Effect of silver nitrate incorporation into heat polymerized acrylic resin on some mechanical properties

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ABSTRACT

Background: Polymers are very rarely used in their form. These modifications are carried out in order to improve the properties of polymers.Recently silver have been used successfully as antimicrobial (medical and dental) biomaterials that can prevent caries and infection of implants. The aim of the present *in vitro* study is to evaluate the effect of addition of silver nitrate to acrylic resin in different concentrationsthrough several tests part of these are: The effect of this additive on impact strength, transverse strength, and tensile strength of $AgNO_3$ – loaded resin, and to assess any effect of addition of silver nitrate on coloration of acrylic resin.

Materials and methods: Different concentrations of silver nitrate (9.375, 15, 30, 60, 120, 150, 300, 600 and 900 ppm) were prepared from stock solution of 1000 ppm silver nitrate. The specimens were prepared in accordance with the manufacturer's instructions and the tested silver nitrate solution was added to the acrylic resin powder and monomer in a fixed volume (0.2ml). Controls devoid of silver nitrate were included.

Results: Fourier transform infra-red confirmed that there was no chemical bond between the Poly methyl methacrylate and silver nitrate. There was insignificant increasing (P=0.05) in impact strength observed when compared with control group. In transverse strength test, significant reduction was show (P<0.001). While for tensile strength there was insignificant reduction with 9.375(P=0.05NS) and 15(P=0.42NS) ppm silver nitrate. However, it was significant above 15 ppm (P<0.001). Darkening of silver nitrate -loaded resins were shown to be started with concentration of silver nitrateof 300 ppm and above.

Conclusions: The additions of silver nitrate to acrylic resins yield good color stability and mechanical properties, depending on the concentration of silver nitrate.

Keywords: Silver nitrate, acrylic resin, infra-red spectra, strength, coloration. (J Bagh Coll Dentistry 2014; 26(4):78-85).

INTRODUCTION

Little information is available about the impact of silver nitrate into heat polymerized acrylic resin. So this prompted us to shed light on this research.

There is a need for effective broad -spectrum antimicrobial resin materials in dentistry; it is well-known that removable denture bases fabricated from heat-polymerized acrylic resins may act as a reservoir for microorganisms and contribute to re-infection in denture wearers [1]. For elderly and institutionalized patients with limited motor skills and special needs, this treatment is further complicated because of some factors such as loss of memory, difficulty in rendering appropriate cleaning for their oral cavities.Unfortunately, current standers of treatment such as the use of antimicrobial mouthwashes, proper –tooth brushing technique have limited success or side -effects due to problems with patient compliance and the development of antibiotic resistance strains of bacteria. Thus a broad- spectrum antimicrobial resin is needed [2].

Silver ions have been reported to inactivate important enzymes and affect the application mechanism of the DNA in bacteria. Ag ions have been reported to attach to the outer membrane and affect the permeability as well as induce structure changes in the cell – ultimately leading to cell death .In addition; Ag does not cause resistant bacterial strains to develop [3,4].

For dental application, the development of other methods of drug elution, such as Ag-Zeolite and SiO_2 filler were incorporated into urethane acrylic monomer in different amount to develop a new temporary filling materials with antibacterial activity against some oral bacterial growth [5], silver containing materials like Novaron, Amenitop and AIS were incorporated into light activated resin composites attended to decrease the frequency of secondary caries around the restorations [6]. The sol-gel derived silica glass powders containing silver are believed to be useful as an antibacterial material for medical applications such as filler of composite resin for dental restoration [7], and the incorporation of nanometer-sized silver-supported antimicrobial agent into denture base materials to investigate the distributionand to study the release mode of silver ions from the base [8,9]. There are few studies about the addition of silver particles to denture base resin have been published [8,9] . So the aim of the present *in vitro* study is to evaluate the effect of addition of silver nitrate to acrylic resin in different concentrationsthrough several tests part of these are: The effect of this additive on impact strength, transverse strength, and tensile strength of $AgNO_3$ – loaded resin, and to assess any effect

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of addition of silver nitrate on coloration of acrylic resin.

MATERIALS AND METHODS

Preparation of silver nitrate ($AgNO_3$) concentrations for studying samples

Different concentrations of $AgNO_3$ solutions were prepared from stock solution of 1000ppm of $AgNo_3$. Serial concentrations were prepared: (15, 30, 60,120ppm), (9.375, 150,300,600 ppm) and 900ppm.The prepared concentrations were confirmed by Atomic Absorption spectrophotometer (Phoenix -986/ AA spectrophotometer, UK) and stored in dark bottles wrapped with aluminum foil.

$AgNO_3$ – loaded resin specimens fabrication

For impact strength test, specimens with a bar shaped specimen with dimensions of (80mm x 10mm x 4mm) length, width, thickness respectively [10].

For transverse strength test, a bar shaped specimens with dimension of (65mm X 10mm X 2.5mm) length, width, thickness respectively [11].

For tensile strength test, flatdumbbell shaped specimens with dimensions (16± 1mm length; 3± 0.2 mm width and 2± 0.2 mm thickness at the parallel segment [12]. The patterns invested in flaks with dental stone. After setting of the stone, the flasks were opened and patterns removed, leaving cavities that were used as matrixes for the fabrication of heat polymerized acrylic resin specimens.

For each assay, 60 specimens were fabricated, and assigned to 10 groups (n=6) according to the concentrations of silver nitrate solutions: zero (control);(9.375,15,30,60,120,150,300,600,and 900ppm). For this, the heat cure denture base resin(Non – veined acrylic, powder and liquid, Ivoclar Vivadent AG, Italy) was mixed according to manufacturer instruction, P/L ratio: 2.25g of powder was mixed with 1ml liquid (0.8ml monomer + 0.2ml $AgNO_3$ solutionof each concentration). Specimens devoid of silver nitrate were included as control.These were mixed manually, by the same operator. The material were packed and polymerized following the manufacturer's instructions.

Visual inspection of $AgNO_3$ – loaded resin samples

Samples were evaluated visually by comparing the tested samples with the control group.

Characterization of $AgNO_3$-loaded resins

The Fourier transform infra –red (FTIR) spectra was performed (on IR Affinity-1/Shimadzu Corporation/Japan spectrophotometer) using KBr and Caesium Iodid (CsI) pellets to determine whether or not functional groups of the $AgNO_3$ have been attached to the heat cured PMMA by analyzing the characteristic vibrations of functional groups [22].

Impact strength test

The test was measured using Charpy type impact testing instrument The specimen was supported horizontally at its ends and strucked by a free swinging pendulum released from a fixed height in the middle. A pendulum of 2 joules testing capacity was used. The scale reading gave the impact energy absorbed to fracture the specimen in joules when struck by sudden blow.The Charpy impact strength of unnotched specimen was calculated in KJ/m^2 according to Anusavice [13] as given by the following equation:

$$\text{Impact strength} = \frac{E}{b.d}$$

Since:
E: is the impact absorbed energy in joules.
b: is the width in millimeters of the test specimens.
d: is the thickness in millimeters of the test specimens.

Transverse strength test

The test was measured usingInstron testing machine, each specimen

was positioned on bending fixture, consisting of two parallel supports (50)mm apart, the full scale load was 50kg, and the load was applied with cross head speed of 1mm/min by rod placed centrally between the supports making deflection until fracture occurred.

The transverse bend strength was calculated using the following formula [13]:

$$\text{Transverse strength (MPa)} = \frac{3Pl}{2bd^2}$$

Since:
P: is the peak load.
l: is the span length.
b: is the sample width.
d: is the sample thickness.

Tensile strength test

The test was measured using Tinius Olsen testing machine at a cross head speed of 0.5 mm/min and with 50 mm grip – to – grip distance. The force at the failure was recorded in Newton (N) and the tensile strength values were calculated from the following equation:

$$\text{Tensile strength } (N/mm^2) = \frac{F\ (N)}{A\ (mm^2)}$$

Since:

F: Maximum load at failure (Newton).

A: Cross sectional area (mm^2).

RESULTS

Visual inspection of $AgNO_3$ – loaded resin samples

As the concentration of $AgNO_3$ increased, the prepared $AgNO_3$ –loaded resin samples start to show visually some darkening started at 300 ppm $AgNO_3$ and above Figure (1).

Characterization of $AgNO_3$-loaded resins

The results of FTIR (Fourier transform infra – red) spectra of PMMA and $AgNO_3$ –loaded resins in KBr and Caesium Iodid (CsI) discs, showed no change in the shape of absorption peaks between PMMA(control) and $AgNO_3$ –loaded resinsindicating no chemical bond between the PMMA and $AgNO_3$ Figures(2-3-4-5).

Impact strength test

As shown in Table 1-2, the mean impact strength was highest in the group with 60 ppm $AgNo_3$ (12.8 KJ/ m^2) and lowest in the control group (10.6 KJ/m^2). The difference in mean impact strength between the concentrations of $AgNO_3$ and control group was statistically insignificant. Compared to control the lowest concentration of $AgNO_3$ (9.375ppm) was associated with an average increase in impact strength of 0.1KJ/m^2. The effect of this very low concentration was evaluated as weak (Cohen's d = 0.17). This effect was statistically insignificant .The 60 ppm $AgNo_3$ was associated with highest increase in mean impact strength of 2.2.This effect was statistically significant which rated as a strong effect (Cohen's d = 2.63) .

Transverse strength test

As shown in table 3- 4, the mean transverse strength was highest in the control group (77.8 MPa) and lowest in the group with 120 ppm of $AgNO_3$ (55.4MPa). The difference in mean transverse strength between the concentrations of $AgNO_3$ and control group was statistically significant.

Compared to control the lowest concentration of $AgNO_3$ (9.375 ppm) was associated with an average reduction in transverse strength of (14MPa), the effect of this very low concentration was evaluated as strong (Cohen's d = 4.18).This effect was statistically significant .The strongest effect was with 120 ppm $AgNO_3$ (reduction in transverse strength) (Cohen's d greater than 6).

Tensile strength test

As shown in table 5-6, the mean tensile strength was highest in the control group (54 MPa) and lowest in the group with 60 ppm $AgNO_3$ (36.8MPa). The difference in mean tensile strength between the concentrations of $AgNO_3$ and the control group was statistically significant. Compared to control the lowest concentration of $AgNO_3$ (9.375ppm) was associated with an average reduction in tensile strength of 5 MPa.

However, this effect was statistically insignificant. The 15 ppm $AgNO_3$ was associated with very small and statistically insignificant reduction in tensile strength of 2.1MPa. On the other hand, the $AgNO_3$ concentration associated with strongest effect (reduction in tensile strength) was the 60 ppm (Cohen's d greater than 4).

Table 1: Descriptive data of impact strength test (KJ/m^2)

Study groups (concentration of added AgNO3 in ppm)				
	Control	**9.375 ppm**	**15 ppm**	**30 ppm**
Range	(9.67 to 11.11)	(9.94 to 11.62)	(10.53 to 12.23)	(9.78 to 13.51)
Mean	10.6	10.7	11.5	11.8
SD	0.65	0.56	0.63	1.54
SE	0.27	0.23	0.26	0.63
N	6	6	6	6
Difference in mean compared to control	Reference	0.1	0.9	1.2
Cohen's d	Reference	0.17	1.37	1.03
P (LSD)	Reference	0.88[NS]	0.24[NS]	0.1[NS]

Table 2: Descriptive data of impact strength test (KJ/m^2).

Study groups (concentration of added AgNO3 in ppm)				
	60 ppm	**120 ppm**	**150 ppm**	**P (ANOVA)**
Range	(11.27 to 13.72)	(9.25 to 12.66)	(8.86 to 15.17)	0.05[NS]
Mean	12.8	10.7	11.8	
SD	0.95	1.57	2.09	
SE	0.39	0.64	0.85	
N	6	6	6	
Difference in mean compared to control	2.2	0.1	1.2	
Cohen's d	2.63	0.12	0.78	
P (LSD)	0.006	0.85[NS]	0.11[NS]	

Table 3: Descriptive data of transverse strength test (MPa)

Study groups (concentration of added AgNO3 in ppm)				
	Control	**9.375 ppm**	**15 ppm**	**30 ppm**
Range	(74.4 to 81.6)	(57.6 to 67.2)	(56.4 to 72)	(60 to 74.4)
Mean	77.8	63.8	67.0	66.4
SD	2.78	3.83	5.65	5.76
SE	1.13	1.56	2.31	2.35
N	6	6	6	6
Difference in mean compared to control	Reference	-14.0	-10.8	-11.4
Cohen's d	Reference	-4.18	-2.42	-2.51
P (LSD)	Reference	<0.001	0.001	<0.001

Table 4: Descriptive data of transverse strength test (MPa)

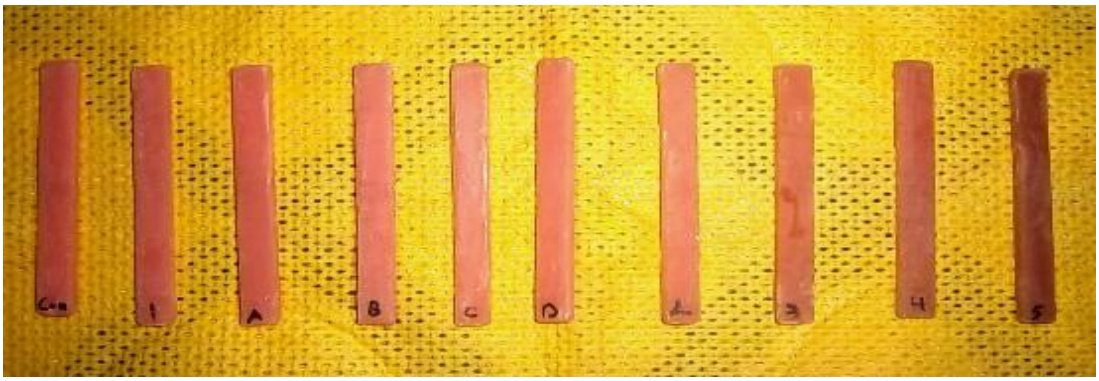
	Study groups (concentration of added AgNO3 in ppm)			
	60 ppm	120 ppm	150 ppm	P (ANOVA
Range	(58.5 to 79.2)	(48 to 57.6)	(57.6 to 76.8)	<0.001
Mean	64.8	55.4	69.6	
SD	7.37	3.75	6.57	
SE	3.01	1.53	2.68	
N	6	6	6	
Difference in mean compared to control	-13.0	-22.4	-8.2	
Cohen's d	-2.33	-6.77	-1.61	
P (LSD)	<0.001	<0.001	0.012	

Table 5: Descriptive data of tensile strength test (MPa)

Study groups (concentration of added AgNO3 in ppm)				
	Control	**9.375 ppm**	**15 ppm**	**30 ppm**
Range	(49.54 to 62.5)	(46.06 to 55.2)	(39.71 to 57.8)	(38.84 to 53.7)
Mean	54	49	51.9	44
SD	4.82	3.3	6.64	5.18
SE	1.97	1.35	2.71	2.12
N	6	6	6	6
Difference in mean compared to control	Reference	-5.0	-2.1	-10.0
Cohen's d	Reference	-1.21	-0.36	-2.00
P (LSD)	Reference	0.05[NS]	0.42[NS]	<0.001

Table 6: Descriptive data of tensile strength test (MPa)

	Study groups (concentration of added AgNO3 in ppm)			
	60 ppm	**120 ppm**	**150 ppm**	**P (ANOVA)**
Range	(31.48 to 41.69)	(38.25 to 43.4)	(38.3 to 45.56)	<0.001
Mean	36.8	40.7	41.5	
SD	3.37	2.1	3.34	
SE	1.38	0.86	1.36	
N	6	6	6	
Difference in mean compared to control	-17.2	-13.3	-12.5	
Cohen's d	-4.13	-3.58	-3.01	
P (LSD)	<0.001	<0.001	<0.001	



Control 9.37 15 30 60 120 150 300 600 900 ppm

Fig. 1: $AgNO_3$ –loaded resinsfrom left to right: control, (9.375, 15, 30, 60, 120, 150, 300, 600, and 900 ppm).

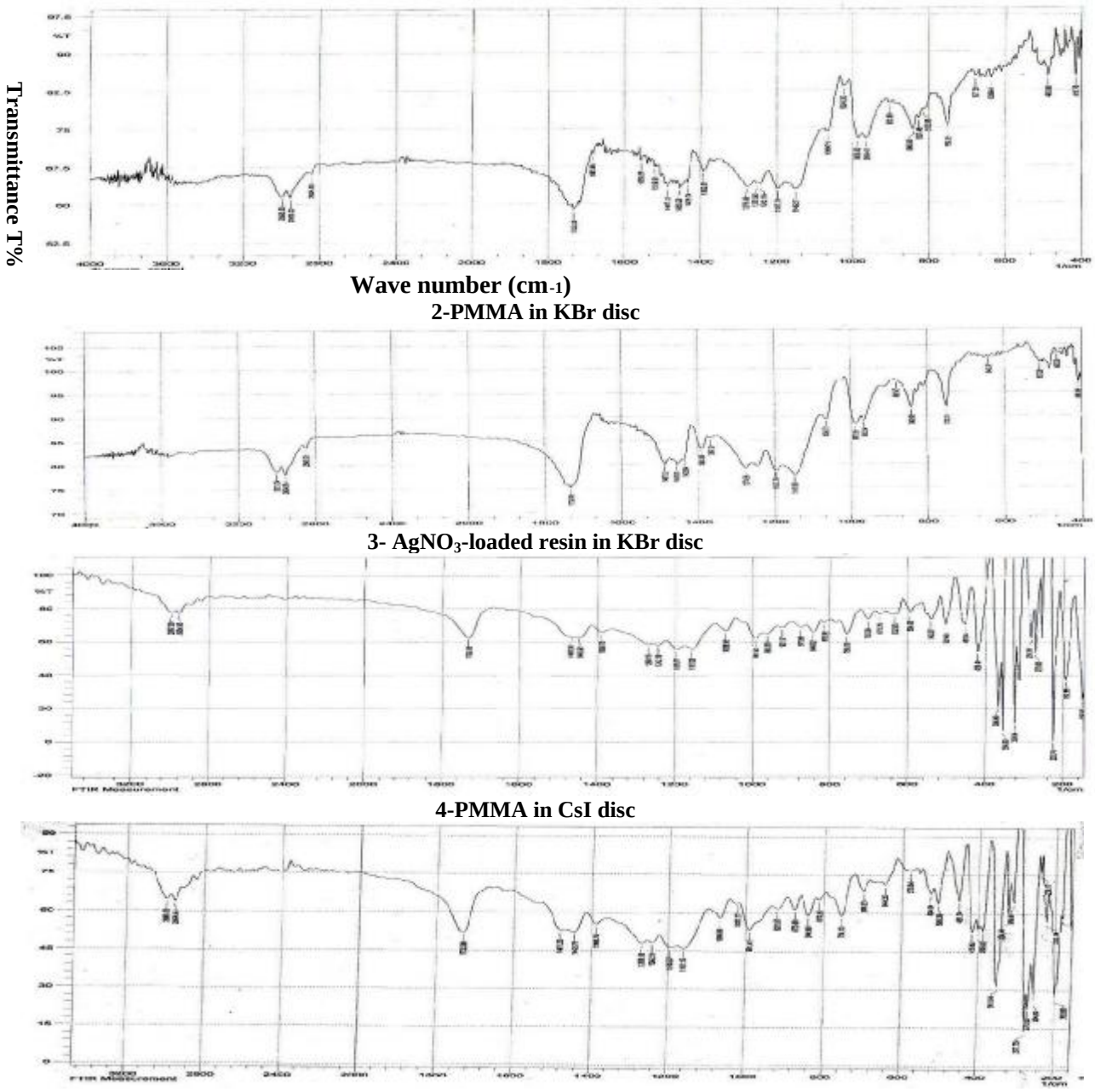


Fig. 2: FTIR spectrum

DISCUSSION

Visual inspection of $AgNO_3$ – loaded resin samples

It is believed that the discoloration for $AgNO_3$ loaded resins which was observed at 300 ppm $AgNO_3$ and above as illustrated in figure (1) was due to the presence of metal oxides from antibacterial metal ions during an oxidation-reduction reaction that occurs during a polymerization reaction, as well as the oxidation of the silver ions on the material surface [14,15].

It was also reported that by adding such antibacterial agent, due to the Ag^+ in it, the color tone of the denture base resin varies[16].

Characterization of $AgNO_3$-loaded resins

Since there is no change in the shape of absorption peaks between PMMA(control) and $AgNO_3$ – loaded resin samples as illustrated in the results of FTIR Figures(2-3-4-5) thus there is no chemical bond between the PMMA and $AgNO_3$ [22].

Impact strength test

The results of impact strength for the different concentrations of $AgNo_3$ shows in significant increase in impact strength (P= 0.05 NS) when compared with control as shown in Table (1-2).The 60ppm $AgNO_3$ was associated the highest increase in impact strength by 2.2KJ/ m^2 .This

could be due to the slow curing process allows greater number of nucleation sites to form and smaller particle sizes, thereby generating more particles [2], the total particle / matrix interfacial surface area available for energy dissipation increase, the critical stress for particle /matrix debonding also increase [17]. Also The increasing in the impact strength could be due to the presence of residual monomer [18,16]. This plasticizing effect render the fabricated acrylic resin samples more capable to absorb energy on impact and are more resistant to fracture[13].

The result of this study disagrees with Casemiro *et al.* [8] who added (2.5-10%) by wet Ag- Zeolite as a powder to acrylic dental resin resulted decrease in impact strength.

Transverse strength and Tensile strength tests

Among the specimens fabricated, the addition of silver nitrate in different concentrations reduces tensile strength (above 15 ppm $AgNO_3$) as shown in Table (5-6) and transverse strength Table (3-4) when compared with control as the concentration of silver nitrate increased, this is probably due to Ag^+ ions being reduced as the concentration of Ag increase, generating atom clusters and smaller particle size during the curing process which compete with complete polymerization process[2]. The plasticization effect of the resultant residual monomer will reduce the molecular binding force. On the other side, the results of FTIR Figures (2-3-4) showed no chemical bonding between PMMA and $AgNO_3$.Therefore we suppose that Ag^+ ions attack the double bond in the alkene group of the monomer molecule and will convert it to residual monomer [18]. This process will reduce the molecular binding force between the reactant molecules and allows greater deformation upon stretching or flexion through exhibiting multiple micro fractures that weaken the $AgNO_3$ – loaded resin samples [19,20].

Some other studies also showed that adding an antibacterial agent may affect the material properties, Kuroki *et al.* [16] have reported that there were significant differences of residual monomer in the samples treated by adding antimicrobial agents (Zeomic, BacteKiller, Novaron) although it was insignificant between the control and samples.

Fan *et al.* [2] found that by adding 0.15% (w/w) AgBz (silver benzoate) and above there was decrease in the degree of curing, result in reduction in Rockwell hardness for light cure resin. Nakanoda *et al.* [14] have reported that, as a result of tensile tests and bending tests, adding Silver-Zeolite to a heat-curing resin tends to decrease the material property depending on the additive concentrations of antibacterial agent of Zeomic.

There was in significant reduction in tensile strength with the lowest concentrations of $AgNO_3$ (9.375 and 15ppm) compared with control as shown in Table 5. This outcome is in agreement with Wakasa *et al.* [21] who reported that when the antimicrobial agent (Zeomic) is added to self – cure acrylic resin between 1% and 2%, the polymerization behavior of the resin is not inhibit.

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