

[DOI] 10.12016/j.issn.2096-1456.2022.08.012

· 综述 ·

储存温度与使用温度对粘接剂及复合树脂性能影响的研究进展

余帆, 饶南荃, 吕长海, 刘波

昆明医科大学附属口腔医院儿童口腔科, 云南 昆明(650106)

【摘要】 粘接剂及光固化复合树脂的性能与牙体缺损的修复效果密切相关,因此改善粘接剂与复合树脂的各项性能以提高充填成功率是近年来牙体修复领域的研究重点,目前研究已证实温度可改变粘接剂及光固化复合树脂的部分性能,对修复效果产生影响。适宜的储存温度是材料拥有良好性能的保障,自酸蚀粘接系统应冷藏保存,光固化复合树脂应根据所含成分、比例等决定将其冷藏或保存于室温中,而酸蚀-冲洗粘接系统适宜的储存温度尚不明确。正确地使用温度可改善材料的流动性、单体转化率、粘接强度及抗压强度等,以此提高充填修复的质量。然而粘接剂与光固化复合树脂种类繁多,在储存、使用过程中温度的改变对其影响程度不一,各材料储存、预冷及预热的温度范围仍需探讨,并且目前多数实验在体外进行,所得结论可能与实际临床应用中有所差别。因此,不同温度下储存、使用的粘接剂与复合树脂在口腔内的应用效果需进一步研究。

【关键词】 自酸蚀粘接系统; 酸蚀-冲洗粘接系统; 光固化复合树脂; 储存温度; 使用温度; 预冷; 预热; 材料性能

【中图分类号】 R78 **【文献标志码】** A **【文章编号】** 2096-1456(2022)08-0604-05

【引用著录格式】 余帆, 饶南荃, 吕长海, 等. 储存温度与使用温度对粘接剂及复合树脂性能影响的研究进展[J]. 口腔疾病防治, 2022, 30(8): 604-608. doi:10.12016/j.issn.2096-1456.2022.08.012.

The effect of storage temperature and application temperature on the properties of adhesives and resin composites YU Fan, RAO Nanquan, LV Changhai, LIU Bo. Department of Pediatric Dentistry, School and Hospital of Stomatology, Kunming Medical University, Kunming 650106, China

Corresponding author: LIU Bo, Email: 465926503@qq.com, Tel: 86-13330466612

【Abstract】 The properties of adhesives and light-cured resin composites are closely related to the repair of dental defects. Therefore, improving the properties of adhesives and resins composite to increase the success rate of filling has been the focus of research in the field of prosthodontics in recent years. Current studies have confirmed that temperature can change the properties of adhesives and light-cured resin composites, affecting their repair effect. A proper storage temperature ensures the good performance of materials: the self-etching adhesive system should be refrigerated, and the light-cured resin composite should be refrigerated or stored at room temperature according to its composition, proportion and other properties; however, the appropriate storage temperature for the etch-and-rinse adhesive system is not clear. The appropriate application temperature could improve the fluidity, monomer conversion, bonding strength, compressive strength and other properties of the materials to improve the quality of filling restoration. However, there is a wide variety of adhesives and resin composites, and the effect of temperature on each material is different. Thus, it is still necessary to explore the temperature range for material storage, precooling and preheating. Few studies have been performed in vivo, and the clinical restorative effects of adhesives and resin composites stored and used at different temperatures need to be further studied.

【收稿日期】 2021-05-26; **【修回日期】** 2022-02-11

【基金项目】 云南省科技厅科技计划项目[2018FE001(-074)]; 云南省教育厅科学研究基金项目(2021Y344)

【作者简介】 余帆, 硕士研究生, Email: 1250683961@qq.com

【通信作者】 刘波, 主任医师, 本科, Email: 465926503@qq.com, Tel: 86-13330466612



微信公众号

【Key words】 self-etching adhesive system; etch-and-rinse adhesive system; light-cured resin composite; storage temperature; application temperature; precooling; preheating; material property

J Prev Treat Stomatol Dis, 2022, 30(8): 604-608.

【Competing interests】 The authors declare no competing interests.

This study was supported by Science and Technology Plan Project of Yunnan Science and Technology Department [No. 2018FE001(-074)]; Scientific Research Fund Project of Yunnan Education Department (No. 2021Y344).

粘接剂及光固化复合树脂因操作简便、色泽美观等原因,被广泛应用于牙体缺损的充填治疗中。虽然粘接剂及复合树脂各方面性能已有了很大改进,但其成分复杂,在储存过程中易受温度、湿度、光照强度等因素的影响而难以长期保持稳定,在术后也会性能欠佳而导致修复失败。近年来研究发现,温度可改变粘接剂及复合树脂的部分性能,进而对修复效果产生影响。本文就储存温度及使用温度对粘接剂、复合树脂性能的影响作一综述,以期临床治疗提供参考。

光固化复合树脂需与粘接剂联合使用才能获得较高的粘接强度,但粘接系统成分复杂,尤其是自酸蚀粘接系统将功能单体、引发剂、偶联剂等多种成分混合在一起,其自身稳定性难以得到保证^[1]。为提高粘接强度,使用稳定的成分以及改善材料的储存环境等方法被提出^[2]。就合适的储存环境而言,温度是较为重要的影响因素之一,材料制造商通常建议将粘接剂保存在室温(25℃左右)或低温下(表1)。

表1 常见粘接剂的储存温度

Table 1 Storage temperatures of commercial adhesives

Name of adhesive		Storage temperature
3M	Adper™ Single Bond 2	Room temperature
	Single Bond Universal Adhesive	2-25℃
	Adper™ Easy One	For now, unknown; if the adhesive cannot be used within 6 months after opening, please keep it in the refrigerator
SHOFU	BeautiBond	1-10℃, and the adhesive should be restored to room temperature before application
Ivoclar Vivadent	Tetric N-Bond Universal	2-28℃
Kuraray	TMS3 BOND	2-28℃

1 储存温度对粘接剂性能的影响

研究发现自酸蚀粘接剂中的酸性单体会发生水解反应,当水解反应发生后,一方面酸性单体的

结构会改变,其化学、物理性质受到影响;另一方面,水解产物会污染混合层,使纳米级树脂突形成不全^[3]。储存温度的升高会加快水解反应的发生,使粘接剂中H⁺浓度不断增加,而pH值的改变又会促进此进程,从而形成恶性循环,使得粘接剂的pH值、纳米压痕硬度及粘接强度显著降低,最终影响粘接效果^[4]。因此多数学者建议自酸蚀粘接剂不使用时应室温或者低温保存^[5]。为进一步探究粘接剂适宜的储存温度,Ozer等^[6]将三种自酸蚀粘接剂分别于低温(6±2)℃及室温(19±2)℃下保存3个月,结果表明室温保存的粘接剂其粘接强度均显著低于低温保存的粘接剂。由此可知,为确保在临床应用中具有最佳的粘接性能,自酸蚀粘接剂应冷藏保存。但需要注意的是粘接剂即使储存于低温环境下,仍不可避免地存在水解反应,故建议自酸蚀粘接剂在有效期内尽快使用。

2 使用温度对粘接剂性能的影响

2.1 预冷对粘接剂性能的影响

预冷是指预先将材料置于制冷设备中,待温度降低到一定程度后将其取出并立即使用。5℃的Prime & Bond NT(酸蚀-冲洗粘接系统)、Adper Prompt L-Pop(自酸蚀粘接系统)与20℃时相比,5℃时粘接剂的粘接强度显著降低,同时通过对实验结果分析可知,预冷效果与粘接系统的类型无明确关系^[7]。这是由于粘接剂需依赖适当的流动性才能渗透到牙本质小管和胶原纤维网中形成微机械固位,但低温保存后粘接剂的黏度显著增加,阻碍了粘接剂的溶解、渗透^[8];其次,粘接能力还有赖于溶剂的挥发,温度降低后溶剂挥发受到限制,粘接剂的吸水性大大增强^[9],大量的水分不仅会激发牙体组织内胶原酶对树脂基质的水解作用^[10],还会造成相分离现象。相分离过程影响单体聚合,还会在混合层下层形成树脂缺乏而富含水分的水树结构,来自粘接剂、牙本质小管及唾液的水分可在水树通道内随意移动,使未完全聚合的树脂单体浸出,从而加快粘接界面的老化^[11]。

尽管将粘接剂储存在冰箱中有利于材料的保存,但冷藏保存的粘接剂应在室温环境下至少放置 20 min 再应用于临床,然而粘接剂反复冷藏是否会对粘接性能造成影响仍有待进一步研究。

2.2 预热对粘接剂性能的影响

预热是指预先将材料置于加热设备中,待加热到一定温度后将其取出并立即使用。Panavia F 2.0(自酸蚀粘接剂)预热至 60 ℃后对牙本质表现出较强的粘接力^[12],另有研究表明 68 ℃的 Opti-bond FL、Kerr Corp(酸蚀-冲洗粘接系统)在使用 1 周及 6 个月其牙本质粘接强度均较室温对照组高^[13]。粘接强度的提升是由于温度升高后,粘接剂的黏度降低,良好的流动性可促使均匀混合层的形成;其次,粘接剂预热后溶剂、水分挥发加快,余留水分及溶剂减少,水解反应被限制;此外,功能单体内自由基的迁移随温度升高而加快,转化率提高后残留单体的塑化作用减弱,从而获得良好的粘接效果^[14]。

然而,Transbond XT 和 NeoBond(正畸粘接剂)在 36 ℃下较 20 ℃获得更高的黏质粘接强度,但加热至 55 ℃时,其粘接强度反而下降^[2]。学者们认为这是由于粘接剂的某些单体成分在高温下不仅会发生化学变性,还会过早聚合,形成污染粘接面的聚合物颗粒^[15],溶剂的加速挥发也会导致单体

渗透不全,从而影响粘接强度。

由此可知,预热效果主要与粘接剂所含成分及含量相关,与粘接系统尚无明确关系。此外,粘接剂预热应有一定的温度限制,否则将会缩短粘接剂的使用效期,但目前粘接剂多加热至 36 ~ 60 ℃之间,明确的温度限制需进一步研究。

3 储存温度对复合树脂性能的影响

复合树脂不宜储存于 37 ℃的高温环境,但对于 2 ℃的低温环境,则应根据树脂所含成分、比例等决定是否适宜储存^[16]。复合树脂在 37 ℃下其抗弯强度显著降低是由于长期存储于高温环境下,树脂单体会出现基团断裂、氧化水解、结晶形成等情况,在这些情况下自由基的加成聚合受到限制,即使存在大量未反应的单体,聚合程度也会大大降低,最终只能提供有限的机械性能。

储存温度不仅会影响复合树脂的抗弯强度,还会影响其剪切模量和弯曲模量,研究发现大块树脂的剪切模量和弯曲模量随储存温度的升高而逐步下降^[17]。由此可知,虽然不同类型复合树脂的适宜温度各不相同,但长期储存于高温下有损材料的性能,还可能会加速材料老化,故储存时应将其冷藏或保存于室温中(表 2)。

表 2 常见复合树脂的储存温度

Table 2 Storage temperatures of commercial resin composites

Name of resin composite		Storage temperature
3M	Filtek™ Z250XT Universal Restorative	Room temperature; the validity of the resin composite can be extended when stored at 4 ℃; the resin composite should be restored to room temperature before application
	Filtek™ Z350XT Universal Restorative	Room temperature; if the resin is refrigerated, it should be restored to room temperature before use; storage temperatures often higher than 27 ℃ may shorten validity
	Filtek™ Z350XT Flowable Restorative	Same as above
	Filtek™ P60	15-17 ℃
SHOFU	Beautifil e Posterior	1-30 ℃
	Beautifil Flow Plus F00	1-30 ℃
	Beautifil Flow Plus F03	1-30 ℃
Dentsply	SDR	4-25 ℃
Kerr	Sonic Fill	Room temperature
Ivoclar Vivadent	Tetric N-Flow	2-28 ℃

4 使用温度对复合树脂性能的影响

4.1 预冷对复合树脂性能的影响

Charisma 和 DurafillVS 两种复合树脂预冷至 4 ℃后,其顶部硬度显著低于 23 ℃时的硬度,研究者从而认为制冷条件无法提供树脂活化所需的初

始活化能,故建议冷藏的树脂材料在使用前应恢复到室温^[18]。但其他学者发现 4 ℃的复合树脂可发生聚合反应,并且预冷不会影响复合树脂的抗弯强度及光固化 24 h 后的硬度^[19],研究还观察到预冷可降低单体的聚合收缩率,进而减小微渗漏,

这是由于预冷类似于“软启动聚合”,即低温增大了复合树脂的粘度,导致聚合反应速度减慢,从而提供一个较长的预凝胶相以增加凝胶前的收缩应力,减少凝胶后收缩,进而减少收缩应力^[20]。由于与发光二极管(Light-Emitting Diode, LED)光固化灯相比,经石英钨卤素(Quart Tungsten Halogen, QTH)光固化灯照射后树脂会产生更大的聚合收缩,故研究者建议将预冷的复合树脂与LED光固化灯联合使用,以在不影响复合材料硬度的情况下将收缩率降至最低^[21]。

4.2 预热对复合树脂性能的影响

树脂材料的流动性对修复体的使用寿命起着重要作用^[22]。流动性不仅直接关系到其处理特性(在修复部位的放置和成型),还关系到材料表面凹陷形变的能力及单体转化的程度。复合树脂预热后,树脂单体或低聚体在热振动的作用下进一步分离,相互之间的滑动更容易^[23],从而使复合树脂的粘稠度降低,流动性增强^[24]。但预热的复合树脂无法达到与流体树脂一样的流动性,因此,在临床应用中预热复合树脂不能取代流体树脂,并且不同种类树脂预热后流动性变化不同,这与树脂类型及所含成分有关^[25]。

复合树脂流动性增强后,单体分子的迁移率及未反应基团的碰撞频率也随之提高,自由基转化被促进^[26],有助于提高转化率。Lempel等^[27]将光固化复合树脂加热到55℃,转化率提高了10%~20%,证实预热对树脂的双键转化有正向影响。此外,研究表明复合树脂经过反复预热或延长预热时间均不会影响其转化、聚合的能力^[28]。研究也表明在相同的光照强度下,预热树脂的光照时间即使减少50%~75%,仍获得与室温复合树脂相似或更好的转化率,由此建议在应用预热树脂时可适当缩短光照时间^[27]。

目前多数学者认为预热可将玻璃化反应推迟到聚合过程的后期,使复合材料在聚合过程中有较长的应力释放机会而减小收缩力,并且在高流动性、高转化率的正面影响下,复合树脂预热最终可很大程度减少收缩力的产生,有效防止微渗漏的发生。但也有部分学者认为温度升高促进了聚合过程,反应会快速到达凝胶点,单体缺乏足够的流动时间而不能起到补偿作用,树脂的聚合收缩率也随单体转化率的增加而增大,从而导致预热的的作用适得其反。此外,加热可能会促进复合树脂的老化,影响修复体的寿命,因此 Marcinkowska

等^[29]建议谨慎使用预热树脂。

在一定温度范围内,预热树脂并不会造成牙髓热损伤,研究发现光固化灯照射20 s后,牙本质温度升高了5.0~6.8℃,而将68℃的复合树脂立即置于窝洞中,牙本质温度仅升高1.3℃^[30]。然而这并不意味着树脂可以无限度加热,因为当温度高于某个极限时,树脂内的反应物会蒸发,光引发剂会降解,牙髓也会受损伤。因此,为了保护牙髓细胞,同时保证修复体的质量,临床上一概不建议将树脂加热至60℃以上^[31]。

5 结 论

综上所述,粘接剂及复合树脂的流动性、转化率、粘接强度等性能与温度密切相关,虽然子弹、胶囊装新型树脂的出现使得材料在短期内用尽已成为可能,但是为保证材料的修复质量,适宜的储存环境和使用温度仍尤为重要。值得注意的是,目前多数实验都在体外进行,所得结论可能与实际临床应用有所差别,并且各类材料因其成分与含量的不同而受温度的影响也有所不同。因此,不同温度下储存及使用的粘接剂、复合树脂在口腔内的应用效果仍需进一步研究。

【Author contributions】 Yu F wrote the article. Rao NQ, Lv CH, Liu B reviewed the article. All authors read and approved the final manuscript as submitted.

参考文献

- [1] Simmer FS, da Silva EM, Bezerra RDSG, et al. Bond stability of conventional adhesive system with MMP inhibitors to superficial and deep dentin[J]. *J Mech Behav Biomed Mater*, 2019, 100: 103402. doi: 10.1016/j.jmbbm.2019.103402.
- [2] Maaßen M, Wille S, Kern M. Bond strength of adhesive luting systems to human dentin and their durability[J]. *J Prosthet Dent*, 2021, 125(1): 182-188. doi: 10.1016/j.prosdent.2019.07.012.
- [3] Münchow EA, da Silva AF, Piva E, et al. Development of an anti-bacterial and anti-metalloproteinase dental adhesive for long-lasting resin composite restorations[J]. *J Mater Chem B*, 2020, 8(47): 10797-10811. doi: 10.1039/d0tb02058c.
- [4] Sutil BGDS, Susin AH. Dentin pretreatment and adhesive temperature as affecting factors on bond strength of a universal adhesive system[J]. *J Appl Oral Sci*, 2017, 25(5): 533-540. doi: 10.1590/1678-7757-2016-0500.
- [5] Carrilho E, Cardoso M, Marques Ferreira M, et al. 10-MDP based dental adhesives: adhesive interface characterization and adhesive stability-a systematic review[J]. *Materials(Basel)*, 2019, 12(5): 790. doi: 10.3390/ma12050790.
- [6] Ozer F, Ovecoglu HS, Daneshmehr L, et al. Effect of storage temperature on the shelf life of self-adhesive resin cements[J]. *J Ad-*

- hes Dent, 2015, 17(6): 545-550. doi: 10.3290/j.jad.a35252.
- [7] Kasraei S, Yarmohamadi E, Ranjbaran Jahromi P, et al. Effect of 940nm diode laser irradiation on microtensile bond strength of an etch and rinse adhesive (single bond 2) to dentin[J]. J Dent (Shiraz), 2019, 20(1): 30-36. doi: 10.30476/DENTJODS.2019.44560.
 - [8] Firouzmandi M, Khashaei S. Knoop Hardness of Self-etch adhesives applied on superficial and deep dentin[J]. J Dent (Shiraz), 2020, 21(1): 42-47. doi: 10.30476/DENTJODS.2019.77805.0.
 - [9] Hardan L, Bourgi R, Kharouf N, et al. Bond strength of universal adhesives to dentin: a systematic review and meta-analysis[J]. Polymers (Basel), 2021, 13(5): 814. doi: 10.3390/polym13050814.
 - [10] Beck F, Ilie N. Antioxidants and Collagen-Crosslinking: benefit on Bond strength and clinical applicability[J]. Materials(Basel), 2020, 13(23): 5483. doi: 10.3390/ma13235483.
 - [11] Lee C, Kashima K, Ichikawa A, et al. Influence of hydrolysis degradation of silane coupling agents on mechanical performance of CAD/CAM resin composites: in silico multi-scale analysis[J]. Dent Mater J, 2020, 39(5): 803-807. doi: 10.4012/dmj.2019-223.
 - [12] Golbari N, Kasraei S, Afrasiabi A, et al. Effect of diode laser (810 nm) irradiation on marginal microleakage of multi-mode adhesive resins in class V composite restorations[J]. J Lasers Med Sci, 2019, 10(4): 275-282. doi: 10.15171/jlms.2019.45.
 - [13] Magne P, Mori Ubaldini AL. Thermal and bioactive optimization of a unidose 3-step etch-and-rinse dentin adhesive[J]. J Prosthet Dent, 2020, 124(4): 487.e1-487.e7. doi: 10.1016/j.prosdent.2020.03.011.
 - [14] Bourgi R, Daoud U, Bijle MN, et al. Reinforced universal adhesive by ribose crosslinker: a novel strategy in adhesive dentistry[J]. Polymers (Basel), 2021, 13(5): 704. doi: 10.3390/polym13050704.
 - [15] Akarsu S, Buyuk SK, Kucukkekenci AS. Effects of adhesive systems at different temperatures on the shear bond strength of orthodontic brackets[J]. J Dent Res Dent Clin Dent Prospects, 2019, 13(2): 103-108. doi: 10.15171/joddd.2019.016.
 - [16] Camargo FSAS, González AHM, Alonso RCB, et al. Effects of polymerization mode and interaction with hydroxyapatite on the rate of pH neutralization, mechanical properties, and depth of cure in self-adhesive cements[J]. Eur J Dent, 2019, 13(2): 178-186. doi: 10.1055/s-0039-1696057.
 - [17] Hassan MA, Zinelis S, Hersberger-Zurfluh M, et al. Creep, hardness, and elastic modulus of lingual fixed retainers adhesives[J]. Materials (Basel), 2019, 12(4): 646. doi: 10.3390/ma12040646.
 - [18] Osternack FH, Caldas DB, Rached RN, et al. Impact of refrigeration on the surface hardness of hybrid and microfilled composite resins[J]. Braz Dent J, 2009, 20(1): 42-47. doi: 10.1590/s0103-64402009000100007.
 - [19] Mandava J, Vegesna DP, Ravi R, et al. Microtensile bond strength of bulk-fill restorative composites to dentin[J]. J Clin Exp Dent, 2017, 9(8): e1023-e1028. doi: 10.4317/jced.53965.
 - [20] Steiner R, Edelhoff D, Stawarczyk B, et al. Effect of dentin bonding agents, various resin composites and curing modes on bond strength to human dentin[J]. Materials(Basel), 2019, 12(20): 3395. doi: 10.3390/ma12203395.
 - [21] Osternack FH, Caldas DB, Almeida JB, et al. Effects of preheating and precooling on the hardness and shrinkage of a composite resin cured with QTH and LED[J]. Oper Dent, 2013, 38(3): E1-E8. doi: 10.2341/11-411-L.
 - [22] Meshram P, Meshram V, Palve D, et al. Comparative evaluation of microleakage around Class V cavities restored with alkasite restorative material with and without bonding agent and flowable composite resin: an in vitro study[J]. Indian J Dent Res, 2019, 30(3): 403-407. doi: 10.4103/ijdr.IJDR_767_17.
 - [23] Almeida LN, Mendes GAM, Favarão IN, et al. Influence of preheating and post-curing on a novel fiber-reinforced composite post material[J]. Braz Oral Res, 2018, 32: e97. doi: 10.1590/1807-3107bor-2018.vol32.0097.
 - [24] Tomaselli LO, Oliveira DCRS, Favarão J, et al. Influence of preheating regular resin composites and flowable composites on luting ceramic veneers with different thicknesses[J]. Braz Dent J, 2019, 30(5): 459-466. doi: 10.1590/0103-6440201902513.
 - [25] Coelho NF, Barbon FJ, Machado RG, et al. Response of composite resins to preheating and the resulting strengthening of luted field-spar ceramic[J]. Dent Mater, 2019, 35(10): 1430 - 1438. doi: 10.1016/j.dental.2019.07.021.
 - [26] Abdulmajeed AA, Donovan TE, Cook R, et al. Effect of preheating and fatiguing on mechanical properties of bulk-fill and conventional composite resin[J]. Oper Dent, 2020, 45(4): 387-395. doi: 10.2341/19-092-L.
 - [27] Lempel E, Őri Z, Szalma J, et al. Effect of exposure time and preheating on the conversion degree of conventional, bulk-fill, fiber reinforced and polyacid-modified resin composites[J]. Dent Mater, 2019, 35(2): 217-228. doi: 10.1016/j.dental.2018.11.017.
 - [28] Yang J, Silikas N, Watts DC. Pre-heating effects on extrusion force, stickiness and packability of resin-based composite[J]. Dent Mater, 2019, 35(11): 1594 - 1602. doi: 10.1016/j.dental.2019.08.101.
 - [29] Marcinkowska A, Gauza-Włodarczyk M, Kubisz L, et al. The electrical properties and glass transition of some dental materials after temperature exposure[J]. J Mater Sci Mater Med, 2017, 28(12): 186. doi: 10.1007/s10856-017-5996-2.
 - [30] Erhardt MCG, Goulart M, Jacques RC, et al. Effect of different composite modulation protocols on the conversion and polymerization stress profile of bulk-filled resin restorations[J]. Dent Mater, 2020, 36(7): 829-837. doi: 10.1016/j.dental.2020.03.019.
 - [31] Daronch M, Rueggeberg FA, Hall G, et al. Effect of composite temperature on in vitro intrapulpal temperature rise[J]. Dent Mater, 2007, 23(10): 1283-1288. doi: 10.1016/j.dental.2006.11.024.

(编辑 罗燕鸿)



官网