

PHENOLIC RESIN MOLDING MATERIAL

1 The present invention relates to a phenolic
resin molding material which has good thermal stability,
which is easy to fill into a molding die, which has
excellent rapid curability, and which is capable of
5 giving a molded article improved in abrasion property in
drilling operation, etc. as well as in mechanical
strength.

 Many of the general phenolic resin molding
materials comprise a novolac type phenolic resin as a
10 main component and hexamethylenetetramine (hexamine) as
a curing agent, and are cured by the reaction of these
two components. Such phenolic resin molding materials
using a novolac type phenolic resin have relatively good
curability in injection molding, but is insufficient in
15 thermal stability in an injection cylinder in said
molding and also insufficient in filling into a molding
die; hence, improvement in continuous moldability has
been required for said phenolic resin molding materials.

 With respect to the curability of said
20 phenolic resin molding materials, it has been studied to
improve the curability by using a high-ortho-novolac
type phenolic resin wherein the proportion of the o-
methylene bond with respect to the phenol nucleus is
high, and phenolic resin molding materials using such a

high-ortho-novolac type phenolic resin are in practical use. However, they are insufficient in thermal stability, etc. in injection molding, and further improvement has been desired.

5 With respect to the filler used in the phenolic resin molding materials using a novolac type phenolic resin, there is used, as an organic filler, mainly wood flour. As the organic filler, there are also used, depending upon applications of the phenolic
10 resin molding materials, pulp, organic fiber, small pieces of cloth, thermoplastic resin powders and the like. When an ordinary organic filler such as wood flour or the like is used, the resulting phenolic resin molding material is insufficient in mechanical strength
15 and electrical properties (particularly, properties after boiling); and these properties can be improved to some extent by adding thermoplastic resin powders, cured thermosetting resin powders or an inorganic filler. Addition of thermoplastic resin powders, however, gene-
20 rally leads to reduction in heat resistance and there is a limit in the amount of said thermoplastic resin powders added. It was also tried to use cured thermosetting resin powders or a combination of the powders with wood flour to obtain improvements in molding
25 shrinkage and electrical properties (e.g. Japanese Patent Application Kokai (Laid-Open) Nos. 57-78444 and 59-105049); however, use of a large amount of cured

1 thermosetting resin powders makes the resulting molded
article hard and fragile and brings about no noticeable
improvements in other properties.

As an inorganic filler, there are used powders
5 of calcium carbonate, clay, silica, alumina, aluminum
hydroxide, glass or the like; glass fiber; and so forth.
As the inorganic filler, there are two types, i.e. a
hard type such as silica, alumina, glass or the like,
and a relatively soft type such as calcium carbonate,
10 clay or the like, and they are selectively used depend-
ing upon applications of and requirements for the
phenolic resin molding material in which said fillers
are used. The inorganic filler exhibits excellent
properties generally in mechanical strength, electrical
15 properties, etc. The inorganic filler, as compared with
the organic filler, is hard and has, in drilling opera-
tion or sliding of the phenolic resin molded article
obtained, a problem of giving abrasion to a material
(e.g., a drill or metal) which comes in contact with the
20 molded article.

The present inventor made an extensive study in
order to reduce or eliminate the above-mentioned
drawbacks of the phenolic resin molding materials using a
novolac type phenolic resin. The present invention makes
25 it possible to provide a molding material which has
excellent thermal stability in injection molding, which
is easy to fill into a molding die, which has rapid

1 curability, and which is capable of giving a molded
article of excellent mechanical strength and excellent
abrasion property (i.e., low in abrasion of the molded
article itself and gives substantially no abrasion to a
5 material which comes in contact with the molded
article).

The present invention provides a phenolic
resin molding material comprising a curable phenolic resin, an
organic filler, an inorganic filler and a liquid sub-
10 stance having a boiling point of 80-150°C, said phenolic
resin comprising, as its main component, a novolac type
phenolic resin wherein the ratio of the o-methylene bond
to the p-methylene bond with respect to the phenol
nucleus ranges from 1.0 to 2.5.

15 In the phenolic resin molding material of the
present invention, the phenolic resin comprises, as the
main component, a novolac type phenolic resin wherein
the ratio of the o-methylene bond to the p-methylene
bond with respect to the phenol nucleus ranges from 1.0
20 to 2.5. This novolac type phenolic resin imparts rapid
curability to the molding material. When the ratio of
the o-methylene bond to the p-methylene bond is smaller
than 1.0, curing is less rapid; a novolac
type phenolic resin wherein the ratio is larger than
25 2.5, is difficult to synthesize. A preferable range of
the ratio is 1.0-1.8, and a novolac type phenolic resin
having such a ratio of o-methylene bond to p-methylene

1 bond not only imparts rapid curability to the resulting
molding material but also allows the molded article
obtained from the molding material to have improved
mechanical and electrical properties.

5 Such a novolac type phenolic resin preferably
has a number-average molecular weight of 600-900. When
the molecular weight is smaller than 600, the resin has
a low melting point, is less convenient to handle, and has
lower curability. When the molecular weight is larger
10 than 900, the resin is less stable during
production.

The so-called high-ortho-novolac type phenolic
resin as mentioned above can be produced by a known
process.

15 The phenolic resin can comprise, besides the
above-mentioned high-ortho-novolac type phenolic resin,
an ordinary novolac type phenolic resin (the so-called
random novolac type phenolic resin) wherein the ratio of
the o-methylene to the p-methylene bond is less than 1.0
20 and/or a resole type phenolic resin (methylol type, or
dimethylene ether type). The proportion of the ordinary
novolac type phenolic resin and/or the resole type
phenolic resin varies depending upon requirements for the
molding material to be obtained, but is less than 50% by
25 weight, preferably 10-40% by weight based on the total
phenolic resins. Use of such a resin composition makes
possible improvements in mechanical strength and
electrical properties and can achieve a lower cost.

1 The phenolic resin molding material of the
present invention comprises a liquid substance having a
boiling point of 80-150°C so that said material can have
improved thermal stability in an injection cylinder, be
5 easily filled into a molding die, and be capable of
giving a molded article of stable and improved pro-
perties.

The liquid substance may, for example, comprise one
or more liquids selected from methyl ethyl ketone, methyl
isobutyl ketone, toluene, xylene, water and propanol. Of
these, particularly preferable are methyl ethyl ketone,
toluene, water and propanol.

15 Use of a liquid substance as defined above prevents
the resulting molding material, molten in an injection
cylinder, from overheating by evaporation of the liquid
substance, and, furthermore, allows the molding material
to have higher flowability and lower melt torque. As a
result, the molding material has improved thermal
20 stability in an injection cylinder and can be easily
filled into a molding die.

The amount of the liquid substance used is
advantageously 0.5-4% by weight based on the whole mold-
ing material. When the amount is less than 0.5% by
25 weight, the above-mentioned effect is obtained to a lesser
extent; when the amount is more than 4% by weight, there is
obtained no higher effect due to the amount exceeding 4% by

1 weight and the molded material obtained has a larger shrinkage ratio. The amount of the liquid substance used is preferably 0.5-2.5% by weight.

Then, description is made on the filler.

5 One of the features of the present invention is to use an organic filler and an inorganic filler in combination, part of the organic filler preferably comprising a powder derived from one or more cured thermosetting resins. The cured thermosetting resin powders include not only
10 powders of a cured thermosetting resin but also powders obtained by grinding a cured thermosetting resin molding material or a thermosetting resin laminate or decorative laminate. The thermosetting resin may comprise, for example, one or more resins selected from phenolic resins, melamine resins, epoxy resins, urethane resins and unsaturated polyester resins. Phenolic resin, melamine resin and epoxy resin are generally used.

Use of only an ordinary organic filler such as wood flour or the like gives a molded article which is less hard, less dimensionally accurate and less
20 satisfactory in strength and abrasion.

These drawbacks can be significantly alleviated by using, as a part of the organic filler, cured thermosetting resin powders. The cured thermosetting resin powders are hard as compared with other organic fillers
25 but soft as compared with metals such as iron, aluminum or the like; therefore, said powders give no abrasion against a material (a drill or metal) which comes in

contact with the powders in drilling operation or sliding of the molded article produced from the present molding material comprising the powder.

The proportion of the cured thermosetting resin powders used in the organic filler is preferably 10-40% by weight. When the proportion is less than 10% by weight, the effect of using said powders is low; when the proportion is more than 40% by weight, the molded article obtained is relatively hard and fragile, which is not preferable.

The organic filler may comprise, for example, one or more fillers selected from wood flour, pulp, organic fiber, small pieces of cloth and thermoplastic resin powders. The choice of filler depends upon the application of the resulting molding material. Such fillers may be used in addition to or instead of the cured thermosetting resin powders.

An inorganic filler is used in combination with the above-mentioned organic filler. Use of an inorganic filler in combination can give improvements in strength, dimensional accuracy, electrical properties, etc. The inorganic filler may comprise, for example, one or more fillers selected from calcium carbonate, talc, clay, silica, alumina, aluminum hydroxide, magnesium hydroxide and glass. Depending upon the kind and amount of the inorganic filler used, the molded article obtained is hard and gives abrasion against a material (a drill or

metal) which comes in contact with the molded article during drilling operation or sliding of the molded article. Hence, in the present invention, the inorganic filler preferably comprises one or more fillers selected from calcium carbonate, talc, clay, aluminum hydroxide and magnesium hydroxide. All of those fillers are soft. The proportions of the organic filler and the inorganic filler may be 60 to 80% by weight and 40 to 20% by weight, respectively. The inorganic filler is used in an amount of 20 to 40% by weight based on the total fillers, when advantageous abrasion properties are required.

The phenolic resin molding material of the present invention is preferably obtained by melt-kneading a blend of resin(s), fillers, additives, etc. using rolls, a co-kneader, an extruder or the like, followed by pelletization or cooling and grinding.

The resulting phenolic resin molding material may be molded by an ordinary method such as injection molding or the like.

The phenolic resin molding material of the present invention exhibits rapid curability in molding because it comprises a high-ortho-novolac type phenolic resin as the main component of the phenolic resin, and has improved thermal stability in an injection cylinder and is easily filled into a molding die because it comprises a liquid substance having a boiling point of 80-150°C. Thereby, in injection molding, the present phenolic resin molding

material has a shorter molding cycle and enables continuous molding, and the molded article obtained therefrom has stable and improved properties.

Further, since the present phenolic resin molding material uses an organic filler and an inorganic

1 filler in combination, the molded
article obtained therefrom is improved in mechanical
strength and abrasion property. When calcium carbonate,
talc, clay, aluminum hydroxide or magnesium hydroxide,
5 all of which are soft, is used as the inorganic filler,
the molded material obtained is further improved in
abrasion property. Additional advantages are obtained
when part of the organic filler comprises a cured
thermosetting resin powder.

10 The present invention is hereinafter described in
more detail by way of Examples and Comparative Examples.
Examples 1-4 and Comparative Examples 1-3

Phenolic resin molding materials were obtained
by kneading the components shown in Table 1, in accord-
15 ance with the compounding recipes shown in Table 1,
using hot rolls. In Table 1, the numerical figures are
by parts by weight.

In Comparative Example 1, a random novolac was
used as the phenolic resin; a wood flour was used as the
20 filler; and further toluene was used. In Comparative
Example 2, the same random novolac was used as the
phenolic resin; and the same wood flour and calcium
carbonate were used as the filler. In Comparative
Examples 1 and 2, magnesium oxide as a curing accele-
25 rator was not used as in Examples. In Comparative
Example 3, a high-ortho-novolac was used as the main

1 component of the phenolic resin; the same wood flour and
calcium carbonate were used as the filler; and magnesium
oxide was used as usual. No liquid substance having a
boiling point of 80-150°C was used in any of Comparative
5 Example 2 and 3. Although any curing agent suitable for
curing phenolic resins may be used for the materials of
the invention, hexamine was used for all the Examples.

The molding materials obtained in each Example and
each Comparative Example were measured for curability
10 (minimum curing time in which no blister appeared),
thermal stability (thermal stability in an injection
cylinder), moldability (easiness of filling into a
molding die), abrasion resistance (drill abrasion index)
and bending strength. The results obtained are shown in
15 Table 2.

Table 1
Compounding for molding materials

Components	Example				Comparative Example		
	1	2	3	4	1	2	3
High-ortho-novolac type phenolic resin	30	30	35	30	0	0	30
Random novolac type phenolic resin	12	12	7	12	42	42	12
Hexamine	8	8	8	8	8	8	8
Wood flour	28	28	28	28	42	28	28
Cured thermosetting resin powders	6	6	6	6	0	0	0
Calcium carbonate	8	8	8	8	0	14	12
Magnesium oxide	0	0	0	0	0	0	2
Liquid substance	2 (Toluene)	2 (Propanol)	2 (Toluene)	2 (Water)	2 (Toluene)	0	0
Releasing agent (stearic acid)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Coloring agent (black dye)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Curing assistant (calcium hydroxide)	3	3	3	3	3	3	3

Notes High-ortho-novolac type phenolic resin

Ratio of o-methylene bond to p-methylene bond = 1.2

Number-average molecular weight = 800

Random novolac type phenolic resin

Ratio of o-methylene bond to p-methylene bond = 0.8

Number-average molecular weight = 850

Cured thermosetting resin powders

Examples 1, 3 and 4: powders of a melamine resin decorative laminate

Example 2: Powders of cured product of a wood flour-containing phenolic resin molding material

Table 2
Test Results

Properties	Example				Comparative Example		
	1	2	3	4	1	2	3
Minimum curing time in which no blister appeared (seconds)	10	8	8	10	15	15	10
Thermal stability in an injection cylinder (minutes)	300	300	300	300	300	240	220
Moldability (easiness of filling)	○	○	○	○	△	X	△
Drill abrasion index	1.5	1.5	1.5	1.5	1.5	1.5	2.0
Bending strength (N/mm ²)	95.2	98.9	96.1	96.7	73.2	84.2	93.4

Notes Rating of moldability (easiness of filling)

○: good

△: unfilled portion remains slightly

X: unfilled portion remains

1 Incidentally, impact strength and insulation
resistance were measured, but there was no difference in
these properties among the test samples.

[Measurement methods]

- 5 (1) Minimum curing time in which no blister appeared

Test samples [60 mm ϕ x 4 mm (thickness)] were
molded by injection molding with the die temperature set
at 180°C. The curing time was shortened by one second
each from 20 seconds. The curing time one second before
10 the curing time in which blister appeared, was taken as
minimum curing time in which no blister appeared. The
time in which the thickness of a test sample (molding)
as measured using a micrometer increased by more than
0.05 mm, was taken as curing time in which blister
15 appeared.

- (2) Thermal stability in an injection cylinder:

Molded articles for test purpose each of 170 g
were produced by injection molding with the in-cylinder
temperature set at 85°C. In this case, the time in
20 which the molding material stayed in the cylinder from
the metering to the injection, was taken as staying time
in the cylinder. This in-cylinder staying time was
prolonged, for example, from 30 seconds to 60 seconds,
90 seconds,; and the longest in-cylinder staying
25 time which made injection possible, was taken as in-
cylinder thermal stability.

- (3) Moldability (easiness of filling)

1 Injection molding (injection pressure = 1,250
kgf/cm²) was conducted from the die length (100 mm)
direction with the test die (100 mm x 5 mm x 2 mm)
temperature set at 180°C, and moldability (easiness of
5 filling) was rated.

(4) Bending strength, Charpy impact strength and
insulation resistance:

Were measured in accordance with JIS K 6911.

(5) Drill abrasion index

10 A hole was made in a 2 mm-thick aluminum plate
using a drill, at 500 rpm (rotation of the drill edge)
and at 1 mm/min (descending speed of the drill edge),
and shape (A) of stress wave of the drill edge was
measured. Then, using this drill and under the same
15 conditions, 10 holes were made at 10 positions in each
of 3 mm-thick test samples prepared from the molding
materials of each Example and each Comparative Example;
thereafter, a hole was made again in the 2 mm-thick
aluminum plate, and shape (B) of stress wave of the
20 drill edge was measured. Drill abrasion index was taken
as a ratio of (A) to (B), i.e. (A)/(B).

The molding materials obtained in Examples 1-4
had excellent rapid curability, good thermal stability
and good moldability, and gave molded articles of high
25 bending strength and excellent abrasion property. The
molding materials obtained in Comparative Examples 1 and
2 contained only a random novolac as the phenolic resin,

1 and therefore were slow in curing, and gave molded
articles inferior in bending strength. The molding
material obtained in Comparative Example 3 used a high-
ortho-novolac and hence had relatively rapid curability,
5 but was inferior in thermal stability and moldability;
and the molded article produced therefrom had a good
bending strength owing to the use of magnesium oxide but
showed poor abrasion property.

As clear from the above Examples, the phenolic
10 resin molding material of the present invention has
excellent rapid curability, is superior in thermal
stability in an injection cylinder, and is easy to fill
into a molding die; hence, the molding material can be
molded in a shorter cycle and enables even continuous
15 molding.

Further, the present phenolic resin molding
material can provide a molded article of good mechanical
strength and yet of excellent abrasion property.
Therefore, the molded article enables good drilling ope-
20 ration and are superior also in abrasion during sliding
and die abrasion during molding. Further, the molded
article is at least equal to those produced from conven-
tional molding materials, in electrical properties and
dimensional accuracy.

CLAIMS

1. A phenolic resin molding material comprising a curable phenolic resin, an organic filler, an inorganic filler and a liquid substance having a boiling point of 80 to 150°C, said phenolic resin comprising, as its main component, a novolac type phenolic resin wherein the ratio of the o-methylene bond to the p-methylene bond with respect to the phenol nucleus ranges from 1.0 to 2.5.

2. A molding material as claimed in claim 1, wherein the organic filler comprises 10 to 40 % by weight of cured thermosetting resin powder.

3. A molding material as claimed in claim 2, wherein the thermosetting resin comprises one or more resins selected from phenolic resins, melamine resins, epoxy resins, urethane resins and unsaturated polyester resins.

4. A molding material as claimed in any one of claims 1 to 3, wherein the organic filler comprises one or more fillers selected from wood flour, pulp, organic fiber, small pieces of cloth and thermoplastic resin powders.

5. A molding material as claimed in any one of claims 1 to 4, wherein the inorganic filler comprises one or more fillers selected from calcium carbonate, talc, clay, silica, alumina, aluminium hydroxide, magnesium hydroxide and glass.



6. A molding material as claimed in claim 5, wherein the inorganic filler comprises one or more fillers selected from calcium carbonate, talc, clay, aluminium hydroxide and magnesium hydroxide.

7. A molding material as claimed in claim 6, wherein the proportions of the organic filler and the inorganic filler are 60 to 80 % by weight and 40 to 20 % by weight, respectively.

8. A molding material as claimed in any one of claims 1 to 7, wherein the liquid substance comprises one or more liquids selected from methyl ethyl ketone, methyl isobutyl ketone, toluene, xylene, water and propanol.

9. A molding material as claimed in any one of claims 1 to 8, wherein the liquid substance is present in an amount of 0.5 to 4 % by weight based on the whole molding material.

10. A molding material as claimed in any one of claims 1 to 9, wherein the phenolic resin consists of (a) a novolac type phenolic resin wherein the ratio of the o-methylene bond to the p-methylene bond with respect to the phenol nucleus ranges from 1.0 to 2.5 and (b) a novolac type phenolic resin wherein the ratio of the o-methylene bond to the p-methylene bond is less than 1.0.

11. A molding material as claimed in claim 10, wherein the novolac type phenolic resin (b) wherein the ratio of the o-methylene bond to the p-methylene bond is



less than 1.0, is present in an amount of 10 to 40 % by weight based on the total phenolic resins.

12. A molding material as claimed in claim 1, substantially as described in any one of the Examples herein.

13. The use of a liquid substance having a boiling point of 80 to 150°C to improve the thermal stability and/or ease of introduction into a molding die of a molding material comprising a resin and fillers as specified in claim 1 and/or to give a molded article, produced from such a molding material, of stable and improved properties.

14. A molding process wherein a molding material as claimed in any one of claims 1 to 12 is used.

15. A molded article obtained from a molding material as claimed in any one of claims 1 to 12 or by a process as claimed in claim 14.

