

# Boron Nitride Particle Filled Paraffin Wax as a Phase-Change Thermal Interface Material

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*Wax (predominantly tricosane paraffin wax, with a melting temperature of 48°C) filled with hexagonal boron nitride (BN) particles (5–11 μm) was found to be an effective phase-change thermal interface material. The thermal contact conductance, as measured with the interface material between copper surfaces, decreased with increasing temperature from 22 to 48°C, but increased with increasing temperature from 48 to 55°C. The melting of the wax enhanced the conductance, due to increased conformability to the mating surfaces. For a given BN volume fraction and a given temperature, the thermal contact conductance increased with increasing contact pressure. However, a pressure above 0.30 MPa resulted in no significant increase in the conductance. The conductance increased with BN content up to 6.2 vol. %, but decreased upon further increase to 8.6 vol. %. The highest conductance above the melting temperature was  $18 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ , as attained for a BN content of 4.0 vol. % at 55°C and 0.30 MPa. Below the melting temperature, the highest conductance was  $19 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ , as attained for a BN content of 6.2 vol. % at 22°C and 0.30 MPa.*  
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## Introduction

Heat dissipation is important in the electronic industry in relation to the miniaturization of electronics and electronics packaging. Much attention has been given to the development of materials with high thermal conductivity for electronic devices and heat sinks for the purpose of alleviating the heat dissipation problem [1–3]. Another issue involved in heat dissipation is how to efficiently remove the heat from an electronic device to a heat sink. Both the surface of a heat sink and that of an electronic device are not smooth enough to avoid air gaps at the interface between heat sink and device. Air has a very low thermal conductivity of  $0.027 \text{ W/m} \cdot ^\circ\text{C}$ . The current strategy to resolve this problem is using a thermal interface material between the two components so as to fill in the surface irregularities, eliminate the air pockets and gaps, and consequently facilitate the heat transfer. Desired properties of thermal interface materials include high thermal conductivity, good thermal stability during thermal cycling, and high fluidity. Fluidity is essential for conformability to the topography of the mating surfaces. It is also important for spreadability, which is needed to obtain a small thickness of the interface material.

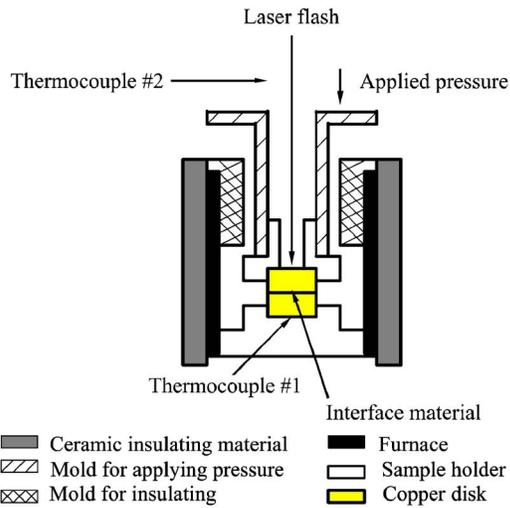
Thermal interface materials can roughly be classified as coatings [4–7], thermal fluids [8], thermal grease [9–11], and resilient thermal conductors [12,13]. Metals such as tin, aluminum, silver and copper [4,6] are often used as coating materials because of their low hardness, which increases the total contact area of the joint, and their high thermal conductivity, which enhances the heat transfer from heat source to heat sink. However, metal coatings usually need to be sintered, electroplated, or deposited on the desired substrate surfaces, and the processing is more complicated than using other thermal interface materials. Thermal greases (pastes) are most commonly made of silicone with thermally con-

ductive particle fillers [9,14]. The main disadvantages of silicone greases are low fluidity, messiness and difficulty of removal by dissolution. A resilient thermal conductor often requires an applied pressure to hold it between the mating surfaces and hence is sometimes inconvenient for use. Mineral oils are attractive in their fluidity and are often used as thermal fluids. A common disadvantage of using a thermal fluid or a thermal grease is that it tends to flow out, whether it is in service or not. As shown in our previous research, which evaluated by calorimetry various phase change materials for use as thermal interface materials [15], a paraffin wax is a potentially good thermal interface material. It is in the solid state at room temperature and changes to the liquid state around 48°C. Hence, high conformability can be attained at service temperatures above the melting temperature of the wax. Moreover, it is stable during thermal cycling. The use of phase change materials as thermal interface materials has been mentioned in a few patents [16–18].

Various thermal contact conductance ( $\text{W/m}^2 \cdot ^\circ\text{C}$ ) models have been derived for rough surface contacts [19,20] and elastic contacts [21] in which no thermal interface material that was based on a liquid or a semi-solid was used. Experimental thermal contact conductance measurement has been conducted on various thermal interface materials such as solder, mineral oil, sodium silicate/BN, silicone/ZnO, silicone/BN, polymer/ZnO, and epoxy/graphite [22]. Boron nitride (BN) particles are effective as a thermally conductive filler for thermal interface materials [22]. Little research work has been done on the effect of temperature on the thermal conductance of thermal interface materials, even though temperature is an important variable in thermal management.

By using paraffin wax as the base material and hexagonal boron nitride particles as the thermally conductive filler, thermal interface materials with various volume fractions of BN have been developed in the present work. The aim of this work is to investigate the effects of pressure, temperature, and BN content on the thermal contact conductance of a phase-change thermal interface material.

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**Fig. 1 Experimental set-up for thermal contact conductance measurement**

### Experimental Methods

The hexagonal boron nitride (BN) particle used as a thermally conductive filler is Polartherm 180 from Advanced Ceramics Corp., Cleveland, OH. Their size range is about 5–11  $\mu\text{m}$ . The thermal conductivity is about 280 W/m.k. The paraffin wax, predominantly tricosane paraffin ( $\text{C}_{23}\text{H}_{48}$ ), was supplied by Crystal, Inc. -PMC, Lansdale, PA. Its melting temperature is 48°C, as shown by calorimetry [15].

The thermal interface material is the paraffin wax mixed with boron nitride, as prepared by mixing the wax and boron nitride particles in the weight ratio of 0, 5, 10, 15, and 20 wt. % (corresponding to 0, 1.9, 4.0, 6.2, and 8.6 vol. %). The mixture of wax and BN particles was put in an aluminum pan and heated to 60°C in a water bath. Manual mixing was conducted for 15 min after the wax had melted. The resulting paste (a thermal interface material) was sandwiched by two copper disks. The thickness of the thermal interface material was about 30  $\mu\text{m}$ , as measured by a micrometer by subtracting the total thickness of the sandwich from the thickness of the two copper disks. Both copper disks had diameter 12.68 mm and thickness 1.05 mm. Various pressures (0.08, 0.18, 0.30, and 0.43 MPa) were applied on the sandwich. The same pressure was applied during sandwich preparation and testing.

The transient laser flash method was used to measure the thermal contact conductance across two copper disks with a thermal interface material between them. A Coherent General Everpulse

Model II Nd glass laser with a pulse energy up to 15 J, a pulse duration of 0.4 ms and a wavelength of 1.06  $\mu\text{m}$  was used for impulse heating. Both surfaces of each copper disk were polished with 0.05  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  powders. The top surface of the upper copper disk (disk #1 in the experimental set-up, as shown in Fig. 1) had been electroplated with black nickel in order to increase the absorption of laser beam. An E-type thermocouple (#1) was attached to the bottom surface of copper disk #2 in order to monitor the temperature change after the upper surface of copper disk #1 had been hit by the laser beam. Another E-type thermocouple (#2) was set about 10 cm above the sample assembly in order to monitor the time of emergence of the laser beam. Both E-type thermocouples were connected to a National Instruments DAQPAD-MIO-16XE-50 data acquisition board, which was connected to a computer. NI-DAQ software coded in Visual Basic was used in the computer to monitor the response of both E-type thermocouples simultaneously. The time ( $t_{0.5}$ ) for the temperature to rise to half of the temperature difference between the maximum temperature and the initial temperature from thermocouple #1, was used in the finite element program ABAQUS to calculate the thermal contact conductance [22,23]. The time lag of the thermocouple caused by the systematic error for  $t_{0.5}$  was determined by using a standard NBS 8426 graphite disk and a pure copper disk [24], which then was used to correct the  $t_{0.5}$  for each sample.

A resistance furnace, also shown in Fig. 1, was used to heat the sample. The furnace was electrically disconnected during laser flash and data acquisition. The pressure was applied by using steel rings, which were put on the top of the mold, as shown in Fig. 1.

### Results

Table 1 gives the variation with temperature of the thermal contact conductance for wax/BN thermal interface materials with 0, 1.9, 4.0, 6.2, and 8.6 vol. % BN. No pressure was applied. The thermal contact conductance was significantly increased by the presence of BN, even at a BN content of 1.9 vol. %. Increase of the BN volume fraction enhanced the thermal contact conductance. A BN content of 6.2 vol. % resulted in the highest thermal contact conductance in Table 1. Further increase of the BN content to 8.6 vol. % decreased the thermal contact conductance, due to the decrease in fluidity (as shown by the feel during manual mixing) and the consequent reduction in conformability. That the contact conductance is maximum at an intermediate content of BN particles has been previously reported for the case of polyethylene glycol (liquid) as the base material of BN pastes [23].

For a given BN content, the thermal contact conductance decreased with increasing temperature up to 48°C, and then increased as the temperature increased from 48 to 55°C. Further increase of the temperature above 55°C decreased the thermal contact conductance slightly in most cases.

**Table 1 Variation of thermal contact conductance ( $10^4 \text{ W/m}^2 \text{ }^\circ\text{C}$ ) with temperature for various thermal interface materials under no pressure with a thermal interface material thickness of 30  $\mu\text{m}$**

Temperature (°C)	Thermal interface materials				
	Wax	Wax/BN (1.9 vol. %)	Wax/BN (4.0 vol. %)	Wax/BN (6.2 vol. %)	Wax/BN (8.6 vol. %)
22	0.63±0.03	1.92±0.08	3.75±0.13	6.32±0.12	5.58±0.26
30	0.57±0.05	1.33±0.11	3.39±0.20	4.77±0.24	4.02±0.14
40	0.42±0.03	1.18±0.09	2.80±0.19	3.65±0.11	2.94±0.15
45	0.39±0.05	0.99±0.07	2.08±0.08	3.25±0.16	1.95±0.12
48	0.40±0.04	0.92±0.10	2.20±0.11	3.16±0.16	1.88±0.13
50	0.43±0.06	1.02±0.06	2.37±0.05	3.97±0.13	2.35±0.18
55	0.48±0.07	1.38±0.05	2.70±0.10	4.89±0.12	3.21±0.14
60	0.47±0.06	1.42±0.09	2.61±0.15	4.74±0.21	3.07±0.16

**Table 2 Variation of thermal contact conductance ( $10^4 \text{ W/m}^2 \text{ }^\circ\text{C}$ ) with temperature for various thermal interface materials under a pressure of 0.18 MPa**

Temperature ( $^\circ\text{C}$ )	Thermal interface materials			
	Wax	Wax/BN (4.0 vol. %)	Wax/BN (6.2 vol. %)	Wax/BN (8.6 vol. %)
22	3.90±0.20	14.35±0.41	15.02±0.56	7.62±0.35
30	2.51±0.33	13.33±0.51	13.03±0.71	7.08±0.28
40	2.16±0.32	12.21±0.32	12.35±0.64	5.82±0.29
45	2.11±0.27	10.75±0.27	11.41±0.69	5.08±0.31
48	2.03±0.18	9.43±0.50	10.55±0.79	3.77±0.17
50	2.46±0.45	11.21±0.38	11.96±0.62	4.21±0.15
55	2.87±0.49	13.02±0.43	16.07±0.73	5.71±0.21
60	3.09±0.33	13.07±0.57	16.15±0.82	5.61±0.27

The relationship between temperature and the thermal contact conductance of wax filled with BN at different volume fractions under a pressure of 0.18 MPa is given in Table 2. Comparison of Tables 1 and 2 shows that the increase in pressure from 0 to 0.18 MPa greatly enhanced the thermal contact conductance. The enhancement was particularly pronounced if the BN content was low (e.g., 4.0 vol. %). The effect was small at 8.6 vol. % BN.

Further increase of the applied pressure from 0.18 to 0.30 MPa further enhanced the thermal contact conductance (Table 3), though the enhancement caused by increasing the pressure from 0.18 to 0.30 MPa was small (though substantial) compared to that caused by increasing the pressure from 0 to 0.18 MPa. As shown in Tables 1–3, wax/BN (8.6 vol. %) gave lower thermal contact conductance than wax/BN (6.2 vol. % BN). The thermal contact conductance was lower at 4.0 vol. % BN than at 6.2 vol. % in all of Tables 1–3, except for the highest two temperatures (55 and 60 $^\circ\text{C}$ ) in Table 3. This exception may be caused by both the larger extent of thickness reduction of the interface material as the pressure increased and the greater ease of thinning when the BN content was lower.

The variation with temperature of the thermal contact conductance for wax/BN thermal interface materials is also shown in Fig. 2 for an applied pressure of 0.08 MPa. Figs. 2(a) and 2(b) correspond to wax/BN (4.0 vol. %) and wax/BN (8.6 vol. %), respectively. It is clear that the thermal contact conductance decreased with temperature up to 48 $^\circ\text{C}$  and then increased. Heating over 55 $^\circ\text{C}$  may have a slightly negative effect on the thermal contact conductance, as in the case of Fig. 2(b). Figures 3(a) and 3(b) show corresponding results for a pressure of 0.43 MPa. The increase in thermal contact conductance above 48 $^\circ\text{C}$  was even clearer at the higher pressure, especially at a low BN content of 4.0 vol. % (Fig. 3(a)).

Figure 4 shows the variation with the BN content of thermal contact conductance for various temperatures and a pressure of 0.30 MPa. The conductance increased with increasing BN content up to 4.0 or 6.2 vol. % and then decreased upon further increase beyond 6.2 vol. %. For a given BN volume fraction, the conductance decreased with increasing temperature up to 48 $^\circ\text{C}$  and then increased upon further increase of the temperature to 55 $^\circ\text{C}$ .

The relationship between thermal contact conductance and pressure is shown in Fig. 5 for a BN content of 4.0 vol. %. The conductance increased with increasing pressure up to 0.30 MPa. Further increase in pressure to 0.43 MPa resulted in relatively little increase, if any, in the conductance. At 55 $^\circ\text{C}$ , the conductance at a pressure of 0.43 MPa was even less than that at 0.30 MPa, possibly due to the outflow of wax at this combination of high temperature and high pressure.

The thermal contact conductance for wax/BN (6.2 vol. %) in this work is  $19 \times 10^4 \text{ W/m}^2 \text{ }^\circ\text{C}$  at 22 $^\circ\text{C}$  under 0.30 MPa, which is close to the values of  $21 \times 10^4$ ,  $19 \times 10^4$  and  $19 \times 10^4 \text{ W/m}^2 \text{ }^\circ\text{C}$ . attained, respectively, by solder, polyethylene glycol filled with BN and sodium silicate filled with BN [22,23].

## Discussion

Compared to boron nitride, wax has a very low modulus. It is soft and easy to change shape. Boron nitride has a higher thermal conductivity. The addition of BN to wax increases its strength and thermal conductivity. Therefore, wax filled with more BN gives a higher thermal contact conductance at the same temperature and pressure. However, the addition of BN also reduces the fluidity, thus decreasing the conformability and the thermal contact conductance.

As mentioned above, the addition of BN (up to 6.2 vol. %) to

**Table 3 Variation of thermal contact conductance ( $10^4 \text{ W/m}^2 \text{ }^\circ\text{C}$ ) with temperature for various thermal interface materials under a pressure of 0.30 MPa**

Temperature ( $^\circ\text{C}$ )	Thermal interface materials			
	Wax	Wax/BN (4.0 vol. %)	Wax/BN (6.2 vol. %)	Wax/BN (8.6 vol. %)
22	6.51±0.34	15.69±0.55	19.01±1.03	11.33±0.45
30	4.72±0.51	15.11±0.39	15.46±0.78	8.91±0.44
40	3.65±0.56	14.35±0.51	14.67±0.53	7.57±0.51
45	3.40±0.33	13.53±0.25	14.04±0.61	6.18±0.36
48	3.41±0.41	9.98±0.50	12.99±0.72	5.49±0.45
50	4.32±0.39	11.07±0.44	13.91±0.41	7.48±0.22
55	4.85±0.42	17.91±0.86	17.11±0.36	8.61±0.40
60	4.76±0.65	18.19±0.91	16.89±0.84	8.73±0.54

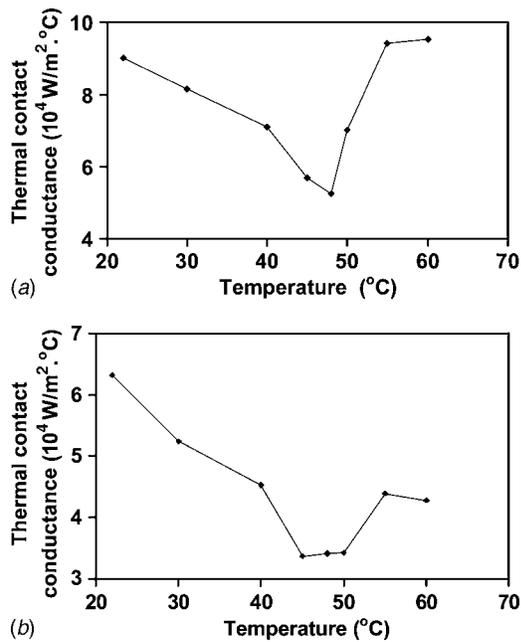


Fig. 2 Variation with temperature of the thermal contact conductance of wax filled with (a) 4.0 vol. % BN and (b) 8.6 vol. % BN. The pressure is 0.08 MPa.

wax enhanced the thermal contact conductance. A higher content of BN (8.6 vol. %) resulted in a lower thermal contact conductance (Tables 1–3), due to its negative effect on the fluidity and conformability.

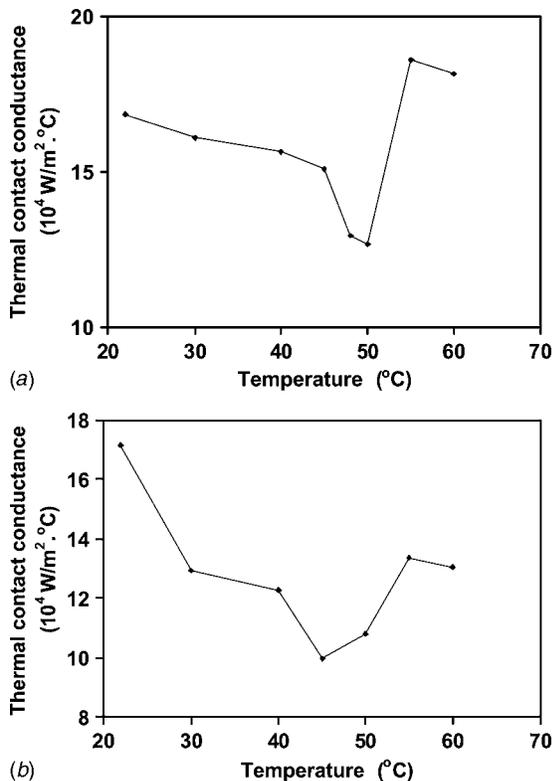


Fig. 3 Variation with temperature of the thermal contact conductance of wax filled with (a) 4.0 vol. % BN and (b) 8.6 vol. % BN. The pressure is 0.43 MPa.

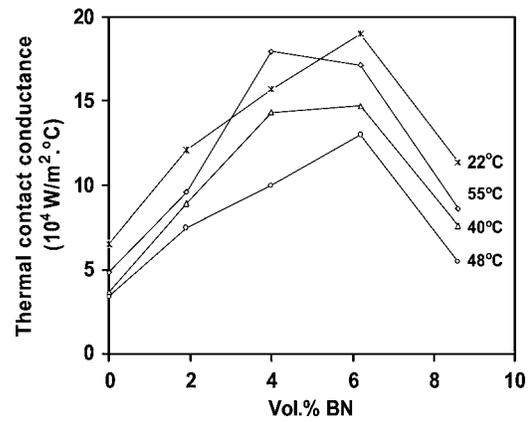


Fig. 4 Variation with BN volume fraction of the thermal contact conductance of wax/BN at different temperatures. The pressure is 0.30 MPa.

Heating the interface materials up to  $48^\circ\text{C}$  decreased the thermal contact conductance. This is because the wax expands upon heating, with a thermal expansion coefficient of  $38 \times 10^{-6}/^\circ\text{C}$ , as measured in this work at  $15\text{--}30^\circ\text{C}$  and a heating rate of  $15^\circ\text{C}/\text{min}$ , using a Perkin-Elmer Corp. TMA7 Thermal Mechanical Analyzer. On the other hand, the wax becomes a liquid when the temperature is above  $48^\circ\text{C}$ . Melting increases the fluidity and conformability of the interface material and consequently enhances the thermal contact conductance. The conductance minima in Figs. 2 and 3 may be due to these reasons. The addition of BN particle to paraffin wax may change the melting point [15]. Thus, the actual conductance minimum may not be exactly at  $48^\circ\text{C}$ .

Increasing the pressure enhanced the thermal contact conductance for the following possible reasons. Firstly, high pressure can reduce the volume of voids between the two copper disks. Secondly, reduction in thickness of the interface material occurs under a high pressure, especially when the thermal interface material is in the liquid state. However, the combination of a high pressure (above 0.30 MPa) and a high temperature ( $55^\circ\text{C}$ ) results in a decrease in thermal contact conductance.

## Conclusions

The effectiveness of hexagonal boron nitride particle ( $5\text{--}11 \mu\text{m}$ ) filled wax (a phase change material, predominantly tricosane paraffin) as a thermal interface material between copper surfaces was demonstrated. The thermal contact conductance, as measured by the laser flash method, decreased with increasing temperature from  $22$  to  $48^\circ\text{C}$  (presumably due to thermal expansion).

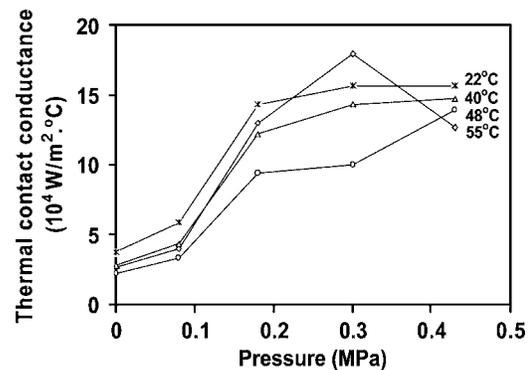


Fig. 5 Variation with pressure of the thermal contact conductance of wax filled with 4.0 vol. % BN. The temperature ranges from  $22$  to  $55^\circ\text{C}$ .

sion of the wax), but increased with increasing temperature from 48 to 55°C. The change in trend at 48°C was due to the melting of the wax at this temperature. The melting enhanced the conformability of the interface material. At a given temperature, the thermal contact conductance increased with increasing BN content up to 6.2 vol. % (due to the thermal conductivity of BN), but decreased upon further increase of the BN content to 8.6 vol. % (due to increased viscosity and the consequent reduced conformability). For a given BN content and a given temperature, the thermal contact conductance increased with increasing contact pressure. However, a pressure above 0.30 MPa resulted in no significant increase in the conductance, possibly due to the out-flow of the wax having reached its limit. The highest conductance attained above the melting temperature of the wax was  $18 \times 10^4 \text{ W/m}^2 \text{ }^\circ\text{C}$ , which was close to the value of  $21 \times 10^4 \text{ W/m}^2 \text{ }^\circ\text{C}$  previously reported for solder. This highest value was attained for a BN content of 4.0 vol. % at 55°C and 0.30 MPa. At a lower pressure of 0.18 MPa, the highest conductance was  $16 \times 10^4 \text{ W/m}^2 \text{ }^\circ\text{C}$ , as attained for a BN content of 6.2 vol. % and a temperature of 55°C. With no pressure, the highest conductance was only  $5 \times 10^4 \text{ W/m}^2 \text{ }^\circ\text{C}$ , as attained for a BN content of 6.2 vol. % and a temperature 55°C. Below the melting temperature of the wax, the highest conductance was  $19 \times 10^4 \text{ W/m}^2 \text{ }^\circ\text{C}$ , as attained at 22°C for a BN content of 6.2 vol. % and a pressure of 0.30 MPa.

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