traditional camphorquinone/ amine systems in dental materials. This selection, therefore, enabled us to focus only on the differences in polymerization kinetics and material properties associated with the monomers, while maintaining an initiation rate that was approximately the same across the various samples, including the controls. Additionally, these resin systems may be affected differently by filler systems and therefore studying these systems in resin form enabled us to focus only on differences in the resin systems.

Materials and Methods

Materials

Dicyclopentadiene, trimethylolpropane triacrylate, phenothiazine (PTZ), triallyl-1,3,5triazine-2,4,6-(1H,3H,5H)-trione (TATATO) and the photoinitiator, 2,2-dimethoxy-2phenylacetophenone (DMPA) were purchased from Aldrich. 2,2-bis[4-(2-hydroxy-3methacryloyloxypropoxy)phenyl]propane (BisGMA), ethoxylated bisphenol-A dimethacrylate (EBPADMA), and triethylene glycol dimethacrylate (TEGDMA) were donated by Esstech Inc. (Essington, PA). Pentaerythritol tetra(3-mercaptopropionate) (PETMP) was donated by Evans Chemetics (Waterloo, NY). Unless otherwise specified, all monomers were used as received. Chemical structures of all monomers utilized in this study are shown in Figure 1.

Norbornene Synthesis

To synthesize the TMPTN norbornene, a 1.1:1 stoichiometric excess of cyclopentadiene from freshly cracked dicyclopentadiene was added to an addition funnel connected to a three-necked round bottom flask, containing acrylate and 2000 ppm of PTZ. The flask was purged with nitrogen, submerged in an oil bath, and heated to 80 °C. The contents of the addition funnel were then added dropwise. Aliquots were removed and analyzed by FTIR to monitor for reaction conversion. The reaction was stopped once the acrylate peak (1636 cm⁻¹) was completely consumed. Excess cyclopentadiene and dicyclopentadiene were removed by vacuum filtration, and the purity of the monomer was determined using NMR. Additional synthesis details are given elsewhere [29].

Methods

All thiol-ene samples were composed of 1:1 stoichiometric mixtures of thiol to ene functional groups. The BisGMA/TEGDMA and EBPADMA/TEGDMA control resins were 70/30 wt% mixtures of the two monomers. All analyses were conducted using 0.1 wt% DMPA as the photoinitiator and are irradiated using 15 mW/cm² of UV light with an EXFO Acticure (Mississauga, Ontario, Canada) pass through a 320 – 500 nm filter. Irradiation intensity was measured by an International Light, Inc. Model IL1400A radiometer (Newburyport, MA) at the sample surface.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was utilized for kinetic analysis using a Nicolet 750 Magna FTIR spectrometer (Madison, WI) with a KBr beam splitter and an MCT/A detector. Series scans were recorded at a rate of approximately two scans per second for 300 seconds. Data was collected in the near-infrared (7000 – 4000 cm⁻¹) with samples placed between glass slides with a 1.0 mm glass spacer. Functional group conversions were monitored utilizing the methacrylate absorption peak at 6164 cm⁻¹, the allyl ether absorption peak at 6132 cm⁻¹, and the norbornene absorption peak at 6020 cm⁻¹. Methacrylate and allyl ether peak absorbances are overlapped and a Gaussian fitting peak deconvolution method was utilized to determine individual functional group conversions. Norbornene functional groups did not exhibit a strong enough absorption in the near infrared region to accurately deconvolute functional group conversion in EBPADMA/ PETMP:TMPTN systems. For each system, experiments were performed in triplicate.

Flexural Properties

Samples were prepared using teflon molds measuring $2 \text{ mm} \times 2 \text{ mm} \times 25 \text{ mm}$ and were cured under identical conditions as in the FTIR analysis. Polymer flexural strength and modulus were calculated using a 3-point flexural test, carried out with a hydraulic universal test system (858 Mini Bioix, MTS Systems Corporation, Eden Prairie, MN, USA) using a span width of 10 mm and a crosshead speed of 1 mm/min. For each formulation, at least five replicate experiments were performed.

Shrinkage stress

Experiments were performed with a tensometer (American Dental Association Health Foundation), which monitors stress development using cantilever beam deflection theory. Simultaneous conversion measurements are facilitated using remote near-IR transmitted through the polymer sample via fiber optic cables. A detailed description of the tensometer and measurement technique for polymerization shrinkage stress is found elsewhere [31,32]. Samples measuring 6 mm in diameter and 1.5 mm in thickness were irradiated for 600 seconds, and the stress and conversion were monitored for a total of 1200 seconds in all of the experiments. For each composition, experiments were performed in triplicate.

Statistical analysis

The experimental results were analyzed using one-way analysis of variance (ANOVA) based on triplicate specimens for FTIR and shrinkage stress, and five specimens for flexural modulus and strength testing. Multiple pairwise comparisons were further conducted using Tukey's test with a significance level of 0.05.

Results

A thiol-norbornene system (PETMP/TMPTN) was evaluated for shrinkage, shrinkage stress, flexural strength, and flexural modulus relative to a thiol-ene system (PETMP/TATATO) and two dimethacrylate controls (BisGMA/TEGDMA and EBPADMA/TEGDMA). Results are

given in Table 1. The thiol-norbornene resin exhibited a polymerization shrinkage stress of 2.2 \pm 0.2 MPa, which was greater than the shrinkage stress for PETMP/TATATO (1.6 \pm 0.1 MPa), but less than that for the BisGMA/TEGDMA and EBPADMA/TEGDMA control resins (2.6 \pm 0.2 MPa and 2.8 \pm 0.2 MPa). The flexural modulus of the thiol-norbornene resin was 1.3 \pm 0.1 GPa, which was less than both the PETMP/TATATO (1.7 \pm 0.2 GPa) and the BisGMA/TEGDMA controls (2.2 \pm 0.1 GPa and 1.7 \pm 0.1 GPa). The flexural strength of the thiol-norbornene resin was 72 \pm 13 MPa, which was equivalent to the PETMP/TATATO and EBPADMA/TEGDMA resins (76 \pm 8 MPa and 80 \pm 3 MPa), but less than BisGMA/TEGDMA (112 \pm 9 MPa).

To improve the lower flexural modulus and strength of the thiol-ene systems, the PETMP/ TMPTN and PETMP/TATATO systems were evaluated in ternary methacrylate-thiol-ene systems. The methacrylate-thiol-ene systems contained 70 wt% EBPADMA as the primary dimethacrylate component and 30 wt% thiol-ene as the reactive diluent. EBPADMA was utilized as the primary component due to its lower viscosity as compared to BisGMA. Polymerization shrinkage stress, flexural modulus, and flexural strength results for the methacrylate-thiol-ene systems are presented in Table 1. The methacrylate-thiol-ene systems, EBPADMA/PETMP:TATATO and EBPADMA/PETMP:TMPTN, exhibited flexural modulus values equivalent to that of BisGMA/TEGDMA. Both the EBPADMA/ PETMP:TATATO and EBPADMA/PETMP:TMPTN systems exhibited slightly reduced flexural strength as compared to BisGMA/TEGDMA, although the reduction for the EBPADMA/PETMP:TMPTN system was not statistically significant. The EBPADMA/ PETMP:TATATO system exhibited shrinkage stress of 1.1 ± 0.1 and the EBPADMA/ PETMP:TMPTN system exhibited shrinkage stress of 1.1 ± 0.2 MPa relative to 2.6 ± 0.2 MPa for BisGMA/TEGDMA. Shrinkage stress versus methacrylate conversion for each one of these systems is plotted in Figure 3.

In Figure 2 the polymerization kinetics are presented for both binary thiol-ene and ternary methacrylate-thiol-ene systems. The final conversions and time to reach 90% of final conversion are given in Table 2. The thiol-norbornene system achieved $93 \pm 1\%$ conversion relative to $90 \pm 1\%$ for the PETMP/TATATO system and only $56 \pm 1\%$ and $67 \pm 1\%$, respectively for the BisGMA/TEGDMA and EBPADMA/TEGDMA control systems under these same conditions. The thiol-norbornene system achieved 90% of final conversion in only 1.2 ± 0.4 seconds versus 4.3 ± 0.1 seconds for the PETMP/TATATO system and 57 ± 9 and 39 ± 5 seconds, respectively, for the BisGMA/TEGDMA and EBPADMA/TEGDMA systems. Both of the methacrylate-thiol-ene systems exhibit increased methacrylate functional group conversion (83 \pm 1% for EBPADMA/PETMP:TATATO and 89 \pm 3% for EBPADMA/ PETMP:TMPTN) relative to the BisGMA/TEGDMA and EBPADMA/TEGDMA controls. In the EBPADMA/PETMP:TATATO system, the allyl ether functional group conversion was 38 \pm 1%. Norbornene functional group conversion could not be determined. The time to reach 90% of final conversion was significantly faster for the methacrylate-thiol-ene systems than for the dimethacrylate controls; 26 ± 1 seconds for EBPADMA/PETMP:TATATO and $17 \pm$ 4 seconds for EBPADMA/PETMP:TMPTN.

Discussion

The thiol-ene systems exhibit increased polymerization rate and overall functional group conversion as well as reductions in shrinkage stress relative to the dimethacrylate control resins. However, the evidence to date suggests that currently available binary thiol-ene resins exhibit significantly reduced flexural modulus and strength as compared to the pure dimethacrylate controls. Utilizing a ternary methacrylate-thiol-ene system offers a unique approach to combine advantages of both methacrylate and thiol-ene systems. Relative to the BisGMA/TEGDMA control resin, the methacrylate-thiol-ene systems exhibit a 27% increase in methacrylate

conversion for the EBPADMA/PETMP:TATATO system and a 15% increase in methacrylate conversion for the EBPADMA/PETMP:TMPTN system. Flexural modulus is equivalent to BisGMA/TEGDMA for both methacrylate-thiol-ene systems with slight reductions in flexural strength. In addition shrinkage stress is reduced 58% for both the EBPADMA/ PETMP:TATATO and EBPADMA/PETMP:TMPTN systems. The methacrylate-thiol-ene resins studied here combine increased functional group conversion, equivalent polymerization rates, and equivalent flexural modulus with modest reductions in flexural strength and dramatic reductions in shrinkage stress, thereby making them ideal candidates for use in dental restorative materials.

Interestingly, the shrinkage stress in the methacrylate-thiol-ene systems is actually less than the corresponding thiol-ene systems despite containing 70 wt% EBPADMA. The increased reductions in shrinkage stress in the methacrylate-thiol-ene systems are due to the thiol-ene component acting as a solvent in the initial stages of the polymerization, which are dominated by methacrylate homopolymerization and chain transfer, thereby further decreasing shrinkage stress due to a pseudo two stage hybrid polymerization. Significant stress development does not occur until ~30% methacrylate conversion in the EBPADMA/PETMP:TATATO system and ~60% methacrylate conversion in the EBPADMA/PETMP:TMPTN system. This beneficial effect has been previously observed in a hexanediol dimethacrylate/ PETMP:TATATO system [33].

Given the promising initial results of the methacrylate-thiol-ene systems, they should also be tested for additional properties that are relevant for dental restorative materials such as, biocompatibility, water sorption/solubility, and refractive index. Additionally, both of the systems evaluated in this work will be evaluated in systems cured with visible light and as composite systems.

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Figure 1.

Chemical structures of monomers utilized in this study along with their abbreviations.

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Figure 2.

Average functional group conversion versus time for (a) BisGMA/TEGDMA, EBPADMA/ TEGDMA, PETMP/TATATO, and PETMP/TMPTN and (b) BisGMA/TEGDMA, EBPADMA/PETMP:TATATO, and EBPADMA/PETMP:TMPTN. All samples are 70/30 wt % BisGMA/TEGDMA, EBPADMA/TEGDMA, or methacrylate/thiol-ene, contain 0.1 wt% DMPA and are irradiated for 300 seconds at 15 mW/cm² UV light. Cramer et al.



Figure 3.

Average polymerization shrinkage stress versus methacrylate conversion for 70/30 wt% mixtures of BisGMA/TEGDMA, EBPADMA/TEGDMA, EBPADMA/PETMP:TATATO, and EBPADMA/PETMP:TMPTN. Samples contain 0.1 wt% DMPA and are irradiated at 21 mW/cm² for 600 seconds.

Table 1

Polymerization shrinkage stress, flexural modulus, and flexural strength for thiol-ene, methacrylate-thiol-ene, and methacrylate resins. Thiol-ene samples are stoichiometric, methacrylate/thiol-ene samples are 70/30 wt% methacrylate/thiol-ene, and BisGMA/TEGDMA and EBPADMA/TEGDMA samples are 70/30 wt%. All samples contained 0.1 wt % DMPA and are irradiated at 15 mW/cm² (300 seconds for flexural samples and 600 seconds for shrinkage stress). Within each column, the letters indicate statistically significant differences (P < 0.05) as determined by a one-way ANOVA and a Tukey post-hoc pair-wise comparison test.

Resin	Stress (MPa)	Flexural Modulus (GPa)	Flexural Strength (MPa)
PETMP/TMPTN	2.2 ± 0.2^{a}	1.3 ± 0.1^{a}	72 ± 13^{a}
ΡΕΤΜΡ/ΤΑΤΑΤΟ	1.6 ± 0.1^{b}	1.7 ± 0.2^{b}	76 ± 8^a
EBPADMA/PETMP:TATATO	$1.1\pm0.1^{\rm c}$	2.1 ± 0.1^{c}	95 ± 1^{b}
EBPADMA/PETMP:TMPTN	$1.1\pm0.2^{\rm c}$	2.1 ± 0.1^{c}	$101\pm3^{b,c}$
BisGMA/TEGDMA	$2.6\pm0.2^{a,d}$	2.2 ± 0.1^{c}	112 ± 9^{c}
EBPADMA/TEGDMA	2.8 ± 0.2^{d}	1.7 ± 0.1^{b}	80 ± 3^a

Table 2

Functional group conversions and polymerization rates for thiol-ene and methacrylate-thiol-ene resins for 1 mm thick samples (near-IR). BisGMA/TEGDMA and EBPADMA/TEGDMA samples are 70/30 wt%, thiol-ene samples are stoichiometric, and methacrylate/thiol-ene samples are 70/30 wt% methacrylate/thiol-ene. Samples contain 0.1 wt% DMPA and are irradiated for 300 seconds at 15 mW/cm² UV light. Within each column, the letters indicate statistically significant differences (P < 0.05) as determined by a one-way ANOVA and a Tukey post-hoc pair-wise comparison test.

Resin	Methacrylate Conversion	Ene Conversion	Time to Reach 90% Conversion
BisGMA/TEGDMA	56 (1)		57 (9) ^a
EBPADMA/TEGDMA	67 (1)		39 (5) ^b
PETMP/TATATO		90 (1)	4.3 (0.1) ^c
PETMP/TMPTN		93 (1)	1.2 (0.4) ^c
EBPADMA/PETMP:TATATO	83 (1)	38 (1)	26 (1) ^d
EBPADMA/PETMP:TMPTN	89 (3)		17 (4) ^d