Studies on Polyfunctional Cyclophosphazene Monomers for Dental Use (2)

—Physical Properties of Polymers—

by

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Abstract

The present studies were aimed at the development of monomers for dental resins, for which the authors substituted the 8 Cl atoms in $P_4N_4Cl_8$ with hydrophobic groups (Ph, TF and OF) and a polymerizing group (EMA), and bulk-polymerized them in order to examine their physical properties. Attention was focused on the relationship between the number of substituted hydrophobic groups and the mechanical properties, thermal expansion coefficient, polymerization shrinkage, contact angle, refractive index, water sorption and solubility to establish a basis for the practical use of cyclophosphazene monomers as dental resin monomers. The results obtained were as follows: compressive strength, transverse strength and hardness under dry conditions decreased in accordance with the increased number of substituted hydrophobic groups, but their degree of decrease in mechanical strength under wet conditions (after immersion in water) was small, proving that in comparison with PNC-EMA 4006, having no hydrophobic group, the mechanical properties under wet conditions were improved. It was found that by hydrophobic group substitution, contact angle increased and water sorption decreased. On the other hand, thermal expansion coefficient increased in accordance with the number of substituted hydrophobic groups, but polymerization shrinkage in all cases was very small, 3.09–9.08 vol%. Solubility also showed low values, 0.053–0.160 wt% when the number of substituted hydrophobic groups was 1–2.

Introduction

With the aim of strengthening the matrix of dental resins, the authors have

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synthesized various kinds of monomers possessing the -P=N- heterobond in their skeleton, and examined their properties^[1-4].

The monomers were prepared by substituting the 6 Cl atoms of hexachlorocyclotriphosphazene ($\text{P}_3\text{N}_3\text{Cl}_6$), with 2-hydroxyethylmethacrylate (HEMA), having polymerizing properties. It was proved that the compounds obtained by bulk-polymerization of these monomers showed preferable physical properties^[5] in comparison with those of conventional resins.

Then, in the previous study^[6], the authors used octachlorocyclotetraphosphazene ($\text{P}_4\text{N}_4\text{Cl}_8$), which belongs to the same family as hexachlorocyclotriphosphazene, reacting it with HEMA by the method of ANZAI and OHASHI^[1] to synthesize monomers having -P=N- in the skeleton. Likewise, 1-6 of the 8 Cl atoms were substituted with hydrophobic groups and then 7-2 of them with the methacryloxyethoxy group (EMA), a polymerizing group. Thus, 13 kinds of monomers^[6] were synthesized.

Hydrophobic groups used in the previous study were the phenoxy group (Ph), 2,2,2-trifluoroethoxy group (TF) and 2,2,3,3,4,4,5,5-octafluoropentoxy group (OF), 3 kinds in all.

From the results of IR and XMA, it was proved that the 13 kinds of monomers were all what the authors had expected to obtain. It also was proved that these monomers, colorless or light yellow, transparent, oily and with a viscosity of 3.8-7.0 poise, could be widely applicable as dental resin monomers.

The aim of the present study was to polymerize the monomers obtained in the previous study in order to determine their respective properties. The authors examined in particular the relationship between the number of substituted hydrophobic groups and the mechanical properties, thermal expansion coefficient, polymerization shrinkage, contact angle, refractive index, water sorption and solubility, to establish a basis for the practical use of cyclophosphazene monomers as dental resin monomers.

Materials and Methods

1. Materials

Thirteen kinds of monomers synthesized in the previous study were used. These were PNC-EMA monomer (4006, code no. used in the previous study) obtained by substituting the 8 Cl atoms of $\text{P}_4\text{N}_4\text{Cl}_8$ with EMA, PNC-Ph-EMA monomers, by substituting respectively 1.00 (4046), 2.00 (4043), 2.87 (4038) and 4.00 (4042) Ph groups, PNC-TF-EMA monomers, by substituting respectively 1.00 (4034), 2.10 (4012), 4.20 (4013) and 6.20 (4014) TF groups, and PNC-OF-EMA monomers, by substituting respectively 1.00 (4035), 2.00 (4017), 4.00 (4028) and 6.00 (4024) OF groups.

2. Bulk-polymerization method of compound formation

Compounds with 0.3 wt% of BPO mixed, sealed in a vacuum flask, were transferred to a vacuum drying oven (Yamato Science, DPF-31) for polymerization for 6 h at 60°C and then for 2 h at 120°C, and then taken out after being left to cool.

3. *Methods for measurement of physical properties*

1) Measurement of compressive strength

Compressive strength was measured using a universal testing machine (Minebea TCM-5000A). Specimens were $5\phi \times 10$ mm in size, and the measurement conditions were: cross-head speed 1 mm/min and load cell 5,000 kg. Five specimens each, either dry or wet (immersed in water at 37°C for 7 days), were measured to obtain the respective averages.

2) Measurement of transverse strength

As for compressive strength, transverse strength of specimens $3 \times 3 \times 40$ mm in size, was measured using a TCM-5000A by the 3-point transverse testing method, with a fulcrum distance of 30 mm and a cross-head speed of 1 mm/min. Five specimens each, either dry or wet, were measured to obtain the respective averages.

3) Measurement of hardness

Knoop hardness was measured. The Knoop indenter used was set on a micro Vickers hardness tester (Akashi), and measurement was carried out with a load of 50 (or 25) g and a pressure time of 30 s. Hardness was expressed in H_k . Specimens (surface mirror-ground), $9\phi \times 10$ mm in size, and three dry and wet samples, respectively, were prepared, and the hardness of each was measured at 4 different points to obtain an average.

4) Measurement of thermal expansion coefficient

Thermal expansion coefficient was measured using a thermal mechanical analyzer (Rigaku), with quartz glass as the standard substance. Specimens as well as the standard substance were $5\phi \times 10$ mm in size, and measurement was carried out under the following conditions: constant load 2 g, heating rate 5°C/min and TMA-RANGE 250 μ m. Specimens were heated from room temperature to 130°C to obtain the thermal expansion curve, from which the trend (i.e., thermal expansion coefficient) was determined by the method of least squares.

5) Specific gravity of polymers and polymerization shrinkage

Specific gravity of polymers, d_{30}^{30} , was measured using a specific gravity bottle (Hubbard type). The size of the specimens was the same as that for the hardness test and 5 specimens were placed into the bottle for measurement. From the values obtained and the specific gravity of the monomers, polymerization shrinkage (vol%) was calculated.

6) Measurement of contact angle

Contact angle to water of the bulk polymers was measured with a goniometer-type contact angle meter (Erma, G-I) at a room temperature of 23°C. Specimens, $25 \times 17 \times 2$ mm in size were polymerized on smooth, clean slide-glasses. A water drop, 0.05 ml, was then placed on the surface of each specimen and after 1 min, the contact angles of the water drop on both sides were measured at 5 different points to obtain an average.

7) Measurement of refractive index

Refractive index, n_D^{25} , of polymers was measured with an Abbe refractometer, using specimens $5 \times 12 \times 15$ mm in size. Measurement was carried out

through 1-bromonaphthalene medium (Wako) set between the specimens and the specimen stand. Two specimens were measured to obtain an average.

8) Measurement of water sorption and solubility

Five specimens, each $5 \phi \times 10$ mm, were prepared for water sorption and solubility tests. The specimens were first put into a vacuum drying oven at 60°C until they reached constant weight (W_o). Then, they were immersed in pure water at 37°C and taken out after 1, 3 and 7 days. They were weighed immediately after wiping off the extraneous water to obtain their wet weight (W_w). Then, those immersed in water for 7 days were placed again in the vacuum drying oven at 60°C to obtain their constant weight (W_d). Water sorption was calculated using the relation $(W_w - W_o)/W_o \times 100$, and solubility in Figs. 1–15. Those of PNC-EMA (4006) are also shown in the respective figures.

Results and Discussion

Mechanical properties, thermal expansion coefficient, polymerization shrinkage, contact angle and refractive index of the 13 kinds of bulk polymers are shown in Table 1, their water sorption and solubility in Table 2 and their physical properties in Figs. 1–15. Those of PNC-EMA (4006) are also shown in the respective figures.

1. Compressive strength

Figures 1, 2 and 3, respectively, show the compressive strength of the bulk polymers PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA in that order. As shown in the figures and Table 1, the compressive strength of the bulk polymers PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA, both dry and wet, decreased with the increase in the number of substituted hydrophobic groups (decrease in the number of substituted EMA groups). Again in all cases, the wet specimens had a smaller compressive strength than the dry ones. On comparing these bulk polymers having 1–4 hydrophobic groups, it was found that in the case of PNC-TF-EMA, containing TF, both dry and wet specimens showed comparatively large compressive strengths. However, for practical use, a large compressive strength is desirable even in wet conditions. Specimens with a hydrophobic group substitution number of 1, i.e., PNC-Ph-EMA 4041, PNC-TF-EMA 4034 and PNC-OF-EMA 4035, showed comparatively large values of 2034–3114 kg/cm^2 under wet conditions, showing an improving effect on water-resisting properties.

2. Transverse strength

Figures 4, 5 and 6, respectively, show the transverse strength of the bulk polymers PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA, in that order. As shown in the figures and Table 1, as in the case of compressive strength, the transverse strength of the bulk polymers PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA, both dry and wet, decreased in accordance with the increase in the number of substituted hydrophobic groups (decrease in the number of substituted EMA groups). In all cases, the wet specimens had a smaller transverse strength than the dry ones. Especially, with an increased number of hydrophobic groups, the strength showed

Table 1 Some physical properties of PNC-EMA, PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA polymers

Polymer	Code	Compressive Strength (kg/cm ²)	Transverse Strength (kg/cm ²)	H _K	Thermal Expansion Coefficient ($\times 10^{-6}/^{\circ}\text{C}$)	Polymerization Shrinkage (vol %)	Contact Angle (deg)	n _D ²⁵
PNC-EMA	4006 DRY	4,574 (276)	542 (80)	40.5 (1.8)	66.9	9.36	62.0 (1.3)	1.5095
	WET	3,200 (374)	380 (33)	20.0 (0.9)				
PNC-Ph-EMA	4041 DRY	3,606 (149)	548 (88)	17.5 (1.5)	78.4	5.83	43.2 (2.6)	1.5336
	WET	3,109 (186)	282 (106)	17.0 (0.7)				
	4043 DRY	2,822 (116)	352 (95)	12.9 (0.9)	101.4	7.97	49.9 (2.3)	1.5440
	WET	2,116 (321)	191 (31)	12.0 (0.3)				
	4038 DRY	2,205 (39)	370 (10)	10.1 (0.4)	121.0	6.32	81.3 (2.4)	1.5483
	WET	1,566 (157)	245 (22)	8.4 (0.3)				
	4042 DRY	1,796 (175)	297 (22)	6.5 (0.5)	135.4	5.15	73.7 (2.3)	1.5544
	WET	1,382 (209)	130 (14)	6.4 (0.3)				
PNC-TF-EMA	4034 DRY	3,905 (109)	480 (69)	19.9 (1.3)	79.0	6.42	63.6 (10.7)	1.5080
	WET	3,114 (226)	435 (46)	19.5 (0.8)				
	4012 DRY	3,350 (359)	440 (26)	19.4 (0.5)	84.1	7.41	74.3 (3.1)	1.4909
	WET	2,706 (385)	446 (91)	16.6 (1.0)				
	4013 DRY	2,051 (43)	349 (53)	13.6 (0.8)	132.6	7.40	103.6 (2.8)	1.4521
	WET	1,758 (229)	303 (72)	9.5 (0.5)				
	4014 DRY	788 (102)	218 (20)	5.3 (0.3)	202.6	9.08	119.0 (4.4)	1.4209
	WET	601 (57)	207 (19)	4.5 (0.3)				
PNC-OF-EMA	4035 DRY	3,512 (240)	577 (94)	17.5 (1.2)	88.0	8.98	68.8 (2.4)	1.4952
	WET	2,874 (146)	355 (65)	16.2 (0.5)				
	4017 DRY	2,169 (404)	323 (42)	13.0 (0.3)	115.4	7.79	47.3 (2.1)	1.4680
	WET	1,704 (192)	192 (49)	11.5 (0.6)				
	4028 DRY	1,116 (74)	139 (83)	6.8 (0.1)	155.6	6.89	96.5 (4.5)	1.4370
	WET	825 (226)	137 (27)	6.7 (0.2)				
	4024 DRY	451 (34)	75 (13)	3.2 (0.2)	201.6	3.09	94.0 (2.8)	1.4180
	WET	213 (36)	18 (5)	2.9 (0.3)				

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Table 2 Water sorption and solubility of PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA polymers

Polymer	Code	Water Scrpption at 7 days (wt%)	Solubility (wt%)
PNC-EMA	4006	2.493	0.161
PNC-Ph-EMA	4041	2.188	0.101
	4043	1.725	0.053
	4038	1.453	0.153
	4042	0.876	0.676
PNC-TF-EMA	4034	2.163	0.121
	4012	1.700	0.139
	4013	1.102	0.028
	4014	0.536	0.025
PNC-OF-EMA	4035	1.822	0.131
	4017	1.278	0.160
	4028	0.598	0.163
	4024	0.360	0.180

Fig. 1 Compressive strength of PNC-Ph-EMA polymers

Fig. 2 Compressive strength of PNC-TF-EMA polymers

Fig. 3 Compressive strength of PNC-OF-EMA polymers

Fig. 4 Transverse strength of PNC-Ph-EMA polymers

Fig. 5 Transverse strength of PNC-TF-EMA polymers

Fig. 6 Transverse strength of PNC-OF-EMA polymers

Fig. 7 Knoop hardness of PNC-Ph-EMA polymers

Fig. 8 Knoop hardness of PNC-TF-EMA polymers

a decreasing tendency, both in dry and wet specimens. Therefore, it was considered that samples having more than 4 hydrophobic groups were not suitable for practical use. However, those with a small number of hydrophobic groups, i.e., PNC-TF-EMA 4034, 4012 and PNC-OF-EMA 4035, showed comparatively large values, 355–446 kg/cm² in wet conditions.

3. Knoop hardness

Figures 7, 8 and 9, respectively, show the Knoop hardness values of the bulk polymers PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA, in that order. As shown in the figures and Table 1, the Knoop hardness of PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA, as in the cases of compressive strength and transverse strength, decreased in accordance with the increased number of substituted hydrophobic groups, both in dry and wet samples. Again, the wet samples had a smaller Knoop hardness than the dry ones, but the degree of decrease was small in comparison with that of PNC-EMA 4006. The degree of decrease occurred in the following order: OF=Ph>TF, presumably in accordance with the degree of steric hindrance produced during polymerization by the difference in the bulk density of the hydrophobic group.

Results 1–3 show that the mechanical properties of the 12 kinds of bulk polymers had small values in comparison with those of PNC-EMA 4006. This was presumably caused by the decrease in the ratio of the polymerizing group, substitution with hydrophobic group and by steric hindrance due to the bulk density and the number of hydrophobic groups.

Fig. 9 Knoop hardness of PNC-OF-EMA polymers

Fig. 10 Thermal expansion coefficient of PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA polymers

On the other hand, it was proved that by substitution of the hydrophobic groups, the change in mechanical properties before and after immersion in water became small, in comparison with PNC-EMA 4006, proving that the water-resisting properties were improved.

4. Thermal expansion coefficient

Figure 10 shows the thermal expansion coefficient of the bulk polymers PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA. As shown in the figure and Table 1, the thermal expansion coefficient of the bulk polymers PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA, in all cases, decreased in accordance with the increase in the number of substituted EMA polymerizing groups. Where the number of substituted hydrophobic groups was the same, PNC-TF-EMA showed the smallest value of thermal expansion coefficient, followed by PNC-Ph-EMA and PNC-OF-EMA in that order. This was presumably due to the decrease in the polymerizing groups, in accordance with the increase in the number of substituted hydrophobic groups and the decrease in cross-linking density of the set products caused by steric hindrance of the hydrophobic groups. PNC-TF-EMA 4014, with a large number of substituted hydrophobic groups, showed almost the same thermal expansion coefficient as PNC-OF-EMA 4024. However, the reason for this was not clear.

5. Polymerization shrinkage

Figure 11 shows the polymerization shrinkage of PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA monomers. As indicated in the figure

Fig. 11 Polymerization shrinkage of PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA polymers

Fig. 12 Contact angle of PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA polymers

and Table 1, the polymerization shrinkage of the synthesized monomers showed values in the range of 3.09–9.08 vol%, small in comparison with that of PNC-EMA 4006, 9.36 vol%, but the relationship of this trend to the kinds of substituents and their numbers was not investigated. However, it was proved that the polymerization shrinkage was very small in comparison with that of MMA, 21 vol%^[7].

6. Contact angle

Figure 12 shows the contact angle to water of the bulk polymers PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA. As shown in the figure and Table 1, the contact angle, except in the cases of PNC-Ph-EMA 4041, 4043 and PNC-OF-EMA 4017, was large, compared with that of PNC-EMA 4006, 62.0°, and especially in the case of PNC-TF-EMA, the contact angle increased almost linearly in accordance with the number of hydrophobic groups. However, in the above cases of PNC-Ph-EMA 4041, 4043 and PNC-OF-EMA 4017, the contact angle was small in comparison with the case of PNC-EMA 4006, despite the substitution of the hydrophobic group.

The present experiments at least showed that the contact angle obtained in the case of PNC-TF-EMA 4013, 4014 and PNC-OF-EMA 4028 and 4024, was large in comparison with that between hydrophilic denture base resin and water, 67.4°, and that of normal-type denture base resin, 73.5°^[8].

Fig. 13 Refractive index of PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA polymers

Fig. 14 Water sorption at 7 days of PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA polymers

7. Refractive index

Figure 13 shows the refractive index of the bulk polymers PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA. In the case of PNC-Ph-EMA, the refractive index increased almost linearly in accordance with the increase in the number of substituted Ph groups, but in the cases of TF and OF, it conversely decreased in accordance with the increase in substitution number.

The refractive index of these bulk polymers, in all cases, in comparison with that^[6] of monomers, showed large values, 0.0151–0.0279.

8. Water sorption and solubility

Table 2, Figs. 14 and 15 show the water sorption and solubility of specimens immersed in water for 7 days. Water sorption, for all of PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA, decreased in accordance with the increase in the number of substituted hydrophobic groups. From these values, it was proved that the water sorption of bulk polymers possessing a hydrophobic group, in comparison with that of PNC-EMA 4006, 2.493%, was small. Again, when the substitution number (1–3) of hydrophobic groups was the same, water sorption showed the smallest value in the case of PNC-OF-EMA and approximately the same values for both PNC-TF-EMA and PNC-Ph-EMA. In other words, PNC-EMA, with no hydrophobic group, showed a slightly larger water sorption than denture base resin^[9], and when the number of substituted hydrophobic groups was 1–3, it became approximately the same as that of denture base resin,

Fig. 15 Solubility at 7 days of PNC-Ph-EMA, PNC-TF-EMA and PNC-OF-EMA polymers

while the greater the substitution number, the smaller it became.

Solubility, as shown in Table 2 and Fig. 15, differed in accordance with the types of hydrophobic group. That is, in accordance with the increase in the number of substituted hydrophobic groups, it showed a decreasing tendency in the case of TF, an increasing tendency in the case of OF and became smallest, with a substitution number of 2, in the case of Ph.

Water sorption and solubility of Bis-GMA, which is widely used as a base monomer for composite resins, are 2.48 and 2.66 wt%^[10] respectively, but the water sorption of the present bulk polymers, except for PNC-EMA, 2.49 wt%, were smaller, and the solubility was also smaller in all cases.

As shown above, in the 13 kinds of monomers possessing cyclophosphazene in the skeleton, which were bulk-polymerized, compressive strength, transverse strength and hardness under dry conditions decreased in accordance with the increase in the number of substituted hydrophobic groups, but the degree of decrease in the mechanical strength under wet conditions (after immersion in water) was small, proving that in comparison with PNC-EMA 4006, possessing no hydrophobic group, the mechanical properties under wet conditions were improved. Again, it was found that by substitution of hydrophobic groups, the contact angle increased and water sorption decreased.

On the other hand, the thermal expansion coefficient increased in accordance with the increase in the number of substituted hydrophobic groups, but polymerization shrinkage in all cases was very small, 3.09–9.08 vol%. Solubility also showed small values, 0.053–0.160 wt%, when the number of substituted hydrophobic groups was 1–2.

Ideal compounds for use as dental resins should preferably have mechanical properties showing a small decrease even after immersion in water, and should have a small polymerization shrinkage as well as low water sorption and solubility. Also, in accordance with the purposes for which they are applied, they should have a small thermal expansion coefficient, and if they are applied for light-cured resins, they should preferably have the same refractive index as the filler. Thus, in order to use these compounds practically, the optimum monomers should be selected in accordance with the properties of the 13 kinds of polymers described above.

As shown here, as well as in the previous study, it was proved that the 13 kinds of synthesized monomers were low in viscosity. Furthermore, when bulk-polymerized, the polymers showed high values of physical properties. Consequently, it was proved that by using them alone or together with monomers currently available on the market as monomers for denture base, filling and crown and bridge resins, the matrix of resins could be strengthened. In other words, these compounds are widely applicable as dental resin monomers. The authors therefore plan to examine a practical composition for these compounds in the near future.

Conclusion

The present studies were conducted in order to develop monomers for dental resins, in which the 8 Cl atoms of $P_4N_4Cl_8$ were substituted with hydrophobic groups (Ph, TF and OF) and a polymerizing group (EMA), and bulk-polymerized to examine their physical properties. The results were as follows:

1. Compressive strength, transverse strength and hardness of bulk-polymers decreased in accordance with the increased number of substituted hydrophobic groups.
2. When the bulk polymers were immersed in 37°C water, compressive strength, transverse strength and Knoop hardness decreased in comparison with dry specimens, but the degree of decrease was small in comparison with compounds in which the hydrophobic groups were not substituted.
3. Thermal expansion coefficient of bulk polymers also increased in accordance with the increase in substitution number, the thermal expansion coefficients being $PNC-TF-EMA < PNC-Ph-EMA < PNC-OF-EMA$, in that order.
4. Polymerization shrinkage of the 13 kinds of bulk polymers showed small values, 3.09–9.08 vol%.
5. Contact angle of bulk polymers to water showed a tendency to increase in accordance with the increase in the number of substituted hydrophobic groups.
6. Refractive index of bulk polymers in the case of the Ph hydrophobic group increased almost linearly in accordance with the increase in substitution number, but in the cases of TF and OF, it decreased.
7. Water sorption of bulk polymers, in the case of any hydrophobic substituent, increased with time. However, it decreased with the increase in the number of hydrophobic substituent groups, and when the number of substituents was the same, the order was: $PNC-OF-EMA < PNC-Ph-EMA =$

PNC-TF-EMA.

8. Solubility of the 13 kinds of bulk polymers immersed in water for 7 days showed small values, 0.025–0.676 wt%, in all cases.
9. Among 13 kinds of bulk polymers, the one which was most preferable with regard to mechanical properties, showed the smallest decrease in mechanical properties after immersion in water, and the smallest water sorption, solubility and thermal expansion coefficient, and it was PNC-TF-EMA 4034. In this case, polymerization shrinkage was 6.42 vol%, compressive strength and transverse strength were 3905 and 480 kg/cm² respectively, the Knoop hardness was 19.9, thermal expansion coefficient $79.0 \times 10^{-6}/^{\circ}\text{C}$ and contact angle to water, 63.6°. Again, compressive strength and transverse strength after immersion in 37°C water were 3114 and 435 kg/cm² respectively, and the Knoop hardness 19.5.

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