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Abstract. — For the past decade and a half, many different types of piezoelectric ceramic-polymer composites have been developed intended for transducer applications. These diphasic composites are prepared from non-active polymer, such as epoxy, and piezoelectric ceramic, such as PZT, in the form of filler powders, elongated fibers, multilayer and more complex three-dimensional structures. For the last four years, most of the efforts have been given to producing large area and fine scale PZT fiber composites. In this paper, processing of piezoelectric ceramic-polymer composites with various connectivity patterns are reviewed. Development of fine scale piezoelectric composites by lost mold, injection molding and the relit method are described. Research activities of different groups for preparing large area piezocomposites for hydrophone and actuator applications are briefly reviewed. Initial development of electrostrictive ceramics and composites are also discussed.

Introduction.

The design and fabrication of composite materials optimized for a special application has been the subject of many research programs, with applications ranging from mechanical structures to electronic devices. The drive for the rapid development of composite materials stems from the need for a combination of desirable material properties that often cannot be obtained in single-phase materials. For example, in an electromechanical transducer, one may wish to maximize the piezoelectric sensitivity, minimize the density to obtain a good acoustic matching with water, and also make the transducer mechanically flexible to conform to a curved surface. These properties are partially conflicting in nature, and a single-phase material that simultaneously satisfies these requirements is virtually nonexistent. Thus, in many applications, one might optimize conflicting requirements by combining the most useful properties of two or more phases that do not ordinarily appear together in nature.

Based on this concept, there has been an intensive research effort for the past several years in many universities and industrial research laboratories around the world to develop electrically active ceramic-polymer composites. Initially, the focus was on developing composite
materials with hydrostatic piezoelectric coefficients larger than those of the commonly used lead zirconate titanate (PZT) ceramics. The piezoelectric composites were intended for underwater hydrophone applications in the low-frequency range, where the dimensions of the sample are much smaller than the acoustic wavelength. It has been demonstrated that certain composite hydrophone materials are two to three orders of magnitude more sensitive than single phase PZT ceramics, while satisfying other requirements. The idea of composite materials has been extended to other applications, such as ultrasonic transducers for acoustic imaging, thermistors with both negative and positive temperature coefficients of resistance, and active sound absorbers. This paper is a review of the past as well as current research in the area of composite materials for transducer applications.

1. Transducers.

1.1 Characteristics. — An electromechanical transducer is a device that converts electrical energy into mechanical vibration and vice versa by utilizing piezoelectricity or electrostriction [2]. The direct piezoelectric effect enables a transducer to function as a passive sound receiver or “pickup” by the conversion of acoustic energy into an electrical signal. Applications include hydrophones, which are used to detect low frequency noises under water, and microphones. The converse piezoelectric effect permits a transducer to act as an active sound transmitter or loudspeaker. In particular, a piezo-tweeter is an audio speaker component used to generate high frequency sounds.

A transducer can also perform both active and passive functions nearly simultaneously. When operated in a pulse-echo mode, a transducer element propagates an acoustic wave in a medium, and then is capable of sensing faint echoes returning just a few microseconds later. The echoes are produced when a sound strikes a boundary between two substances possessing different characteristic acoustic impedances. The strength of the echo is proportional to the acoustic impedance mismatch between the two interface materials.

A hydrophone is a passive “smart” listening device used to detect relatively low frequency (< 40 kHz) noises under water. Since the wavelengths of these sounds are much larger than the transducer dimensions, the stress is considered to be effectively hydrostatic [1].

The sensitivity of a hydrophone can be measured by the voltage produced by a hydrostatic pressure wave. A useful parameter in assessing piezoelectric materials for use in hydrophones is the voltage coefficient, \( g_h \), which relates electric field to the applied hydrostatic strain. Another commonly used parameter is the hydrostatic strain coefficient, \( d_h \), which describes the polarization resulting from a change in stress. The \( g_h \) coefficient is related to \( d_h \) by the relation: \( g_h = d_h / (\varepsilon_0 K) \) where \( K \) is the relative permittivity and \( \varepsilon_0 \) is the permittivity of free space. A useful “figure of merit” for hydrophone materials is the product of the voltage coefficient and the hydrostatic strain coefficient: \( d_h g_h \) [3]. The units for this quantity are \( m^2/N \). A more recent proposed figure of merit is \( d_h g_h / \tan \delta \). This relation takes into account not only the piezoelectric properties, but also the dielectric loss tangent [6].

Other desirable properties for hydrophone materials include: i) low density for good acoustic matching with water, ii) little or no variation of \( d_h \) and \( g_h \) with pressure, temperature, and/or frequency, and iii) high physical compliance and flexibility so that the transducer can conform to curved surfaces, and exhibit improved mechanical shock resistance. A high degree of compliance also leads to large damping coefficients which prevent ringing in passive devices.

The other applications of transducers are in biomedical imaging with ultrasonic sound (1-30 MHz). This is widely used by physicians as a critical diagnostic tool. In fact, its world sales market encompasses nearly a billion dollars a year [7]. Its popularity rests in its ability to produce real-time, high resolution three-dimensional images of internal soft body tissue.
without the use of potentially hazardous ionizing radiation. The process utilizes an electromechanical transducer operating in the pulse-echo mode to transmit ultrasonic pulses into the body and also to receive the faint echoes produced by reflections from internal structures. A more detailed discussion on the finer points of biomedical imaging can be found elsewhere [4, 7-10]. The ultrasonic beam transmission capability of a transducer material can be characterized in part by its piezoelectric longitudinal charge coefficient \( (d_{33}) \). A transducer material's echo receiving sensitivity is directly related to its longitudinal piezoelectric voltage coefficient \( (g_{33} = d_{33}/\varepsilon_0 K) \). Large values for both of these coefficients are highly desirable and some researchers use the product of \( d_{33} \) and \( g_{33} \) as a figure of merit for pulse echo transducers [8, 10]. However, of these two piezoelectric coefficients, \( g_{33} \), may be considered to be slightly more critical since a larger \( g_{33} \) value enables the intensity of the ultrasonic beam to be decreased [7]. This limits the possibility, however minimal, for the ultrasonic beam to cause damage to body tissue. The dielectric constant \( (K) \) of a material plays an important role for both low frequency hydrophone and high frequency medical imaging applications. A \( K \approx 100 \) permits a large voltage coefficient and eases the electrical impedance matching (tuning) between the transducer and the system instrumentation [5]. The dielectric loss factor \( (\tan \delta) \) should also be minimized so as to prevent the loss of signal energy [7].

The thickness mode electromechanical coupling coefficient \( (k_t) \) is another value that indicates the energy conversion efficiency and potential sensitivity of a biomedical imaging transducer material. The power transduction capability of a piezoelectric material is better described by \( k_t \) than the piezoelectric coefficients previously discussed [10]. \( k_t \) is defined as the ratio of mechanical energy stored in a thickness mode transducer to the electrical energy supplied or vice versa [11]. The transducer geometry utilized for biomedical imaging is of a thin disk or plate whose fundamental resonance vibration is in the planar mode. However, when clamped laterally and at high frequencies, the thickness resonance mode dominates [10]. For maximum efficiency, a thickness mode transducer should have a minimal planar mode coupling coefficient \( (k_p) \) so that the ratio \( k_t/k_p \) is as large as possible.

The mechanical quality factor \( (Q_m) \) is inversely proportional to the amount of mechanical loss due to internal friction within a transducer material. On one hand, a low \( Q_m \) implies that a material is mechanically « lossy » and that signal energy is being wasted [5]. On the other hand, a low \( Q_m \) is required to limit ringing, enabling the generation of short acoustic pulse lengths, thus offering improved axial resolution [10]. A \( Q_m \approx 2-10 \) is a compromise value that limits ringing within the transducer without external damping layers [10, 13].

The transducer’s acoustic impedance should be near that of body tissue (1.5 MRaysl) for strong acoustic coupling, minimizing the reflection of acoustic signal at the transducer/skin interface. This would reduce the need for synthetic matching layers which are attached to the transducer surface to improve acoustic coupling with the body [13].

The transducer material should be compliant so as to eliminate air pockets at the transducer/skin interface and to be easily shaped for focusing purposes. Finally, its processing should also be adaptable to mass production.

### 1.2 MATERIALS.

Piezoelectric ceramic materials such as lead zirconate titanate (PZT), pure and modified PbTiO\(_3\) and PbNb\(_2\)O\(_6\) have been used extensively for transducer applications. They share many of the same advantages and disadvantages when evaluated for transducer applications. In general, piezoceramics possess the strongest piezoelectric charge coefficients \( (d_{33} \) and \( d_p) \), the largest electromechanical coupling coefficients \( (k_t) \) and relative permittivities \( (K) \), and the lowest dielectric losses \( (\tan \delta) \). As a result, piezoelectric ceramics are the most common transducer materials used today, despite several drawbacks. Their high densities lead to large characteristic acoustic impedances, necessitating the usage of matching layers. The large relative permittivities of these materials facilitate electrical tuning, but also
significantly reduce their piezoelectric voltage coefficients. Piezoceramics also have a large mechanical quality factor ($Q_m$) and require the addition of damping backings to reduce ringing to an acceptable level. Finally, ceramics are brittle, nonflexible and nonconformable.

One single phase piezoelectric material that has been utilized with some success is a piezoelectric polyvinylidene fluoride polymer (PVDF or PVF$_2$) \{(CH$_2$-CF$_2$)$_n\} \; [14, 15]. It has a low density and high flexibility, along with a low dielectric permittivity resulting in a very high voltage coefficient. However, it also has several disadvantages which make its use difficult. Its $d_{33}$ and $d_k$ values are low. In order to pole PVDF, an extremely high electric field is necessary, which limits the thickness of the material \[13, 16\].

The recent development of copolymers consisting of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) has resulted in piezopolymers with properties superior to those of PVDF homopolymer \[17, 19\]. In addition, the processing of the copolymer is less restrictive. No stretching is necessary during poling \[18\] and a reduced poling field (0.7 MV/cm) can be used \[17\]. The decreased $K$ of the copolymer material results in, by far, the greatest voltage coefficients of any single phase piezoelectric material. Its $d_k$ is also larger than that of PVDF. However, the most significant copolymer property improvement is shown in its $k_r(0.3)$. The highest $k_t$ is dependent on both the VDF content and the annealing temperature. Annealing, either prior to or during poling at temperatures above the $T_c$ (~120 °C), serves to enhance the polymer crystallinity \[24\]. The best overall properties were attained in annealed copolymers containing 70-75 mol percent VDF \[24\].

Despite the many advancements made in (PVDF-TrFE) copolymer, there are uncertainties, such as the degree of property pressure dependence, and other drawbacks that remain. The copolymer has a large tan δ (10 %) and small $K$ (6-10). By piezoceramic standards, it has very low $d_{33}$ and $d_k$ coefficients, and its $k_r$, although large for piezopolymers, is still fairly small. Thus, the need for alternative piezoelectric materials for transducer applications remains.

It is apparent then, that some composite material may be designed so as to attain the desired transducer properties. In this way, the best properties from each constituent phase within the composite may be utilized to create an improved transducer material. In general, by replacing a portion of a piezoceramic with a lightweight, flexible, non-piezoelectric polymer, the resulting density, acoustic impedance, mechanical quality factor and dielectric constant can be decreased. If the phases can be arranged so the piezoelectric charge coefficients ($d_k$ and $d_{33}$) and $k_t$ of the composite are maintained at reasonable levels, its voltage coefficients ($g_{11}$ and $g_{33}$) can be substantially improved. As a result, the $d_k$, $g_{11}$ and $d_{33}$ $g_{33}$ figures of merit of the piezocomposites can actually surpass those of single phase materials. For all of these reasons, piezoelectric ceramic/polymer composites have been extensively studied in the past decade and a half for use as transducers in hydrophone and ultrasonic biomedical imaging applications.

2. Piezoelectric composites.

2.1 Connectivity patterns. — The arrangement of the component phases within a composite is critical for the electromechanical properties of composites. Newnham et al. have developed the concept of "connectivity" to describe the manner in which the individual phases are self-connected \[26, 27\]. In a diphasic system, there are ten types of connectivities in which each phase is continuous in zero, one, two or three-dimensions. The ten connectivities shown in figure 1 are denoted as the following: 0-0, 0-1, 0-2, 0-3, 1-1, 1-2, 2-2, 1-3, 2-3 and 3-3. It is conventional for the first digit to refer to the piezoelectrically active phase. Based on the connectivity designs, several important piezoelectric ceramic/polymer composites were developed. Figure 2 represents the schematic diagram of different piezoelectric ceramic/polymer composites. All these composites showed improved piezoelectric properties.
DEVELOPMENT OF PIEZOELECTRIC COMPOSITES FOR TRANSDUCERS

Fig. 1. — Ten different connectivity patterns of diphasic materials.

**Piezoelectric Ceramic-Polymer Composites**

- Particles in a Polymer \((0-3)\)
- PVDF Composite Model \((0-3)\)
- PZT Spheres in a Polymer \((1-3)\)
- Diced Composite \((1-3)\)
- PZT Rods in a Polymer \((1-3)\)

- Sandwich Composite \((1-3)\)
- Glass-Ceramic Composite \((1-3)\)
- Transverse Reinforcement \((1-2-3-0)\)
- PZT-Polymer-Air Composite \((1-3-1)\)
- Moonie \((3-0)\)

- PZT-Air Composite \((3-0)\)
- Honeycomb Composite \((3-1P)\)
- Honeycomb Composite \((3-1S)\)
- Perforated Composite \((3-1)\)
- Perforated Composite \((3-2)\)

- Replamine Composite \((3-3)\)
- BURPS Composite \((3-3)\)
- Sandwich Composite \((3-3)\)
- Ladder Structure \((3-3)\)

Fig. 2. — Schematic diagram of various piezoelectric ceramic-polymer composites.
compared to single phase piezoelectric ceramics. The $d_{33}$ figures of merit of these composites are compared in figure 3. In the following sections, processing and properties of several important piezocomposites with various connectivity patterns are reviewed.

### Comparison of $d_{33}g_{33}$ of Various Composites

<table>
<thead>
<tr>
<th>$d_{33}g_{33}$ ($\times 10^{-15}$ m$^2$/N)</th>
<th>Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>PZT</td>
</tr>
<tr>
<td>1000</td>
<td>PVDF</td>
</tr>
<tr>
<td>1800</td>
<td>PbNb$_2$O$_6$</td>
</tr>
<tr>
<td>2300</td>
<td>0-3 PbTiO$_3$ Composite</td>
</tr>
<tr>
<td>3200</td>
<td>1-3-0 PZT Rod Composite</td>
</tr>
<tr>
<td>3500</td>
<td>PZT Rod Composite with Rigid Electrodes</td>
</tr>
<tr>
<td>8000</td>
<td>3-3 BURPS</td>
</tr>
<tr>
<td>10000</td>
<td>1-3-0 PZT Rods-foamed Polymer Composite</td>
</tr>
<tr>
<td>15000</td>
<td>3-2 Perforated Composite</td>
</tr>
<tr>
<td>20000</td>
<td>Diced Encapsulated Composite</td>
</tr>
<tr>
<td>30000</td>
<td>1-3-1 Composite</td>
</tr>
<tr>
<td>50000</td>
<td>Moonie</td>
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</tbody>
</table>

Fig. 3. — Comparison of $d_{33}g_{33}$ of various composites.

#### 2.2 COMPOSITES WITH 0-3 CONNECTIVITY

In a composite with 0-3 connectivity, a three dimensionally connected polymer phase is loaded with ceramic powder (Fig. 2). The major advantages of 0-3 is its ease of fabrication in a variety of forms including large flexible thin sheets, extruded bars and fibers, and molded shapes. It is also amenable to mass production and may conform to any curved surface. The properties of 0-3 composites are strongly dependent on both the piezoelectric and polymer phases utilized, as well as the fabrication method employed. Many different variations have been attempted, primarily for use in hydrophones and are summarized here.

The first attempts to produce 0-3 composites were made by Kyiatama [32], Pauer [33] and Harrison [34] using PZT as a filler material and polyurethane as a matrix. These early composites had very low $d_{33}$ values.

Several types of flexible piezoelectric composites consisting of PbTiO$_3$ powder and chloroprene rubber were developed by Banno et al. [30, 36, 37] at NTG-NGK, namely PR-303, 304, 305, 306, and 307. PR-305 and 307 showed a figure of merit of $\sim 5 \times 10^{-15}$ m$^2$/N, whereas PR-303, 304, and 306 showed a F.O.M. of $\sim 1 \times 10^{-15}$ m$^2$/N. In addition, the F.O.M. of PR-305 and 307 showed signs of pressure dependence, whereas PR-303, 304 and 306 were pressure independent. In order to explain these variations, several piezoelectric composites consisting of PbTiO$_3$ powder with various particle sizes of 3.3, 7.3, and 31.8 $\mu$m were prepared. In addition, composites consisting of a binary PT ceramic powder with two distinct particle sizes of $A = 7.3$ $\mu$m and $B = 31.8$ $\mu$m
were made. Several conditions were varied, including weight % solids loading. The properties were evaluated at pressures of 0.5 and 15 MPa, and the densities of the composites were measured by the Archimedes method. It was determined that both particle size and relative density affected \( d_h \) values. Larger sized particles seemed to produce higher \( d_h \) values, yet seemed to show moderate pressure dependence attributed to the porosity formation associated with the usage of larger particles. This was confirmed by relative density measurements, which was on the order of 93-96%. Smaller sized particles produced lower \( d_h \) values, but showed little or no pressure dependence, which was attributed to little or no porosity and was confirmed by relative densities approaching 100%. In considering the binary composites, the same effects listed above are applied.

The volume percent ceramic within the composites affected the \( d_h \) values. Composites with 40 volume % ceramic tended to show no pressure dependence. As the volume % of ceramic increased, the pressure dependence became more obvious and the \( d_h \) values decreased with increasing pressure. As with the large monosized particle composites, this too is due to porosity within the composites. More pores become trapped between the particles, causing \( d_h \) to decrease with increasing pressure.

Giniewicz [31] developed 0-3 ceramic powder-polymer composites with a filler material of 0.5PbTiO\(_3\)-0.5Bi(F\(_{0.98}\)Mn\(_{0.02}\))O\(_3\) [PT-BF] composition. Composites prepared conventionally with water quenched PT-BF and Eccogel polymer exhibited a virtually pressure independent \( d_h \). \( g_h \) F.O.M. of 2 700 \( \times \) \( 10^{-15} \) m\(^3\)/N. Hanner et al. [28, 29] developed a 0-3 paint composite containing polymer, piezoceramic powder (60-70 volume %) and the necessary surfactants and dispersants.

All of the piezoceramic filler materials mentioned were prepared by a mixed oxide method in which oxide raw materials are simply mixed together and calcined. Chemically derived piezoelectric powders offer the advantages of high purity, homogeneity on a molecular scale, lower processing temperatures and controlled particle size and distribution [39]. Flexible lead titanate/Eccogel 0-3 composites prepared with highly crystalline, coprecipitated (~3 \( \mu \)m) PT powder exhibited a much larger hydrostatic F.O.M. (4 170 \( \times \) \( 10^{-15} \) m\(^3\)/N) than reported for mixed oxide PT composites [39, 40]. Chemical processing was also used to prepare PT-BF (Mn doped) powder by the coprecipitation of an aqueous citrate-based solution [40]. Composites fabricated by die pressing a mixture of the PT-BF powder and Eccogel polymer exhibited an excellent \( d_h \) \( g_h \) F.O.M. of 4 200 \( \times \) \( 10^{-15} \) m\(^3\)/N [41].

Although the simplicity of 0-3 composite processing is highly desirable, it is difficult to achieve a completely uniform distribution of powder and polymer phases, particularly at higher filler loadings (Fig. 4). Furthermore, the presence of voids within the composites limits the poling field that may be applied by reducing the composite dielectric breakdown strength.

To improve the microstructural homogeneity and decrease the chance of void formation in 0-3 composites, a colloid processing method was developed by Han et al. at Rutgers University [38]. With this technique, piezoceramic powder was dispersed in a dilute polymer solution, allowing a polymer coating to be absorbed onto the powder surface. The addition of nonsolvent drives the polymer out of the solution and precipitates polymer-powder coacervates. Colloidal filtration, followed by die pressing, consolidated the coacervates, forming 0-3 composites with a uniform microstructure (Fig. 4).

Collooidally processed composites composed of coprecipitated PT-BF powder and Eccogel polymer were measured to have the largest \( d_{33} \) (65 pC/N) and highest \( d_h \) \( g_h \) F.O.M. (6 000 \( \times \) \( 10^{-15} \) m\(^3\)/N) of all «true» 0-3 composites. In addition, collooidally processed composites were able to withstand a poling field of up to 150 kV/cm as compared to 120 kV/cm for conventionally prepared composites with the same components. This is indicative of an improved composite microstructure resulting from the colloidal processing.
Han et al. studied the effect of the particle size on dielectric and piezoelectric properties of 0-3 composites [41]. In this study, composites of PT powder with different particle sizes and PVDF copolymer consisting of 90% vinylidenefluoride and 10% hexafluoropropylene were prepared. It was found that $d_{33}$ decreased with the particle size of the filler material. It was also noteworthy that the $d_{33}$ value decreased from 50 to 33 pC/N as the particle size of the PT ceramic changed from 3.5 to 0.5 μm. Unlike the $d_{33}$ behavior, the dielectric constant was found to be almost independent of the particle size of the ceramic filler except for slightly lower values in the composites with very fine particle sizes. The effect of the particle size on dielectric and piezoelectric properties were also investigated by Lee et al. [72]. In this work, PT powder of different particle sizes was mixed with Eccogel polymer and composites were
prepared by conventional die pressing methods. They also observed that the dielectric constant and dissipation factor are not affected by particle size. However, \( d_{33} \), decreased dramatically with particle size.

To investigate the effect of the polymer on resistivity and dielectric properties, Han et al. prepared PT composites with Eccogel polymer, PVDF copolymer, and ethylene-propylene-diene monomer (EPDM) polymer [41]. The PVDF copolymer and EPDM polymer had moderate resistivities (6 \( \times \) 10\(^{14} \) and 10\(^{10} \) ohm-cm, respectively), while the resistivity of the epoxy was lower than that of the PVDF copolymer (10\(^{12} \) ohm-cm). It was found that although higher poling conditions could be applied to the PVDF copolymer and EPDM composites, the highest \( d_{33} \) value was obtained from the epoxy composites. The higher electrical conductivity of the polymer matrix may have created more electric flux paths between the ceramic particles. This in turn increased the electric field acting on the ceramic filler and made poling of the ceramic easier. The dielectric constant of the composite with EPDM polymer was slightly lower than that of the other two types of composites, but the dissipation factor of the composites with epoxy was two times larger than that of the PVDF copolymer and EPDM polymer. The epoxy gave the highest \( d_{33} \) \( g_{33} \) figure of merit (5 600 \( \times \) 10\(^{-15} \) m\(^2\)/N) and the EPDM gave the lowest figure of merit (600 \( \times \) 10\(^{-15} \) M\(^2\)/N). With the consideration of dissipation factor in the figure of merit, the PVDF copolymer gave the highest \( d_{33} \) \( g_{33} \)/tan \( \delta \) of 2 000 \( \times \) 10\(^{-11} \) m\(^2\)/N.

One of the main problems in achieving 0-3 composites with high piezoelectric properties is the difficulty involved in poling the composites. In a 0-3 composite, the electric field which acts on an individual spherical piezoelectric grain is mostly controlled by the dielectric constant of the polymer phase. Since most polymers have a lower dielectric constant compared to piezoelectric ceramic materials, most of the applied electric field will pass through the lower dielectric constant phase. One way to resolve this difficulty with poling is to introduce a third conductive phase between the piezoelectric particles. Sa-Gong [35] prepared such composites by adding carbon, germanium or silicon to PZT. Another approach to ease the poling is to raise the resistivity of the ceramic filler material. This type of composite was prepared for PbTiO\(_3\) powder doped with UO\(_2\) to increase resistivity, allowing a very large (up to 130 kV/cm) poling field to be applied.

The poling of 0-3 composites can also be improved by using the corona poling method [20]. This technique in particular, has been successful in poling PVDF films. In corona poling, charge is sprayed on the surface of an unelctroded sample creating an electric potential between the top sample surface and the ground plate (Fig. 5). If the sample is defective the charge will leak through the film but the sample will not be entirely shortened because of the absence of electrodes. The set-up for the corona poling includes one or more needles to which a large DC potential is applied. These needles act as field intensifiers by ionizing the surrounding gas molecules. The sample is positioned on a heated and grounded metal plate. Heating makes poling easier by lowering the coercive field. The piezoelectric properties of ceramics and composites poled by the corona method are comparable or better than those poled by the conventional poling technique. Using this poling method, one can pole large area samples continuously.

2.3 COMPOSITES WITH 1-3 CONNECTIVITY.— In composites with 1-3 connectivity, the ceramic phase is continuously connected in one dimension while the polymer phase is continuous in all three dimensions (Fig. 2). The first series of 1-3 composites were created by Harrison [13], Pohanka [14] and Safari [15].

Polar glass ceramics, which could be considered to have a 1-3 connectivity have also been investigated for use in hydrophones [13]. These glass ceramics can be thought of as diphasic composites composed of a glassy phase which is continuous in three dimensions, and one or
more crystalline phases, which are continuous in only one dimension. The \( g_h \) and \( d_h g_h \) of these composites are comparable to those of PVDF. However, glass ceramics are especially favorable because they involve no problems with aging or depoling as they are nonferroelectric and exhibit no pressure dependence.

A more common type of 1-3 composite was developed by Klicker [50, 51]. The composite consisted of sintered, extruded rods aligned and embedded in the polymer. In the idealized condition of this composite, the polymer phase is far more compliant than the PZT rods allowing stress to be transferred to the PZT rods. This stress amplification combined with a reduced permittivity, enhances the piezoelectric voltage coefficient.

A simplified method of making 1-3 composites was first investigated by Savakus et al. by dicing a sintered PZT ceramic in a checkerboard pattern to produce an array of PZT columns of desired dimensions and spacing, and then backfilling with polymer [52]. To uniformly distribute stress along the poling direction and to increase piezoelectric properties, thin steel or brass plates were used as end caps [73]. The \( g_h \) coefficient was improved but was highly pressure dependent due to the fact that the cap may have separated at high pressures.

In all 1-3 composites, due to the high Poisson's ratio of the polymer, the internal stress created will oppose the applied stress which reduces the stress amplification. Therefore, the piezoelectric coefficient is not as high as expected. To reduce the Poisson's ratio and increase the piezoelectric properties, Lynn [55] introduced porosity into the polymer by introducing either a foaming agent or glass spheres. Both additives increased the hydrostatic properties, however, the composite with foaming agent in the polymer exhibited a pressure dependence on the piezoelectric properties. This type of composite is named a 1-3-0 where the third number represents the connectivity of the third phase (voids or microglass spheres).

One way to increase the stress amplification in a 1-3 composite is to introduce transverse reinforcement [1, 57]. In this design, the PZT rods are parallel to the poling direction while stiff glass fibers are placed in the transverse directions. The glass fibers carry the stress in the transverse directions, thereby decreasing the \( d_{31} \) coefficient without affecting the \( d_{33} \) coefficient.

Another design developed to counteract the Poisson's ratio problems consists of a 1-3 structure, but without any lateral contact between the polymer matrix and the PZT rods so no charges are generated in the lateral mode [56]. In this design, the stress transfer is carried out by two metallic armature plates used as electrodes as well as providing a reinforcement of the polymer matrix in the transverse directions. To prepare these composites, a polyurethane matrix (Flexcomet 94SA) is cut to the desired size and holes are drilled into it in a square or
hexagonal arrangement, tailored to the required volume ratio. Armature plates of steel are cut to various thicknesses. PZT rods are first aligned and bonded to one of the armature plates with a conductive adhesive (epoxy and silver). The polymer with holes is placed on top and bonded to the armature with the rods such that the PZT rods are standing without any contact with the surrounding polymer. The rods are then ground to the matrix thickness height and the second armature is bonded to the PZT rods and the matrix. Some samples are further reinforced with an epoxy outer shell and all composites are then fully embedded in polyurethane. This type of composite is named a 1-3-1 where the third number refers to the air element introduced to the composites. Typical piezoelectric $d_{33}$ coefficients range from 250 to 400 pC/N. The $d_h g_h$ figure of merit is around $30 \times 10^{-12}$ m$^2$/N. The $d_h g_h$ of composites with thicker armature plates are generally more stable, as are those with a small lateral epoxy shell. Both the armature plate thickness and the epoxy shell lower the stress supported by the lateral edges of the matrix and therefore, limit its lateral strain and the related effects. The $d_h g_h$ of composites with a thinner armature plate decreases with pressure.

Over the past several years many attempts have been made to simplify the assembly process for 1-3 design with the intention of improving manufacturing viability, lowering the material cost and preparing large area composites. The early attempts involved dicing solid blocks and backfilling with polymer [12, 21-24, 52].

Recently, Kim et al. devised a method to fabricate composites which consisted of enclosing PZT rods and soft epoxy in the compartments of a honeycomb structure [60]. The design of this process involved the selection of a stiff corrugated preform made from a stiff epoxy such as polycarbonate (Lexan). The preforms were made in the shape of strips with trapezoidal grooves and ridges that would form a honeycomb when bonded on top of each other with epoxy. The PZT rods used in this study were PZT 5H with diameters of 0.08-0.13 cm. The volume % PZT was varied by changing the rod diameter, introducing dummy rods, or using a combination of rods with different diameters. The latter two approaches resulted in a non-periodic arrangement of rods which was beneficial in attenuating the spurious transverse resonances. The preform honeycomb polymer, in this composite structure, provided mechanical reinforcement to minimize the transverse contribution $d_{33}$ and the soft epoxy reduced the Poisson’s ratio, allowing the ceramic rods to expand and contract. The prototype composite had a rod diameter of 0.08 cm resulting in 17 % ceramic, 70 % Lexan (honeycomb preform) and 13 % Rho-C soft epoxy. The end surfaces were polished to expose the rods and covered with silver paste to adhere to a corrugated alumina cover plate for the best piezoelectric properties. Optimum values of piezoelectric properties of the composites were as follows: $K = 406$, $d_{33} = 564$ pC/N. $g_{33} = 157$ mVm/N. $d_h$, $g_h$, and $d_h g_h$ measured without a cover plate were 135 pC/N, 45 mVm/N, and $6 \times 10^{-15}$ m$^2$/N, respectively.

Ceramic injection molding is a viable process for fabricating PZT ceramics and piezoelectric ceramic/polymer transducers. Some of the advantages offered by the injection molding process are: complex, near net-shape capability for handling many fibers simultaneously; rapid throughput; compatibility with statistical process control; low material waste; flexibility with respect to transducer design; and low cost. The only foreseeable disadvantage is the high initial tooling costs.

Bowen et al. used an injection molding method to produce large area 1-3 ceramic/polymer composites [61]. By using this technique, it is possible to make fine scale piezoelectric fiber-polymer composites for high frequency medical ultrasound and non-destructive applications as well as for underwater hydrophones. The injection molding process overcomes the difficulty of assembling oriented ceramic fibers into composite transducers by net-shape preforming ceramic fiber arrays. Furthermore, the process makes possible the construction of composite transducers with more complex ceramic element geometries than those previously made.
The process consists of injecting a hot thermoplastic mixture of ceramic powder and organic binder into a cooled mold. Precautions such as hard-facing the metal contact surfaces are important to minimize metallic contamination from the compounding and molding machinery. After careful binder removal, firing, and backfilling with polymer follow in typical composite manufacturing fashion. PZT elements with 0.1 and 2 degree taper are made in both 0.5 and 1 mm diameters. The preform size is maintained at 50 x 50 mm to accommodate molding shrinkage. The piezoelectric d_{33} coefficient and dielectric constant of 800 pC/N and 3600, respectively, were an indication that composite properties are comparable to those of optimized PZT 5H (very soft PZT) and prove their negligible sensitivity to iron contamination from the injection molding apparatus. The capability of net-shape molding for fabricating very fine scale preforms has been demonstrated by making 30 μm wide PZT elements.

More recently, Fiber Materials Inc. has demonstrated the applicability of its Ultraloom™ to position individual PZT rods into a tool or mandrel [59]. Large area 1-3 PZT-polymer composites were developed by placing PZT rods into cork type material by application of slight pressure. Glass fiber is then woven in the transverse direction and the entire sample is then impregnated with resin polymer. With this method, they are able to prepare flat samples of 25-50 cm in dimension and cylindrical composites of at least 25-30 cm in diameter and 50 cm in height. Current effort focuses on improving the rate of rod insertion by modifying the Ultraloom to insert several rods at a time. One concept utilizes a serrated tray to prepare up to 30 rods for insertion in a single pass by the machine.

2.4 COMPOSITES WITH 3-0 CONNECTIVITY. — In composites with 3-0 connectivity, PZT ceramic is self-connected in three dimensions while the second phase (polymer, voids) is not connected in any dimension. Ceramic air composites with 3-0 connectivity were first developed by Kahn [62, 63] using a tape casting technique and multilayer ceramic technology. In these studies, a slip consisting of PZT ceramic powder, organic binder, and solvent were tape cast and dried to form thick film tapes (34 μm). A fugitive ink was then screened onto the tapes in a computer generated pattern. 100 layers of tape were then stacked in a chosen configuration and laminated at 55 °C and 2 MPa. The samples were then heat treated to burn out the organic binders and carbon, leaving ordered voids. To prevent defects in the ceramic due to the rapid gas evolution from exothermic reactions during burnout, a well controlled lower partial oxygen pressure was used. Sintering of the samples was then achieved in a covered alumina crucible. The total porosity of the final samples ranged from 15-22% depending on the configuration and size of the ink pattern. The highest hydrostatic piezoelectric values were reported for samples with a crossed bar void configuration. The d_{33} of these composites was 350 pC/N with a dielectric constant of 500. The d_{h} and d_{g} of these samples were 230 pC/N and 13 300 x 10^{-15} m^2/N, respectively.

Another type of 3-0 composite has been fabricated by Pilgrim [64] by hot pressing a mixture of large polymer spheres of polyethylene and PZT powder, thus yielding an irregular array of low K « grains » of polymer surrounded by high K (PZT) boundaries. An exceptionally low acoustic impedance is obtainable using this method.

Recently, researchers at Penn State developed a PZT air composite named « Moonie » [65, 66]. This composite was constructed using metal (brass) end caps with shallow internal cavities which were bonded to a piezoelectric ceramic disk (Fig. 2). The design is based on the concept of a flexational transducer. In this design, the ceramic is excited in an extensional mode and the metal plates in a flexure mode. The metal plates are used as a mechanical transformer of the high impedance of the ceramic to the low impedance of the load. In this manner, the radial displacement of the piezoelectric ceramic is amplified into a large axial motion of the metal end caps. Essentially, the negative flexational motion of the metal arising from the radial motion of the ceramic d_{31} coefficient is added to the positive
longitudinal displacement through \(d_{31}\). This is especially important for hydrophone applications where \(d_h = d_{33} + 2d_{31}\) and thus a very large hydrostatic piezoelectric charge coefficient is evident.

Moonie composite transducers and actuators were made using electroded PZT or PMN-PT ceramic discs (11 mm in diameter and 1 mm thick) and brass end caps (from 11 mm to 13 mm in diameter with thicknesses ranging from 0.2 to 3 mm). Brass was chosen as the metal end cap material for its low thermal expansion coefficient (approximately 15 ppm/°C). Shallow cavities from 6 mm to 8.5 mm in diameter and about 150 \(\mu\)m center depth were machined into the inner surface of each brass cap. The ceramic disc and the end caps were bonded around the circumference, with care being taken not to fill the cavity or short circuit the ceramic electrodes. Three kinds of bonding materials were used: silver foil/paste, lead-tin-silver solder and epoxy resin.

The effective \(d_{31}\) of the composite was found to be inversely proportional to the metal thickness and increased with electroded area of PZT, evidence that all the PZT was contributing uniformly to the displacement. The effective \(d_{33}\) values as high as 4 000 pC/N were obtained with these « Moonie » composites at the center of the brass end caps, where flexural motion is largest. Also, \(d_h \approx \gamma_h\) figure of merit values of \(\sim 50 000 \times 10^{-15}\) m²/N were not uncommon for hydrophones. The lowest flexentional resonance frequency was proportional to the square root of metal thickness and virtually independent of ceramic and bonding layer thickness. This frequency in the PZT-brass composite with the solder bond and without epoxy encapsulation decreased with temperature, which was probably due to the high stress in the PZT ceramic arising from thermal stresses set up by the metal.

The « Moonie » was also examined for its potential as an actuator for micropositioning applications. The displacement of the composite actuator was measured with a Linear Voltage Differential Transducer (LVDT) having a resolution of approximately 0.05 \(\mu\)m, in the low frequency range. The displacement frequency dependence was measured with a double beam laser interferometer and resonant frequencies were obtained with a spectrum analyzer.

The experimental results showed the PMN composite « Moonies » produced a tenfold strain amplification with a displacement of 10 \(\mu\)m under a field of 10 kV/cm. For a 124 layer electrostrictive composite, a 30 \(\mu\)m displacement was feasible under an applied voltage of 150 V. By loading these actuators with weights, forces in excess of 2 kgf were created. The displacement amplification was dependent on the thickness of the metal and the cavity diameter with maximum values as large as 20 \(\mu\)m with a force capability of 0.15 kgf possible for PZT composites.

The « Moonie » actuator appears to make a step function advance in the state-of-the-art for hydrophones, based on its superior electromechanical properties. Further increases in actuator performance are possible using improved materials, design, and the use of multilayer ceramics and multimoonie stacks, all of which are currently under investigation.

2.5 COMPOSITES WITH 3-1 AND 3-2 CONNECTIVITY. — In composites with 3-1 and 3-2 connectivity, the ceramic phase is continuous in all three dimensions while the polymer phase is continuous in one or two dimensions. An early composite in this category is the perforated composite [3] which has been fabricated by drilling holes in sintered PZT blocks and then backfilling with an epoxy polymer. In some of these composites, the perforation was left empty and then capped with an alumina plate and the whole structure was encapsulated in epoxy. These types of composites are referred to as perforated 3-1-0 or 3-2-0 composites. Hole size and volume fraction of PZT had a noticeable effect on the hydrostatic sensitivity of the perforated composites, and the hydrostatic coefficients were improved by decoupling the \(d_{31}\) and \(d_{33}\) coefficients [3]. Large arrays of 3-1 composites were prepared which consisted of
sixteen hundred elements of perforated composites [67]. The $g_h$ of the composite was comparable to that of a single element composite.

The order type of 3-1 composite is the Honeycomb configuration (Fig. 2). The honeycomb PZT was prepared by an extrusion process at Corning Glass Works. In this type of composite, the polymer phase can be continuous in either poling direction (3-1P connectivity) or perpendicular to the poling direction (3-1S connectivity). From these two studies, it was discovered that the stress distribution in a composite was more favorable in lowering the $d_{31}$ coefficient in the 3-1P connectivity composite [68, 69].

2.6 COMPOSITES WITH 3-3 CONNECTIVITY. — In a composite with 3-3 connectivity, the two component phases are each three dimensionally self-connected and in intimate contact with each other. A number of different PZT ceramic/polymer piezocomposites possessing 3-3 connectivity have been fabricated including replamine composites by Skinner [46], BURPS composites by Shrout [47, 48], ladder composites by Miyashita [13] and sandwich composites [74], all of which are illustrated in figure 2. Since the piezoelectric phase is continuous between electrodes in all these composites, poling is facilitated.

The BURPS processing method was adapted by Nagata et al. [13] and Hikita et al. [70] to produce « interconnected porosity » PZT composites. A composite with a 3-3 connectivity pattern was also developed by Zhuang et al. [13]. Their research involved forming a sandwich composite of one PZT/polymer layer surrounded by two solid PZT surface layers.

A completely different fabrication method was developed to make 3-3 composites termed « fired » composites [42, 43]. In this method, piezoceramic powder of PZT and an organic binder were mixed, pressed into pellet form and heat treated to remove the binder, leaving a porous PZT compact and backfilled with polymer. These composites have high $d_{33}$(180 pC/N) and $k_3(0.34)$. Fired composites are not comprised of a connectivity pattern that is truly 0-3. Since some amount of particle-particle interaction occurs during the heat treatment, there is a degree of 3-3 connectivity present within the composites [13].

2.7 FINE SCALE PIEZOELECTRIC CERAMIC FIBER-POLYMER COMPOSITE. — The PZT rod-polymer composite with 1-3 connectivity showed substantial improvement over single phase PZT in its performance as an ultrasonic transducer with water as the load [13]. The improved performance should, however, be extended to a higher frequency range. From the experimental results, it is clear that the strong interaction between the PZT and the epoxy was responsible for the improved performance. This interaction occurred at frequencies where the transverse wavelength in the epoxy was much larger than the periodicity of the lattice. These experimental observations suggest that one of the ways of increasing the efficiency of the composite for operation at high frequency is to scale down the composite structure. This means that the rod diameter and the periodicity of the lattice in the composite structure should be minimized.

Card et al. [49, 53] and Waller et al. [25, 45, 69] were the first researchers to fabricate a fine scale woven PZT fiber/polymer composite by the relic process. These composites have essentially 2-3 connectivity. This process, which is believed to be adaptable for mass production, involves the following steps: i) preparation of an alkoxide PZT stock solution containing stoichiometric amounts of dissolved Pb, Zr, Ti and Nb; ii) homogeneous impregnation of the carbon template with PZT by soaking in the solution; iii) heat treatment to burn out the carbon, transforming the metal ions into a PZT oxide relic that is a replica of the original carbon material; iv) sintering of the PZT relic in a controlled atmosphere to densify the material; v) vacuum backfilling of the PZT relic with a thermally curable polymer.

In both studies, activated carbon fabric (ACC-507, American Kynol, Inc., New York, NY) was used. Activated fabrics consisted of novoloid derived carbon filter twisted into a yarn
which was biaxially woven in two dimensions. The composite fabrication began by soaking as-received woven fabric in the PZT stock solutions for 15 min. The samples were dried at 100 °C/3 h under vacuum, then re-soaked in the PZT solution and dried once more. To burn out the carbon, PZT impregnated woven fabric samples were stacked to a thickness of 20-25 layers and heat treated at 550 °C/10 h and again at 700 °C/4 h. Sintering was performed in a sealed crucible at 1285 °C/2 h with a lead zirconate source to control PbO pressure during sintering. Sintered woven PZT relics were vacuum impregnated with Eccogel (13645-45) epoxy resin polymer.

The amount of weight gain is shown to increase with increasing number of soak/dry cycles. The total amount of PZT absorbed within the carbon fibers after soaking and drying is important. If there is not a sufficient amount of PZT in the fabric, excessive shrinkage and warpage will occur during the carbon burnout step. On the other hand, if there is excessive weight gain after repeated soakings, the woven structure will not be achieved and the spaces between the fibers become clogged with PZT. The optimum solution concentration used in this study was 405 milligrams of PZT per gram of solution.

The series of SEM photomicrographs in figure 6 illustrate the replication process. Figure 6a represents the woven carbon fiber template material. Figure 6b shows how the woven form is preserved in the PZT relic after the sintering stage. A closer view of the relic is shown in figure 6c. Individual fibers of PZT can be seen that corresponds to the individual carbon fibers in the original template. Woven composites were pole in two orientations: parallel and perpendicular to fiber directions, and properties were evaluated for both directions. The dielectric properties of composites with PZT fibers oriented perpendicular to the poling direction are $K = 100$, $d_{33} = 150 \text{ pC/N}$ and $g_1 = 60 \text{ mV/m/N}$.

The relic processing method has been adapted to produce large area composites. The scaling up of the procedure has included studying of variables such as the firing and poling conditions of increasingly larger samples beginning with $1^\prime$ by $1^\prime$, $2.5^\prime$ by $2.5^\prime$ and ending with $4^\prime$ by $4^\prime$. The electromechanical properties of the largest composites are comparable to those of $1^\prime$ by $1^\prime$ samples. Improved processing methods have enabled properties of $K = 140$, $d_{33} = 180 \text{ pC/N}$ and $g_1 = 65 \text{ mV/m/N}$ [71].

The fine scale research was created in order to study the feasibility of constructing different connectivity designs, primarily 1-3, using various carbon filter structures through the relic processing procedure. The three primary fiber structures investigated are the « sandwich », « cigar » and « shell » [71]. The « sandwich » structure incorporates vertical yarns woven into top and bottom carbon fabric layers separated by concentric wooden rings, which are subsequently removed. The desired structure is retained after sintering using an additional support phase (zirconia particles), which is eliminated prior to polymer impregnation. After polishing the top and bottom fabric layers, a structure emulating 1-3 connectivity is created. The « cigar » structure consists of carbon fiber placed parallel to each other and wrapped with a carbon fabric in order to eliminate firing related collapse. A 3-3 connectivity is present due to the cross sintering of the fibers in the planar direction, and vertical direction fiber continuity contributes to the encouraging properties. The « shell » structure is formed simply by wrapping the carbon fabric in a helical fashion around a central point, emulating a 2-3 connectivity. This design yields excellent dielectric and piezoelectric properties ($d_{33} \sim 260 \text{ pC/N}$, $K \sim 220$ and $d_3 \sim 80 \text{ pC/N}$), and offers ease of construction as well as an allowance for a simple modification of its density by controlling the wrapping tightness of the fabric.

Fine scale piezoelectric ceramic-polymer composites were also developed by researchers at Siemens by using a new ceramic processing method [58] called the jet-machining technique. In this method, photoresist was deposited in a unique pattern on the surface of the green PZT pellets using a standard lithographic technique. Ceramic powder of the uncovered area was
Fig. 6. — SEM micrographs of (a) carbon fiber template material (b) sintered relic and (c) close-up of a sintered relic.

removed by jet spraying. The Jet-Machining process cut deep, fine scale, concentric circular grooves with a coupler pattern which are not possible to create with a dicing saw. Firing at high temperature sintered the green pattern into a dense ceramic. The important feature of Jet-Machining is the simplification of fabrication and the creation of complex shapes which are normally made using the dicing technique.

This same team has devised a « lost mold » method for net-shape casting of piezoceramics in which the groove-widths and ceramic-widths can be below ten-microns — well beyond the limit of present diamond wheel machining technology [58]. The ceramic slurry was cast into a plastic mold, dried, and fired. The fired ceramic compact was then flipped over and the space
occupied by the lost mold refilled with a polymer. Grinding, electroding, and poling completed the fabrication of a fine-scale piezocomposite. Composites consisting of PZT rods with a diameter of 100 μm and a thickness of 0.5 mm were prepared by this method. This technique can also form solid-ceramic transducer structures with complex shapes not readily made with a dicing saw. Large scale production of fine-scale structures is feasible; the key is forming the plastic molds which are lost in the firing process. To make molds with very fine scale structures, a deep X-ray synchrotron lithographic technique was used to first form a reusable metal mold with the desired shape of the final ceramic part; the sacrificial plastic mold was then cast from this metal master. Making the plastic molds is a low-cost process, but producing the metal master is costly when very fine scale features are involved.

2.8 Electrostrictive/Ceramic-Polymer Composites. — The electrostrictive materials open up a new direction for transducer applications [75, 76]. By applying an external bias field across the sample, the material becomes piezoelectric. Electrostrictive ceramic-polymer composites with 1-3 connectivity have been developed using the dice and fill method. Deep grooves were cut in a sintered 0.9Pb(Mg1/3Nb2/3)O3-0.1 PbTiO3 [PMN-PT] ceramic disk in a criss-cross pattern and filled with polymer. Composites with 10 and 25 vol. % ceramic were fabricated. Figure 7 shows the dielectric constant and thickness and planar coupling coefficients of the PMN-PT composites. The electromechanical properties of the bulk ceramic

Fig. 7. — Dielectric constant and coupling coefficients of diced 1-3 electrostrictive PMN-PT ceramic/polymer composites.
are also given for comparison. Composites exhibited very high dielectric constants and the $K_v$ value increased linearly with the bias field until saturation of 56% at 5 kV/cm for the composites with 25 vol. % ceramic. The polymer phase had effectively decoupled, causing the planar coupling coefficient to approximate a value of 10% at 5 kV/cm. A higher $K_i/K_p$ ratio translates into a more efficient transducer since there is minimal energy lost through planar vibration. Composites showed mechanical quality response of about 8 at 500 kV/cm [54].

Conclusions.

The development of piezoelectric ceramic-polymer composites has seen much progress in recent years. In this paper, many methods of forming various piezoelectric ceramic-polymer composites have been discussed. 0-3 composites have been generally easier to fabricate, particularly in large areas, but their properties are inferior to other composites. A colloidal processing method improves uniform distribution of powder in 0-3 composites and improves piezoelectric properties. The dice and fill method was seen to be the steadfast method of producing 1-3 composites with much improved properties. However, recent fabrication methods have been seen to be promising methods of producing composites, such as injection molding, the relic method, jet-machining and the lost mold techniques. Moonies are excellent candidates for hydrophone and actuator applications. Initial results on PMN-PT ceramics and composites have been shown to be suitable for transducers with a bias voltage.

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