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EPOXY RESIN BONDED MACHINABLE CERAMICS

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Epoxy resins have been used for a number of years as adhesives, potting compounds, surface finishes, and other applications where a hard thermosetting organic material is required. The high adhesive strength of this material makes it attractive for use as a temporary binder in ceramic bodies which must be formed by machine tool operations. Epoxy resins have the advantages of versatility, good handling characteristics, toughness, low shrinkage, and inertness over other systems such as phenolics, polyesters, or thermoplastic resins.¹

Epoxy resins are characterized by their ability to be transformed from a liquid state to tough, hard solids by a chemically active material known as a curing agent. The choice of the curing agent determines whether this chemical reaction occurs at room temperature, with exothermic heat produced by chemical reaction, or by externally applied heat. The chemical reaction during curing can be represented as shown in Figure 1. This reaction produces a long chain system wherein the molecules are cross-linked to each other. This cross-linking provides the exceptional strength and toughness which these materials possess. If desired, this cross-linked structure may be modified to yield a material which is less brittle or has other desirable properties.

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CURING OF EPOXY RESINS

The technique of epoxy resin-bonding ceramic materials was developed in order to provide a material which had good green strength for machining operations. The investigations reported here were carried out with pure alumina but the same process has been applied to many other materials including sodium iodide, lead zirconate, lead titanate, titania, calcium titanate, strontium titanate, and barium titanate. There is no reason to believe that the system cannot be used with any powdered inorganic material.

The epoxy resin system chosen for bonding ceramics is shown in Figure 2. The Epon 815 is the basic resin. It is somewhat less viscous than others of this series offered by Shell Chemical Company. The diethanolamine is the curing agent. This particular one was chosen because it allows the cure to be initiated only upon heating. This is essential since several handling operations must be performed before the final cure. The cardolite is added as a flexibilizer. It modifies the chain length and cross-linking structure so as to reduce the brittleness of the cured epoxy resin. The amount of flexibilizer is somewhat higher than is found in other epoxy systems. This was done in a deliberate attempt to make the bonded ceramic more resistant to impact stresses. A wide variety of colors may be used in the epoxy. These make it possible to readily distinguish one composition from another. The dyes used are of an organic base which leave no residue after firing. It has been found that dyes which are used for coloring anodized aluminum are excellent for this purpose.

The resin system is formulated as follows: The resin and flexibilizer are mixed together at room temperature using a mechanical stirrer. This mixture, the hardener and the coloring agent are then combined and

EPOXY RESIN FORMULATION

<u>Constituent</u>	<u>Trade Name</u>	<u>Weight Percent</u>
Resin	Epon 815 (Shell Chem. Co.)	69.4
Hardener	Diethanolamine	9.7
Flexibilizer	Cardolite NC-513 (Irvington Varnish and Insulator Co.)	13.9
Color (optional)	Ciba Co.	7.0

Figure 2

heated to 60°C while being stirred. During this operation a slight amount of reaction occurs. This reaction prevents the individual components from segregating, since they are normally imiscible. After cooling, an amount of epoxy resin required for the batch is weighed and dissolved in an organic solvent. Acetone is most often used for this purpose since it is relatively inexpensive and is easily evaporated after mixing. The ceramic powder is then added and the entire batch is thoroughly mixed. If it is desired, this mixing may be done in a ball mill which also serves to reduce the particle size of the ceramic powder. A sufficient amount of acetone is added to produce a rather thin slurry. This ensures that each solid particle will be uniformly coated with epoxy resin.

Following the mixing operation, the acetone is evaporated and the dry powder is screened to produce granules which are suitable for pressing. The compaction of the powder into a suitable shape may be done either by cold pressing in a steel die or by isostatic pressing. The uncured epoxy resin imparts some strength to the material. Pieces as thin as 0.010 inch thick have been successfully pressed.

After pressing, the epoxy resin is cured by heating the piece at 75°C for at least 24 hours. Longer curing times may be desirable for large pieces. It has been noted that the curing operation will continue at room temperature for several weeks after an initial heating at 75°C for 15 hours. After a short cure, the epoxy is somewhat flexible although quite strong. This flexibility may cause difficulties arising from temporary distortion of the piece while it is being held in a lathe chuck during machining. A small amount of springback may occur when the piece is removed from the lathe and a warped fired shape may result.

Machining of the pressed and cured pieces can be done with conventional metalworking tools. Metal-bonded carbide tools such as Kennametal 907 are used since conventional high speed tool materials wear very quickly. Diamond-tipped tools are very satisfactory but are not always available in the proper size or shape. Rough cuts on resin bonded material can be made on a band saw but silicon carbide cut-off wheels are much more satisfactory.

Firing of the machined ware is carried out in a normal fashion. The epoxy burns out completely in an oxidizing atmosphere leaving no residual ash. No difficulty has been experienced with fracturing of the ware due to the volatilization of the epoxy. Binder contents up to 20% have given no trouble in this respect.

A series of tests were made in an attempt to determine an optimum binder content for use with pure alumina. The starting material in this study was Norton 38900 AWIF fused alumina. It was combined with varying amounts of epoxy binder and 500 milliliters of acetone per 1000 grams of alumina. The mixture was ball milled 40 hours, dried, either die pressed at 10,000 psi or isostatically pressed at 30,000 psi, cured, and finally subjected to a number of physical and mechanical tests.

Determinations of green density were made on a series of these samples. The results of these measurements are shown in Figure 3. The density values shown here are expressed as percent of theoretical for the mixture. These curves show that the isostatically pressed alumina had a higher green density. This is due to the higher forming pressure used in this process. A slight decrease in the bulk density is observed when the binder content was increased from 0.5 to 1.0 percent. The reason for this is not known, but it may have arisen from a packing

Figure 3

GREEN DENSITY OF EPOXY BONDED ALUMINA

density difference in these two materials. It is noted that the full theoretical density for the mixture was not reached in the range of binder contents studied. A considerable amount of open porosity remains, even at the highest binder content. Studies of the pore size distribution in the green material has shown that the pores are all smaller than 0.7 micron. The data from this figure were used to calculate the bulk density of these samples on the basis of the theoretical density of alumina. These data are shown in Figure 4. These values are indicative of the density of the material after the epoxy has been burned out during firing. The initial decrease in density with increasing binder content is again noted, but in this case it is more pronounced. The density values reach an apparent maximum at approximately 5 percent binder content. Some decrease in density was observed with the 6 percent addition on the isostatically pressed samples. This was probably due to a dilution effect of the epoxy binder.

A series of modulus of rupture measurements was made on this series of specimens. Test bars measuring $3/8 \times 3/8 \times 2$ inches were prepared by pressing in a steel die at 10,000 psi and by machining stock which had been isostatically pressed at 30,000 psi. The bars were tested in flexure using the third point loading method. A cross-head speed of 0.02 inch per minute was used. The results of these measurements are shown in Figure 5. It is seen that the isostatically pressed material had a higher green strength, particularly at the higher binder contents. In both forming techniques the green strength is quite high, emphasizing the value of the epoxy resin as a binder. A decrease in strength above 6 percent binder is noted. This indicates that perhaps the characteristics of the pure epoxy resin influences

Figure 4

GREEN DENSITY OF EPOXY BONDED ALUMINA

Figure 5

GREEN STRENGTH OF EPOXY BONDED ALUMINA

strength in this range. It has been reported elsewhere² that the use of alumina as a filler in epoxy systems frequently raises the strength. This effect is dependent upon the actual mixture which is used.

A calculation of the thickness of epoxy resin between each alumina grain can be made knowing the surface area of the alumina and the density and weight percent of epoxy binder. The surface area of the alumina as measured by the nitrogen adsorption technique is $3.65 \text{ m}^2/\text{gm}$. The density of the epoxy is approximately 1.1 gm/cc . At an epoxy content of 6 percent, the average thickness of binder between particles is 300 Angstroms.

This same series of epoxy-bonded samples was fired at 1725°C with a 15 hour soak in an oxidizing atmosphere. Mechanical and physical tests were made to determine whether the varying epoxy contents influenced the properties of the fired material. The results of density measurements are shown in Figure 6. These data show that fired density is very much influenced by binder content for those samples which were pressed at 10,000 psi in a steel die. The isostatically pressed samples, however, showed very little dependence on the amount of binder present. This discrepancy is not fully understood. There is a possibility that the two sets of samples were fired at somewhat different temperatures. This may account for the difference, particularly if the isostatically pressed samples had received a higher firing treatment.

The firing shrinkages of these materials are shown in Figure 7. These shrinkage values are based on the fired size of the piece. As with the density values, those samples which were pressed in a steel die show a much more pronounced effect of binder content. The

Figure 6

FIRED DENSITY OF EPOXY BONDED ALUMINA

FIRED AT 1725°C, 15 HOUR SOAK

Fired Density, percent of theoretical

Figure 7

FIRING SHRINKAGE OF EPOXY BONDED ALUMINA

FIRED AT 1725°C, 15 HOUR SOAK

isostatically pressed samples showed almost no variation with binder content except at the ends of the range studies.

Modulus of rupture measurements were made on a series of bars which had been formed by pressing in a steel die at 10,000 psi, cured, and fired at 1725°C for 15 hours in an oxidizing atmosphere. The strengths were measured in a similar manner to the green pieces mentioned earlier. The results of these tests are shown in Figure 8. As is usually the case when ceramic materials are mechanically tested, the individual values vary over a wide range. All of the measured strength values are shown and the averages of each set are connected by straight lines. Relatively few conclusions can be drawn from these data except that perhaps binder contents greater than 3.5 percent lower the fired strength somewhat.

From the preceeding properties it can be seen that a clear-cut choice of optimum binder content cannot be made easily. One would like to keep the binder content low for economic reasons and yet good green strength and fired properties require a binder content in the vicinity of 5 percent. In light of all these measurements, it is apparent that a binder content in the 3 to 5 percent range should be adequate for this type of material. It should be emphasized that a different oxide may require more or less binder depending on its particle size distribution and surface area. One situation has arisen in our experience in which an excess amount of epoxy was used. In this case, removal of the acetone left a powder which resembled a thick slurry and could not be processed further.

Some mention should be made of the cost of the materials used in this process. A summary of approximate cost data is shown in Figure 9.

FIRED STRENGTH OF EPOXY BONDED ALUMINA

FIRED AT 1725°C, 15 HOUR SOAK

Figure 8

COST OF EPOXY BINDERS

Per Pound of Alumina

Containing 5% Epoxy

<u>Material</u>	<u>Unit Price</u>	<u>Lot Size</u>	<u>Quantity</u>	<u>Cost</u>
Epoxy	\$1.00/lb.	1 gal.	0.0345 lb.	\$0.035
Hardener	\$2.10/lb.	1 lb.	0.0049 lb.	\$0.010
Flexibilizer	\$1.00/lb.	1 gal.	0.0070 lb.	\$0.007 ¹
Color	\$3.00/lb	5 lb.	0.0035 lb.	\$0.011
Acetone	\$0.53/gal.	55 gal.	0.0515 gal.	\$0.027
				<u>\$0.090</u>

Figure 9

A price of approximately 9 cents per pound of fired alumina is calculated from these figures. This figure can, of course, be lowered by purchasing the ingredients in larger quantities and by utilizing a lower binder content. An equivalent percentage of polyethylene glycol binder costs 3 cents per pound of alumina.

The use of epoxy resins as binders for ceramic materials is not without its drawbacks. Those working with these materials should be aware of the possible toxic effect of the uncured resin mixture. The hardeners used in epoxy resins are primary skin irritants as well as being sensitizing agents. The hardener used in the formulation described here is one of the least harmful of all hardeners, but nevertheless, the possibility of its contacting the skin should be avoided. The powder containing the uncured resin should not be allowed to become airborne and suitable protective clothing should be worn when handling the powder. The cured resin, on the other hand, is not a known hazard and no special precautions are needed when handling the epoxy-bonded ceramic after the curing operation.

Epoxy resin-bonded ceramics have been found to be extremely useful for a wide variety of applications where a particular shape must be formed from a pressed block. This process has also been used for die pressing simple shapes which require good mechanical strength but do not need to be fired. The technique described here has provided a fabrication technique for many problems which otherwise would have been difficult to solve.

References

1. Henry Lee and Kris Neville, "Epoxy Resins", McGraw-Hill, 1957, p. 305.
2. Ibid, p. 227.