Polymerization behavior and thermal characteristics of two new composites at five temperatures: refrigeration to preheating

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PURPOSE. Heat of composite polymerization (HP) indicates setting efficacy and temperature increase of composite in clinical procedures. The purpose of this *in vitro* experimental study was to evaluate the effects of 5 temperatures on HP of two new composites. **MATERIALS AND METHODS.** From each material (Core Max II [CM] and King Dental [KD]), 5 groups of 5 specimens each were prepared and their total HPs (J/gr) were measured and recorded, at one of the constant temperatures 0℃, 15℃, 23℃, 37℃ and 60℃ (2 × 5 × 5 specimens) using a differential scanning calorimetry (DSC) analyzer. The data were analyzed using a two-way ANOVA, a Tukey's test, an independent-samples t-test, and a linear regression analysis (α=0.05). **RESULTS.** No polymerization reactions occurred at 0℃; then this temperature was excluded from statistical analyses. The mean HP of the remaining 20 KD specimens was 20.5 $\pm$ 14.9 J/gr, while it was 40.7 $\pm$ 12.9 J/gr for CM. The independent-samples t-test showed that there were significant differences between the HP of the two materials at the temperatures 15℃ (*P*=.0001), 23℃ (*P*=.0163), 37℃ (*P*=.0039), and 60℃ (*P*=.0106). Linear regression analysis showed statistically significant correlations between environment temperatures and HP of CM (R^2=0.777). **CONCLUSION.** Using CM is advantageous over conventional composite because of its better polymerization capacity. However due to its high HP, further studies should assess its temperature increase *in vivo*. Preheating KD is recommended. Refrigerating composites can negatively affect their polymerization potential. **[J Adv Prosthodont 2011;3:216-20]**

KEY WORDS: Dental Materials; Composite Resins; Polymerization; Differential Thermal Analysis; Differential Scanning Calorimetry (DSC)

INTRODUCTION

Application of chair-side core build-up materials can reduce working time, expenditures, and the tissues needed to be removed in the conventional approach in order to fit the cast post and core into the canal.[1] Being naturally weaker than amalgam,[2] composite core build-up materials need to reach their optimum physicomechanical properties. These are highly attributed to degree of conversion (DC).[3] The DC is the ratio of single carbon-carbon bonds in a polymer structure to double carbon-carbon bonds among monomers.[4] It indicates the percentage of monomer-to-polymer conversion and is a qualitative and quan-

titative index for the extent of the polymerization.[3,5] Mechanical-physical characteristics and clinical performance of dental composites are compromised by a low DC;[5] the residual monomers might act as plasticizers, reducing mechanical properties and increasing swelling.[4,6] Due to cross-linkage in the polymer structure, the DC is associated with surface hardness, flexural strength, fracture toughness, flexural modulus, tensile strength, and wear resistance.[6,7] According to the manufacturers, the composites should be stored at room temperature, whereas many clinicians store them in refrigerator to prolong product shelf life or improve composite carvability.[8,9] Both room and refrigerator temperatures are not appropriate for complete poly-

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merization,[4,6,8] and preheating the composite is advocated as a method to increase monomer conversion, improve marginal adaptation, reduce paste viscosity, and to shorten curing times.[6,7,9-11]

Another critical factor for dental materials is temperature rise during the exothermic chemical reactions.[12] Due to being highly vascular, periodontal tissues can be severely affected by thermal injuries. Only a temperature rise over 10℃ on the external surface of the root (= 47℃) is tolerable by the tissues.[13,14] Thus heated core composite materials can undermine the vitality of periodontal tissues during dental treatments. These indicate that considering heat produced during restorative procedures of different types and brands of chair-side post and core materials are of great importance.[13-15]

The heat of polymerization (HP) is proportional to the percentage of reacted monomers.[3,5] If there is no other thermal sources in the reaction (such as light curing units), the energy released during composite polymerization is directly associated with both the DC and the increase in the temperature of adjacent tissues during chair-side operations. This energy may be measured by differential scanning calorimetry (DSC) which is a thermal analysis method and can provide the variation of enthalpy in the exothermic polymerization reaction, indicating thermal and physical characterizations.[5,16] The DSC is known as a highly sensitive approach and as one of the most reliable direct methodologies for assessment of thermal and physical characterizations of the materials such as DC.[5,16-19] It is of significance to evaluate thermal characteristics (such as the effect of preheating and refrigeration as well as the possibility of harmful temperature increases) and polymerization efficacy of newly marketed core build up materials. However, thermal characteristics of composites are largely unknown,[9] and the literature lacks any studies on HP and thermal properties of core build up materials. The aim of this study was to assess the exothermal characteristics and relative DC of two commonly used self-cure composites, none of which had been assessed before, as well as the effect of 5 environmental temperatures on composite polymerization behaviors, using the DSC method.

MATERIALS AND METHODS

Based on a pilot study, the sample size of this *in vitro* experimental study was predetermined as 50 specimens (divided into 10 groups [2 materials × 5 temperatures]) to obtain a test power > 90%. The experiments were performed at five temperatures: refrigerated: 0℃, room temperatures: 15℃ and 23℃, human body: 37℃, and a common preheating temperature: 60℃.[6,9,10] The composites tested consisted of a conventional self-cure composite of Bis-GMA organic matrix filled with silica and opaque glass fillers 5-15 micron in diameter (King Dental Composite [KD], batch number: MK08J KKO3J, King Dental Corp., US) and a newly introduced, widely-marketed core build-up composite (Core Max II [CM], batch number: 432353, Dentsply-Sankin, Tokyo, Japan), which is a type of semi-hybrid composite resin with methacrylic acid, benzoic peroxide, and 78% filler composed of silicon dioxide 3.2 micron in diameter, lanthanum, barium, aluminium, and zirconium.

A DSC thermal analyzer (DSC-60, Shimadzu, Kyoto, Japan) was used to perform the isothermal temperature analysis. For each thermal group of each material, the DSC was adjusted to a definite temperature. According to the manufacturers' instructions, uniform blends of materials were prepared and immediately placed in the DSC aluminium pan (2 × 4.5 mm) and transferred to the sample holder of the instrument. Afterward, to start the measurement of the heat flow, the temperature was immediately altered to the programmed temperature in 20 s.[5] In order to normalize the test conditions for all the material-temperature sets, the isothermal measurements began 2 min after the initial placement of each material on the aluminium pan.[5] The heat generated during polymerization of each material and its peak were recorded and graphically illustrated at each temperature. For calibrating the thermal analyzer, an empty aluminium pan was used as a reference at each temperature. Any difference between the temperature of the sample and the reference was measured and appeared as a peak on the recorder. The empty pan was weighed (Sartorius, Göttingen, Germany) for 3 times and the average was considered its weight. Each specimen was as well weighed as described and its net weight was calculated by subtracting the weight of the pan. None of the reactions lasted for more than 30 minutes. The normalized heat of exothermic reaction caused by the conversion of the monomers of each specimen at each temperature during 30 minutes was calculated by dividing the whole differential energy by the specimen weight.

Descriptive statistics were calculated. The data were analyzed using a two-way analysis of variance (ANOVA), a Tukey's post hoc test, a linear regression analysis, and an independent samples *t*-test. The level of significant was set at 0.05.

RESULTS

None of these materials showed any polymerization reaction at 0℃. Thus the 0℃ groups were excluded from the statistical analyses. The two-way ANOVA revealed that there were significant differences between material groups (*P*=.0001) and between temperature groups (*P*=.0004, Fig. 1, Table 1). The interaction between the variables material and temperature on polymerization efficacy was as well significant (*P*=.0180), indicating that the effect of environment temperature differed significantly for the two materials.

The HPs produced by each material at all temperatures were compared using the Tukey's HSD. Results for CM showed significant differences within most of the pairwise com-
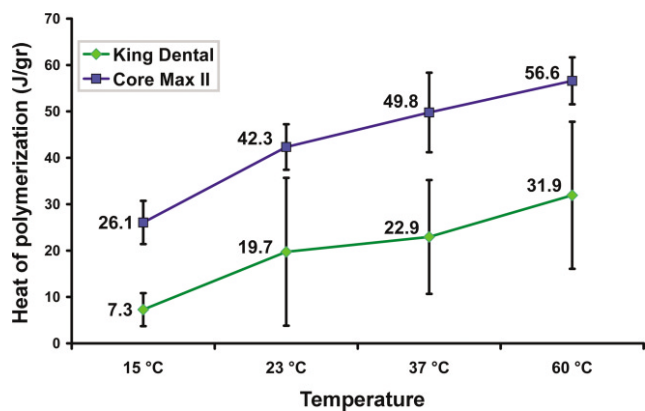
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Fig. 1. Mean (SD) HPs of the tested materials (J/gr) at different temperatures (℃).

Table 2. Results of the Tukey's test, comparing the HPs produced by each material at different temperatures

Compared temperatures (℃)		CM	KD
15	23	0.002	0.446
	37	0.000	0.264
	60	0.000	0.037
23	37	0.250	0.980
	60	0.009	0.466
37	60	0.320	0.690

Table 1. Descriptive statistics for the heat of polymerization during 30 minutes (J/gr)

Material	Temperature (℃)	Mean (J/gr)	SD	Min	Median	Max	CV (%)	Mean 95% CI Low	Up
KD	15	7.27	3.55	4.27	4.98	11.54	48.85	4.16	10.39
	23	19.74	15.94	4.74	10.55	38.10	80.72	5.77	33.71
	37	22.94	12.27	9.69	25.46	39.70	53.49	12.19	33.70
	60	31.92	15.86	22.16	26.55	59.97	49.69	18.02	45.82
CM	15	26.05	4.66	20.29	26.68	32.89	17.89	21.97	30.14
	23	42.33	4.91	34.50	42.07	46.53	11.60	38.03	46.64
	37	49.78	8.57	40.18	51.72	57.98	17.22	42.27	57.30
	60	56.59	5.06	47.79	58.60	60.22	8.94	52.15	61.02

parisons (Table 2). However, most of the HPs produced by KD were not significantly different from each other (Table 2).

The independent-samples t-test showed that there were significant differences between the heat flows from the two materials at 15℃ (*P*=.0001), 23℃ (*P*=.0163), 37℃ (*P*=.0039), and 60℃ (*P*=.0106).

The linear regression analysis showed a significant linear correlation between heat of polymerization and temperature of surrounding environment for CM (R^2 = 0.777), whereas heat of KD polymerization was weakly correlated to environment temperature (R^2 = 0.351).

DISCUSSION

In the present study, the DSC was programmed under isothermal conditions at 5 constant temperatures to evaluate the enthalpy of polymerization as well as the effect of surrounding environment temperatures on the polymerization behavior of the composites. The DSC is a convenient device for measuring the extent of heat produced and reaction kinetics.[18] It is sensitive to small masses of materials and can provide data with sharp peaks, low drift from the baseline, and a linear associ-

ation between the area under the peak and the mass of the specimen.[3,5] It is also a convenient tool for analysis of polymerization of resin monomers, and can measure the extent and rate of polymerization of functional monomers by analyzing the amount of released energy.[3,5,19] It has also been used successfully to predict the incomplete polymerization in commercial dental light cured composites.[18,19]

In the current study, the extent of heat produced during polymerization of Core Max II was significantly more than King Dental composite. In addition, heat of CM polymerization was considerably more affected by the environment temperature. The only significant increase in heat produced by King Dental composite was at 60℃ (compared to the heat flow level at 15℃), where as Core Max II showed a considerable increase in polymerization by increasing the environment temperature. The difference between the materials is attributed to their chemical compositions and viscosities which might affect the polymerization of self-cured composites.[5,8,10,16,20,21] The higher variation observed among KD specimens may be relevant to preparation techniques of the materials (CM was available in the form of powder and liquid with superior homogeneity, KD had 2 pastes), and probably lower viscosity of CM components.

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HP indicates the rate of monomer-to-polymer conversion and polymerization efficacy.[7,18,19] Hence, higher energy released can be also considered an advantage for CM in case the temperature increase does not reach clinically harmful levels. It is shown that temperatures higher than 50℃ for one minute or over 47℃ for five minutes can result in bone resorption and fat replacement, and alkaline phosphatase can be inactivated at 56℃.[15]

It has been shown that the DC can be accelerated by dynamic heating of composite materials.[4,5,7-10,22] This study, as well, showed that preheating the composites may increase the extent of polymerization for both of the composites examined. This may be attributable to reduced viscosity and thus the increased radical mobility, as well as increased collision frequency of unreacted active groups and radicals.[4-6,8] In this study none of the materials showed any reaction at 0℃, which might be due to the absence of any initial activation energy necessary to forming the activated complex (the first 2 phases of composite polymerization [initiation and activation]).[23] According to thermodynamics, the positive effect of preheating on the efficacy of activation and initiation of a reaction might be increased if the material is no more heated (or even be cooled) once the highly-exothermic phase of composite polymerization (propagation) is ongoing.[24]

The composite polymerization procedure is a self-limiting cascade constrained by the rapid formation of a highly cross-linked polymeric network which decreases the mobility of reactive monomers.[6] According to the instructions of the manufactures, CM and KD should be stored at 25 and 22℃ respectively to prevent early evaporation of the solvent.[8] However, they are usually refrigerated to extend their shelf life, and are used immediately after being removed from refrigerator.[8,9] It leads to more reduction in the extent of composite polymerization and so proper quality may not be attained.[4,6,8,9]

Some investigators have recommended preheating to increase monomer conversion and reduce the film thickness of the material and therefore to improve marginal adaptability;[6,7,9,11] whereas according to some others, it might damage adjacent tissues and thus is not recommended.[4] Moreover, residual stress of polymerization shrinkage is also greatly increased with increase in temperature.[6,8,10,20] As was confirmed in the present study, the type of composite has a significant influence on temperature rise during polymerization.[20]

The clinical importance of heat of polymerization depends on the health of the gingival tissues in direct contact with the exothermic release and their susceptibility to inflammation;[12] traumatized and irradiated tissues as well as tissues in some medically compromised and elderly patients might be highly vulnerable to thermal irritations.[12] Nevertheless, in clinical conditions, the temperature increase caused by exothermic reaction of pre-heated self-cure composites is short in duration and is rapidly attenuated by the surrounding soft tissues to endurable levels;[10,25] as only 0.8℃ and 1.8℃ temperature

increases have been observed after placement of 60℃ and 68℃ heated composites, respectively, while light curing the same materials could increase the temperature up to 6℃, which was still tolerable by the tissues.[10,25] As well, the thickness of composite and residual dentin may lower the temperature rise in adjacent tissues,[10,22] so the absence of direct contact with adjacent soft tissue almost guarantees safe practice. Also instead of preheating, the adhesive systems can be taken out of refrigerator and be exposed to room temperature for at least 20 min before they are used, to reach efficacious polymerization rates; and this post-refrigeration period should be longer for materials containing fillers.[8]

In this study, CM released heat during its polymerization twice as much as did the conventional composite (KD). Therefore, unless further clinical studies verify its safe temperature rise and so thermal biocompatibility to previously-irritated tissues, using it in direct contact with recently injured adjacent soft tissues should be approached with caution; also preheating Core Max II should be avoided in such conditions, especially considering the finding that there were no significant differences between its polymerization at 60℃ and 37℃, which could as well enhance the polymerization considerably. Preheating KD, however, might be advantageous; as 60℃ was the only temperature causing heat flows significantly higher than the baseline. Optimum preheating times might vary based on material compositions (e.g., filler ratios) and heating units used.[8,9] Few available works in this regard have demonstrated that 11 minutes of preheating might suffice to elevate composite temperature from about 4℃ to 60℃.[9] After removing from the device, the clinician has little time to apply the warmed composite since it rapidly loses temperature (50% within 2 minutes and 90% within 5 minutes).[9] Finally, it should be noted that while using light-cure composites, clinicians should rely on appropriate light-curing durations rather than depending on preheating.[26]

CONCLUSION

Core Max II showed a much more efficient polymerization capacity; therefore its usage seems to be advantageous over conventional composite. Preheating to 60℃ should be cautioned when the soft tissue is irritated, because of lack of any considerable positive effect on polymerization compared to body temperature as well as odds of imposing harm to soft tissue. Further clinical studies are warranted to assess the latter.

The King Dental composite produced much less heat during polymerization, and showed less efficient polymerization. Warming it to 60℃ is recommended to increase its physico-mechanical properties.

Refrigeration might disrupt composite characteristics. Refrigerated composites should be warmed to (at least) room temperature before application.

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