

Effect of Micro-Additions of Carbon Nanotubes to Polymethylmethacrylate on Reduction in Polymerization Shrinkage

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Abstract

Purpose: Carbon nanotubes are used in dentistry, although there are no adequate scientific data to support their use in acrylic resins. The polymerization shrinkage that occurs with polymethylmethacrylate (PMMA) resins is well known. This study compared the polymerization shrinkage of denture base acrylic resin with and without micro-additions of carbon nanotubes.

Materials and Methods: Two materials were used, PMMA resin and multiwalled carbon nanotubes. Four groups were established of 10 specimens each according to the weight percent of carbon nanotubes dispersed and disintegrated in the monomer: group I (0.5% of carbon nanotubes in monomer), II (0.25%), III (0.125%), and IV (control group, 0%). The polymerization shrinkage of acrylic resin for each group was evaluated based on the distance between the reference points in wax (before polymerization) and in acrylic (after polymerization), measured using a traveling microscope. The data were submitted to Kruskal-Wallis and one-way ANOVA for comparison among the groups, and the results were statistically analyzed.

Results: The Kruskal-Wallis test detected that the different percentages of carbon nanotubes incorporated in the monomer showed significant differences, and the mean ranks of polymerization shrinkage (%) showed differences among all the groups (group IV = 0.126, III = 0.037, II = 0.017, I = 0.006). Hence, the order of severity of polymerization shrinkage was 0% > 0.125% > 0.25% > 0.5% for the amount of carbon nanotubes incorporated in methylmethacrylate.

Conclusion: The present study was done to prove polymerization shrinkage in PMMA resins with micro-additions of carbon nanotubes. The results clearly show reduction in polymerization shrinkage when carbon nanotubes are incorporated into the PMMA resin.

Heat-activated acrylic denture base resins are the best materials currently used for denture prostheses. In acrylic resin the two main unavoidable dimensional changes are expansion and shrinkage.¹ Dimensional changes occur as a result of shrinkage of monomer and release of stress during polymerization.² The extent of dimensional changes in acrylic resin may be due to various factors like technique of polymerization, release of internal stresses due to variation in the coefficient of thermal expansion between resin and gypsum, and thickness of the denture base.³ Despite many changes in the properties of resins, there was no alteration in the shrinkage of the resin.⁴ According to Schadler et al (1998), Allaoui et al (2002), and Wong et al (2003) carbon nanotubes were regarded as the best reinforcement materials in resins.⁵

Polymer physical properties are influenced by changes in temperature and environment and by the composition, structure, and molecular weight of the polymer. Polymer exhibits a tendency to absorb water by a process of imbibition.⁶ Liquid monomer (methylmethacrylate) is mixed with polymer to form plastic dough. A 21% volume shrinkage occurs during polymerization.

Takamata et al⁷ reported that the different thermal expansion coefficients of resin and plaster during flask cooling may increase resin shrinkage, due to the internal stresses developed.

The release of stresses induced after separating the base model causes distortions in the resin and increases the inaccuracy of the denture base to support tissues. Various studies⁸⁻¹⁴ proved that polymerization shrinkage occurred after curing when plain acrylic was used.

Carbon nanotubes are being studied as fillers for augmentation, especially for polymers.^{15,16} By optimizing the interface interaction of the nanotube surface and polymer, the intrinsic properties of nanotubes reinforced in polymers were used. This proper adhesion results in good stress transfer from the polymer to the nanotube, preventing dimensional changes. Therefore, it was chosen for this study.¹⁵

In 1991, Sujio Iijima¹⁷ discovered carbon nanotubes. Structurally these nanotubes are long, thin cylinders of graphite made up of layers of carbon atoms arranged in a hexagonal lattice held together by weak forces called van der Waals. Carbon nanotubes are classified as single-walled varieties (SWNTs), having a single cylindrical wall, and multiwalled varieties (MWNTs), having cylinders within cylinders.

According to Kearns and Shambaugh¹⁸ and Devoret and Dai,¹⁹ carbon nanotubes have a weight percentage of between 0.005 and 5.0 and more typically 0.15 to 2.0. Carbon nanotubes have diameters between 10 and 50 nm and lengths between 10 and 1000 nm.

Augmentation of polymethylmethacrylate (PMMA) resins with carbon nanotubes improves the strength of the prostheses to better withstand the forces of mastication. Due to the excellent strength of this augmented material, it can also be used in fixed partial dentures as well as other prostheses. Carbon nanotubes have tensile strengths up to 4000 times stronger than steel and as much as 200 times stronger than carbon fibers. Carbon nanotubes bond to matrices like PMMA polymer by comparatively weak van der Waals forces. The carbon nanotube/PMMA matrix adhesion strength is very large, such that the bond strength is greater, and the mechanical fatigue strength and compression strength are enhanced.19,20

These carbon nanotubes present in PMMA prevent shrinkage and dimensional changes in the resin during and after polymerization, helping in better denture fit or bone/implant interface. Hence, the augmentation of nanotubes in acrylic resins will improve the mechanical properties of the acrylic, eliminating the need for metal reinforcement in stress-bearing areas. Knowing all the properties of acrylic resins and carbon nanotubes, this study was carried out to compare the polymerization shrinkage of denture base acrylic resin with and without micro-additions of carbon nanotubes.

Materials and methods

The following materials were used for the study:

• A heat-cured acrylic resin denture base material (Trevalon, Dentsply, Surrey, UK) with standard composition powder and liquid.

• Multiwalled carbon nanotubes (Monad Nanotech, Mumbai, India) (Fig 1).

The multiwalled carbon nanotubes used were supplied by Monad Nanotech with the specified dimensions: diameter 20 to 40 nm, length 5 to 15 μ m, Purity >95%, surface area 40 to



Figure 1 Multiwalled carbon nanotubes.



Figure 2 Reference points.

 $300 \text{ m}^2/\text{g}$ comprising of ash 0.2 wt%, amorphous carbon < 3%. A standard edentulous maxillary mold was used. Forty casts were poured using dental stone (Dentsply) with a powder: liquid ratio of 30 ml of water to 100 g powder. Four points were marked on the cast at the following regions 15,21,22 (Fig 2):

- C Incisal papilla
- A1 Deepest part of right hamular notch
- A2 Deepest part of left hamular notch
- B Mid-palatine raphae (center of A1-A2)

A stencil was fabricated with a thermoplastic resin sheet in a vacuum-molding machine on the master cast, and the four reference points were marked with a dark-leaded microtip pencil. The marked areas were drilled with a fine-tapered fissure bur (diameter 1 mm). This stencil was then used to mark the



Figure 3 Brass stubs in wax.

reference points on the other 40 casts to standardize the reference points on all the specimen casts. Care was taken in selecting the wax for the fabrication of the wax denture base. Light pink modeling wax (Cavex, Haarlem, The Netherlands) was selected. This was chosen so as to visualize the dark marked reference point on the cast through the transparent wax. A uniform thickness of 1 mm was verified using a caliper.

Separating medium was applied on the wax denture base. Another stencil was then fabricated with clear self-cured acrylic resin on the wax denture base. Holes of 4 mm diameter were drilled with a straight fissure bur around the above-mentioned four reference points. This stencil was used to locate the placement of the brass stubs and to standardize the same location on the wax denture bases of all 40 specimen casts.

Brass stubs (3 mm length, 3 mm height) were placed on the reference points of the wax denture bases of every cast (Fig 3). Using a surveyor, each of the stubs was surveyed and checked to be parallel to each other and perpendicular to the base of the cast in one plane. The dimensions (in mm) between the reference points of the wax denture bases were measured and recorded using a traveling microscope with a magnification of $10 \times$. A total of five readings (A1-A2, A1-B, A1-C, A2-B, A2-C) were obtained in each of the specimens before curing.

Three groups (group I: 0.5 wt%, group II: 0.25 wt%, group III: 0.125 wt% of multiwalled carbon nanotubes) were weighed using an electronic precision balance. The carbon nanotubes were subject to ultrasonic agitation in an ultrasonic unit of 400 W and 132 KHz power for 5 minutes for uniform dispersion and disintegration of the carbon nanotubes into the monomer (methylmethacrylate). Disintegration is needed because nanotubes have a tendency to firmly adhere to each other in parallel axis arrangement. In this approach, the tip of a sonic dismembranator, that is, an ultrasonic probe used to disrupt cell membranes, is inserted into the mixture of the carbon nanotubes and the liquid methylmethacrylate monomer.²³



Figure 4 Sequence of events CNT – carbon nanotubes, PMMA – polymethylmethacrylate.

The monomer (methylmethacrylate) containing the carbon nanotubes mixed with polymer (PMMA) in a 1:3 ratio by volume was flasked by the conventional technique. Monomer without carbon nanotubes was mixed with polymer and was used to fabricate the control group specimens. A thin K-type thermocouple (Cr/Al) (range -1200) (OMEGA Engineering Systems, Stamford, CT) of 0.25 mm in diameter sheathed with Kapton was used, and the tip of the thermocouple was placed in the palatal region of each specimen to record the temperature changes during packing and curing. The other end of the thermocouple was connected to a digital temperature indicator outside. The measurements were made initially and continued through the process of polymerization.²⁴

A 2 to 3°C difference was acceptable. The curing was followed according to Kawara and Komiyama:²⁵ curing for

 Table 1
 Mean, standard deviation, and test of significance of mean values among four study groups measuring reference points A1-A2, A1-B, A2-B,

 A1-C, A2-C, showing the measurement made between the two reference points in wax and acrylic is not significant in all four groups, but the difference between wax and acrylic is significant (mm)

Distances	Groups	Wax	Acrylic	Difference
A1-A2		5.743±0.076	5.743±0.076	$0.0\pm0.0^{*}$
	11	5.675 ± 0.114	5.764 ± 0.126	$0.089 \pm 0.024^{*}$
	111	5.738 ± 0.140	5.775 ± 0.125	$0.107 \pm 0.054^{*}$
	IV	5.659 ± 0.158	5.871 ± 0.079	$0.212 \pm 0.143^{*}$
A1-B	I	2.390 ± 0.070	3.423 ± 0.083	0.033 ± 0.046
	11	2.513 ± 0.295	3.485 ± 0.202	0.084 ± 0.076
	111	2.471 ± 0.093	3.434 ± 0.088	0.059 ± 0.070
	IV	2.379 ± 0.049	3.500 ± 0.080	0.121 ± 0.094
A2-B		2.353 ± 0.016	2.364 ± 0.031	0.011±0.019*
	11	2.171 ± 0.268	2.279 ± 0.207	$0.139 \pm 0.076^{*}$
	111	2.276 ± 0.073	2.341 ± 0.060	$0.074 \pm 0.075^{*}$
	IV	2.279 ± 0.113	2.371 ± 0.100	$0.143 \pm 0.066^{*}$
A1-C	I	$5.181 \pm 0.051^{*}$	$5.181 \pm 0.051^{*}$	$0.0 \pm 0.0^{*}$
	11	$5.153 \pm 0.079^{*}$	$5.152 \pm 0.044^{*}$	$0.073 \pm 0.027^{*}$
	111	$5.162 \pm 0.083^{*}$	$5.146 \pm 0.034^{*}$	$0.075 \pm 0.040^{*}$
	IV	$5.305 \pm 0.061^{*}$	$5.349 \pm 0.092^{*}$	0.111±0.080*
A2-C	I	5.240 ± 0.080	$5.240 \pm 0.080^{*}$	$0.0 \pm 0.0^{*}$
	11	5.292 ± 0.088	5.211±0.031*	$0.097 \pm 0.038^{*}$
		5.212 ± 0.076	$5.216 \pm 0.065^{*}$	$0.033 \pm 0.038^{*}$
	IV	5.253 ± 0.089	$5.417 \pm 0.082^{*}$	0.164±0.111*

*Significant values.

 Table 2 Mean, standard deviation, and test of significance of mean values among four study groups (mm): average of all five distances (A1-A2, A1-B, A2-B, A1-C, A2-C); the difference between the reference points measured between wax and acrylic is significant

Groups	Wax	Acrylic	Difference
1	3.981 ± 0.019	3.990 ± 0.023	0.006 ± 0.012*
11	3.961 ± 0.064	3.978 ± 0.055	$0.017 \pm 0.014^{*}$
III	3.970 ± 0.060	3.982 ± 0.066	$0.037 \pm 0.021^{*}$
IV	3.975 ± 0.066	4.101 ± 0.046	$0.126 \pm 0.041^{*}$

*Significant values.

90 minutes at 70°C, the temperature then raised to 100°C over the course of 60 minutes, and maintained for 30 minutes. After the polymerization cycle, bench cooling was done for 3 hours before the specimens were deflasked. The distances between the reference points were again measured using a traveling microscope of $10 \times$ magnification. The readings were made by a single operator to reduce error. The distances between A1-A2, A1-B, A1-C, A2-B, and A2-C were noted and were compared with the similar measurements taken before curing. There were 10 specimens per group. The sequence of events used is summarized in Figure 4.

Measurement taking

The readings obtained from the wax and acrylic specimens were tabulated, and the difference in distances between wax and acrylic were also measured. Distances were calculated (i.e., A1-A2, A1-B, A1-C, A2-B, and A2-C) (Table 1). Each reading at the reference point was calculated by a traveling microscope of magnification $10 \times$.

In each specimen a main scale reading (MSR) and a Vernier scale reading (VSR) was obtained in wax (before curing) and in acrylic (after curing). The total reading (TR) was then calculated using a formula: $TR = MSR + (VSR \times LC)$, where LC is the least count having a value of 0.01.

Statistical analysis

Mean, test of significance, and standard deviations were estimated from the specimens for each of the study groups (Table 2). In the present study, p < 0.05 was considered as the level of significance. To calculate the *p*-value Kruskal-Wallis and one-way ANOVA were used. Mann-Whitney U-Test was employed to find out the groups that were significant at the 5% level.

Results

Mean values of the various distances between the reference points were measured and tabulated. The mean distance between A1-A2, A1-B, A1-C, A2-B, and A2-C were evaluated. The mean distance between the wax, acrylic, and the difference between wax and acrylic were evaluated (Fig 5). The mean distances between the reference points in wax values had a mean difference of 0.2 mm, as the stubs were placed manually.

The results indicate that group I (0.5% CNT) showed no visible polymerization shrinkage (%) (mean = 0.006), group II



Figure 5 Comparison of the mean difference between wax and acrylic and the difference between wax and acrylic among the four groups. Group I has 0.00 difference between the reference points measured in wax and in acrylic.



Figure 6 Future of carbon nanotubes.

(0.25% CNT) (mean = 0.017) had some linear changes, group III (0.125%) (mean = 0.037) had a varied amount of linear dimensional inaccuracies, and the control group (0% CNT) (mean = 0.126) showed the maximum amount of polymerization shrinkage.

Discussion

This study evaluated the influence of micro-additions of multiwalled carbon nanotubes in PMMA resin on the polymerization shrinkage of the resin. In the present study, the polymerization shrinkage occurred more in the posterior region (i.e., between reference points A1-A2 of the specimen [mean = 0.126]). These findings are similar to those of previous studies conducted by Firtell et al² and Yeung and Chow,¹¹ who demonstrated that the absence of nanotubes in PMMA resins showed maximum polymerization shrinkage when compared to the presence of nanotubes.

It is also important to emphasize that for the same polymerization cycle, the percent polymerization shrinkage was absent in group I having 0.5% (by wt) of carbon nanotubes. In 1997, Lewis and Mladsi²⁶ proved that incorporating 0.5% of carbon nanotubes in PMMA enhanced the tensile strength and stiffness of resin when compared to 0.25% and 0.125% incorporation of carbon nanotubes. A similar percentage has been shown in this study to inhibit polymerization shrinkage.¹⁹

In the literature, it has already been proven that addition of various quantities of carbon nanotubes to resin improves various properties like tensile strength, impact strength, and stiffness, and that polymerization shrinkage is reduced in composite resins.^{15,19} There is no documented evidence of reduction of polymerization shrinkage in acrylic resin. Hence, the present study was done to prove the inhibition of polymerization shrinkage on PMMA resins incorporating carbon nanotubes, and the results clearly show an absence of polymerization shrinkage when 0.5% of carbon nanotubes are incorporated into the PMMA resin and that there was reduced shrinkage when 0.25% and 0.125% carbon nanotubes were used when compared to 0% carbon nanotube in PMMA resin.

A limitation of this study was that only one denture base resin was polymerized by heat curing. Furthermore, although the method used for analysis of polymerization shrinkage is objective, further research should be conducted to evaluate how these results apply to other studies with comparable methods for the analysis of polymerization shrinkage in resins with microadditions of carbon nanotubes. The clinical implications of this study suggest that micro-additions of carbon nanotubes in PMMA resins can produce denture base resins with reduced or absent polymerization shrinkage based on the percentages of carbon nanotubes added.

We foresee that the carbon nanotubes will find numerous applications and take an important place in the development of emerging technologies in the near future. The ability to render carbon nanotubes biocompatible opens the door to many future directions. For example, coated carbon nanotubes are being evaluated as sensors of analytes produced by cells, and as imaging probes for cultured cells. Furthermore, coated carbon nanotubes might find use as probes for noninvasive imaging in living systems, or as drug delivery particles (Fig 6). At present, researchers are working on these areas to apply carbon nanotubes in emerging technologies.

Conclusion

With the limitations of this in vitro study, the following conclusions were drawn:

- 1. The polymerization shrinkage between the denture bases produced with the micro-additions of multiwalled carbon nanotubes and the dentures bases produced without carbon nanotubes were statistically significant at the 5% level.
- 2. Order of severity of polymerization shrinkage: 0% > 0.125% > 0.25% > 0.5% (wt%) of the amount of carbon nanotubes incorporated in PMMA resin.
- 3. Maximum dimensional changes occurred in the posterior area of the denture base between points A1-A2 (mean = 0.212) in group IV (control, with 0% nanotubes in PMMA resin).
- A1-C, A2-C (mean = 0) between wax and acrylic values in group I proves that dimensional changes are absent between reference points A1-A2 in the posterior area with 0.5% nanotubes on PMMA resin.
- 5. Maximum polymerization shrinkage between reference points A1-C, A2-C, A1-A2, A1-B, and A2-B occurred if acrylic resin was used without incorporating carbon nanotubes (mean = 0.126).
- 6. No visible polymerization shrinkage occurred between reference points A1-C, A2- C, A1-A2, A1-B, and A2-B when acrylic resin was impregnated with 0.5% CNT of the total acrylic used.

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