

APPENDIX

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่

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APPENDIX A

EPOXY RESIN AND FABRICATION OF COMPOSITES

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Epoxy

A common starting material is diglycidyl ether of bisphenol A (DGEBA), which contains two epoxide groups, one at each end of the molecule (Fig. a). Other ingredients that may be mixed with the starting liquidare diluents to reduce its viscosity and flexibilizers to improve the impact strength of the cured epoxy matrix.

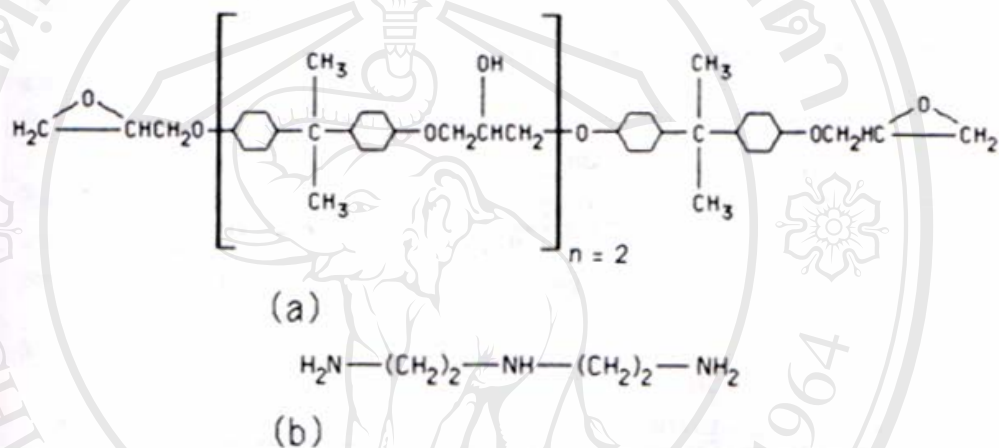


Figure 1 Principal ingredients in the preparation of an epoxy matrix.

(a) A molecule of diglycidyl ether of bisphenol A (DGEBA) epoxy resin.

(b) A molecule of diethylene triamine (DETA) curing agent.

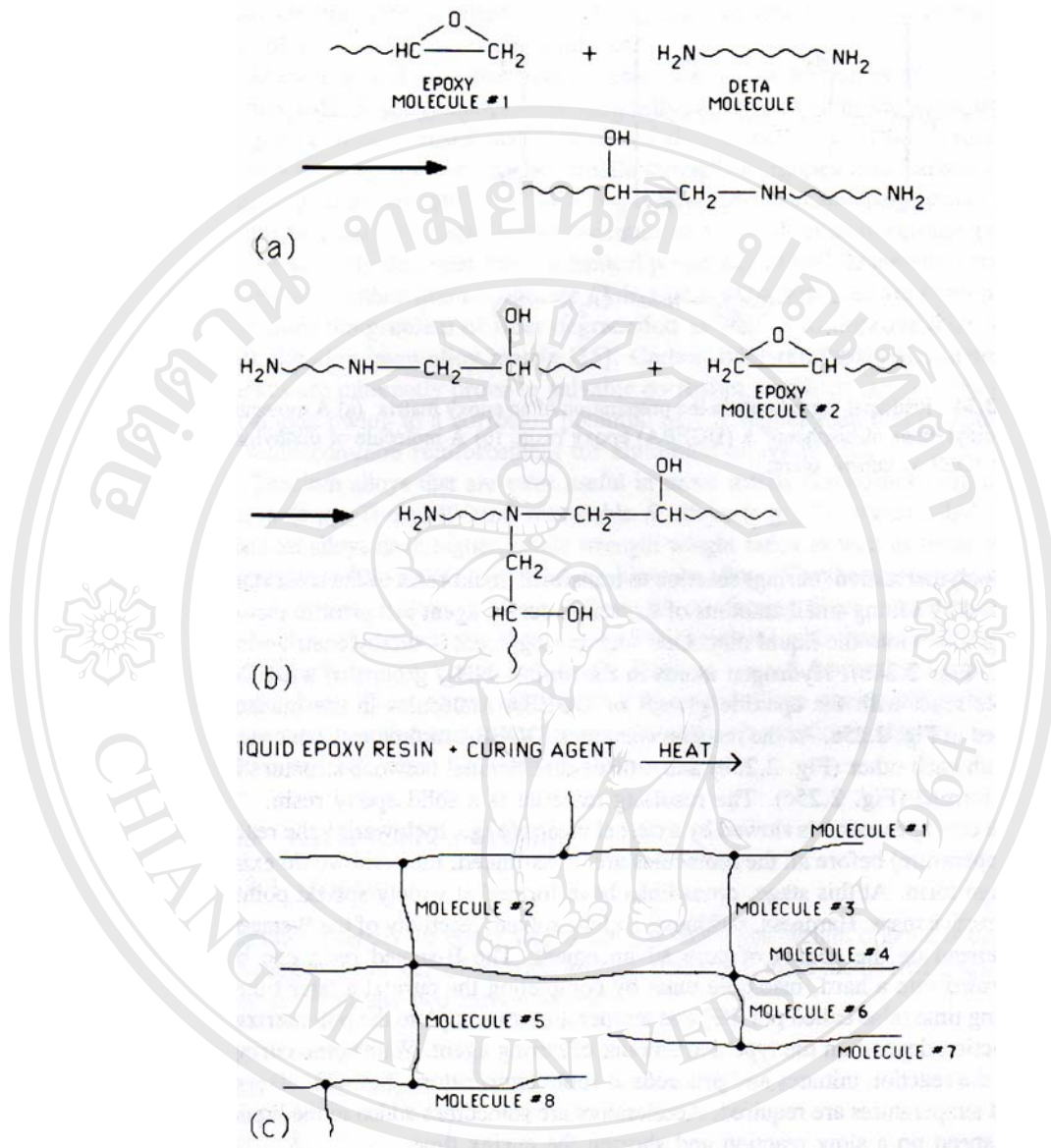


Figure 2 Schematic representation of a cross-linked epoxy resin. (a) Reaction of epoxide group with DETA molecule (b) formation of cross-links and (c) three-dimensional network structure of solid epoxy.

The polymerization (curing) reaction to transform liquid resin to the solid state is initiated by adding small amounts of a reactive curing agent just prior to incorporating fibers into the liquid mix. One such curing agent is diethylenetriamine (DETA, Figure 2b). Hydrogen atoms in the amine (NH₂) groups of a DETA molecule react with the epoxide groups of DGEBA molecules form cross-links with each other (Figure 2b) and a three-dimensional network structure is slowly formed (Figure 2c). The resulting material is a solid epoxy resin.

If the curing reaction is slowed by external means (e.g., by lowering the reaction temperature) before all the molecules are cross-linked, the resin would exist in B-stage form. At this stage, cross-links have formed at widely spaced points in the reactive mass. Hardness, tackiness, and the solvent reactivity of the B-staged resin depend on the degree of cure advancement. The B-staged resin can be transformed into a hard, insoluble mass by completing the cure at a later time.

Curing time (also called pot life) and temperature to complete the polymerization reaction depend on the type and amount of curing agent. With some curing agents, the reaction initiates and proceeds at room temperature, but with others, elevated temperatures are required. Accelerators are sometimes added to the liquid mix to speed up a slow reaction and shorten the curing time.

The properties of a cured epoxy resin depend principally on the cross-link density (spacing between successive cross-link sites). In general, the tensile modulus, glass transition temperature, and thermal stability as well as chemical resistance are improved with increasing cross-link density, but the strain-to-failure and fracture toughness are reduced. Factors that control the cross-link density are the chemical structure of the starting liquid resin (e.g., number of epoxide groups per molecule and

spacing between epoxide groups), functionality of the curing agent (e.g., number of active hydrogen atoms in DETA), and the reaction conditions, such as temperature and time.

The continuous use temperature for DGEBA-based epoxides is 150 °C or less. Higher heat resistance can be obtained with epoxides based on novolac and cycloaliphatics, for example, which have a continuous use temperature ranging up to 250 °C. In general, the heat resistance of an epoxy is improved if it contains more aromatic rings in its basic chain.

Epoxy matrix, as a class, has the following advantages over other thermoset matrices:

1. Wide variety of properties , since a large number of starting materials, curing agents, and modifiers are available
2. Absence of volatile matters during cure
3. Low shrinkage during cure
4. Excellent resistance to chemicals and solvents
5. Excellent adhesion to a wide variety of fillers, fibers, and other substrates

The principal disadvantages are its relatively high cost and long cure time.

Currently, the primary epoxy resin used in the aerospace industry is based on tetraglycidyl diamine diphenyl methane (TGDDM). It is cured with diamine diphenyl sulfone (DDS) with or without an accelerator. The TGDDM/DDS system is used due to its relatively high glass transition temperature (240 °C-260 °C, compared to 180-190 °C for DGEBA systems) and good strength retention even after prolonged exposure to elevated temperatures. Prepregs made with this system can be stored for

a longer time period due to relatively low curing reactivity of DDS in the B-staged resin. Limitations of the TGDDM system are their poor hot/wet performance, low strain-to failure, and high level of atmospheric moisture absorption (due to its highly polar molecules). High moisture absorption reduces its glass transition temperature as well as its modulus and other mechanical properties.

Table 1 Typical Properties of Cast Epoxy Resin (at 23 °C)

Specific gravity	1.2-1.3
Tensile strength, MPa (psi)	55-130 (8000-19,000)
Tensile modulus, GPa (106 psi)	2.75-4.10 (0.4-0.595)
Poisson's ratio	0.2-0.33
Coefficient of thermal expansion, 10 ⁻⁶ m/m per °C (10 ⁻⁶ in./in. per °F)	50-80 (28-44)
Cure shrinkage, %	1-5

Although the problems of moisture absorption and hot/wet performance are reduced by changing the resin chemistry, brittleness or low strain-to-failure is an inherent problem of any highly cross-linked resin. Improvement in tolerant composite laminates. For epoxy resins, this can be accomplished by adding a small amount of highly reactive carboxyl terminated butadiene-acrylonitrile (CTBN) liquid elastomer which forms a second phase in the cured matrix and impedes its microcracking. Although the resin is toughened, its glass transition temperature, modulus, and tensile strength as well as solvent resistance are reduced. This problem is overcome by blending epoxy with a tough thermoplastic resin, such as polyethersulfone, but the

toughness improvement depends on properly matching the epoxy and thermoplastic resin functionalities, their molecular weights, etc.

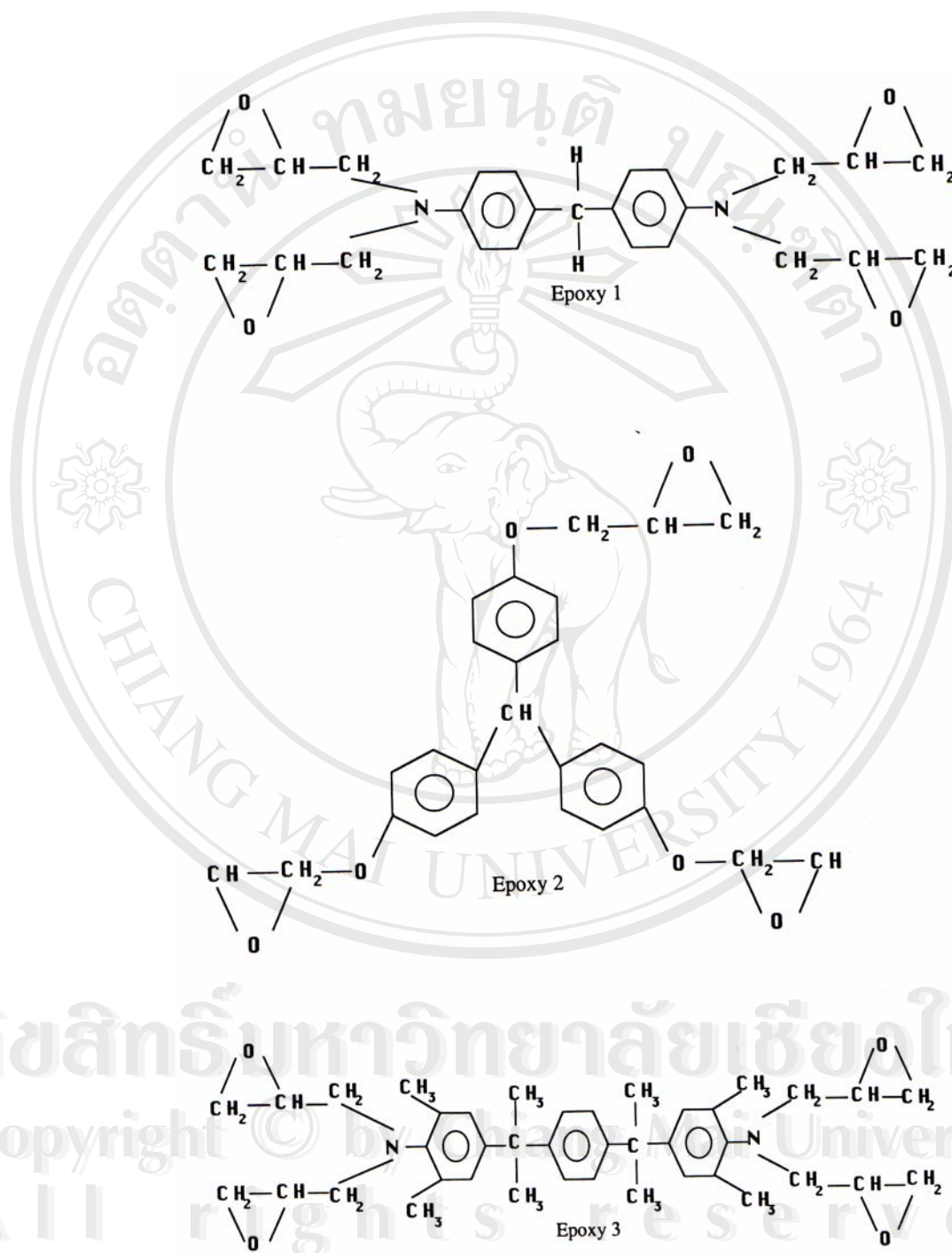


Figure 3 Structures of Epoxy 1-3.

Table 2 Mechanical Properties of High-Performance Epoxy Resin a,b

Property	Epoxy 1	Epoxy 2 (Epon HPT 1072, Shell Chemical)	Epoxy 3 (Tactix 742, Dow Chemical)
T _g °C	262	261	334
Flexural properties (room temperature)	140.7	111.7	124.1
Strength, MPa (ksi)	(20.4)	(16.2)	(18)
Modulus, GPa (Msi)	3.854 (0.559)	3.378 (0.490)	2.965 (0.430)
Flexural properties (hot/wet) ^c			
Strength (% retained)	55	65	-
Modulus (% retained)	64.5	87.3	-
Fracture energy, G _{1c} , kJ/m ² (in.-lb/in ²)	0.09 (0.51)	0.68 (3.87)	0.09 (0.51)
Moisture gain %	5.7	2.6	-

^a All epoxies were cured with DDS.

^b Structures for Epoxies 1-3 are given on Fig.

^c Percent retained of room temperature/dry properties when tested in water at 93 °C after 2-week immersion at 93 °C

Table 3 Effect of CTBN Addition on the Properties of Cast Epoxy Resin

CTBN parts per 100 parts of epoxy ^a	0	5	10	15
Tensile strength, MPa	65.8	62.8	58.4	51.4
Tensile modulus, GPa	2.8	2.5	2.3	2.1
Elongation at break (%)	4.8	4.6	6.2	8.9
Fracture energy, G _{Ic} , kJ/m ²	1.75	26.3	33.3	47.3
HDT, °C (at 1.82 MPa)	80	76	74	71

^aDGEBA epoxy (Epon 828, Shell) cured with 5 parts of piperidine at 120 °C for 16 h

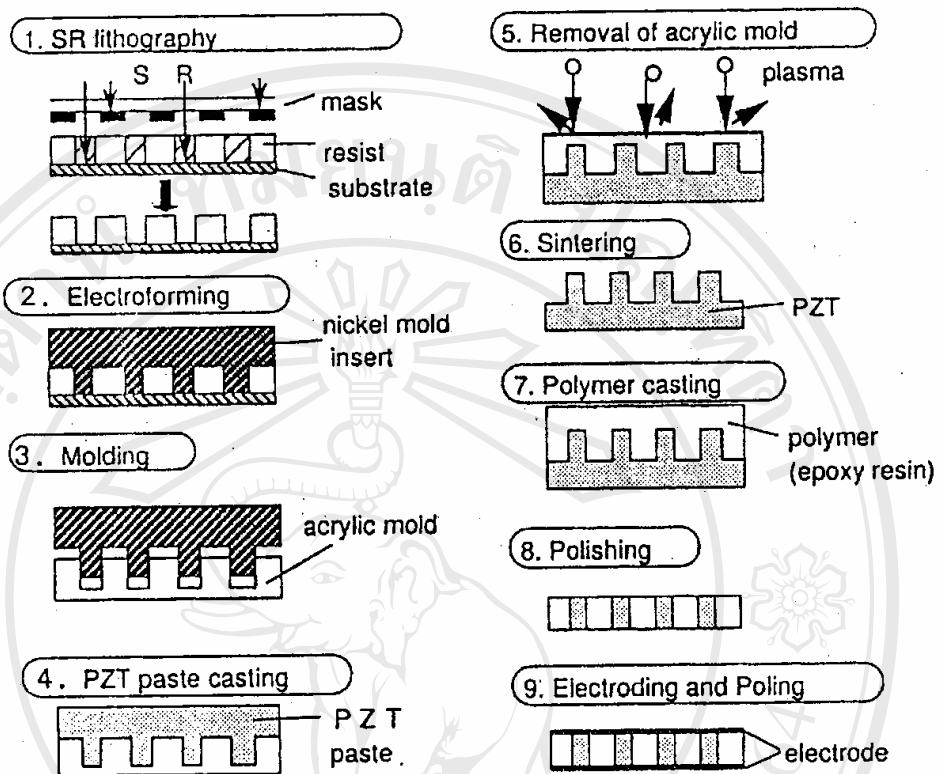


Figure 4 Fabrication of 1-3 composite by LIGA process.

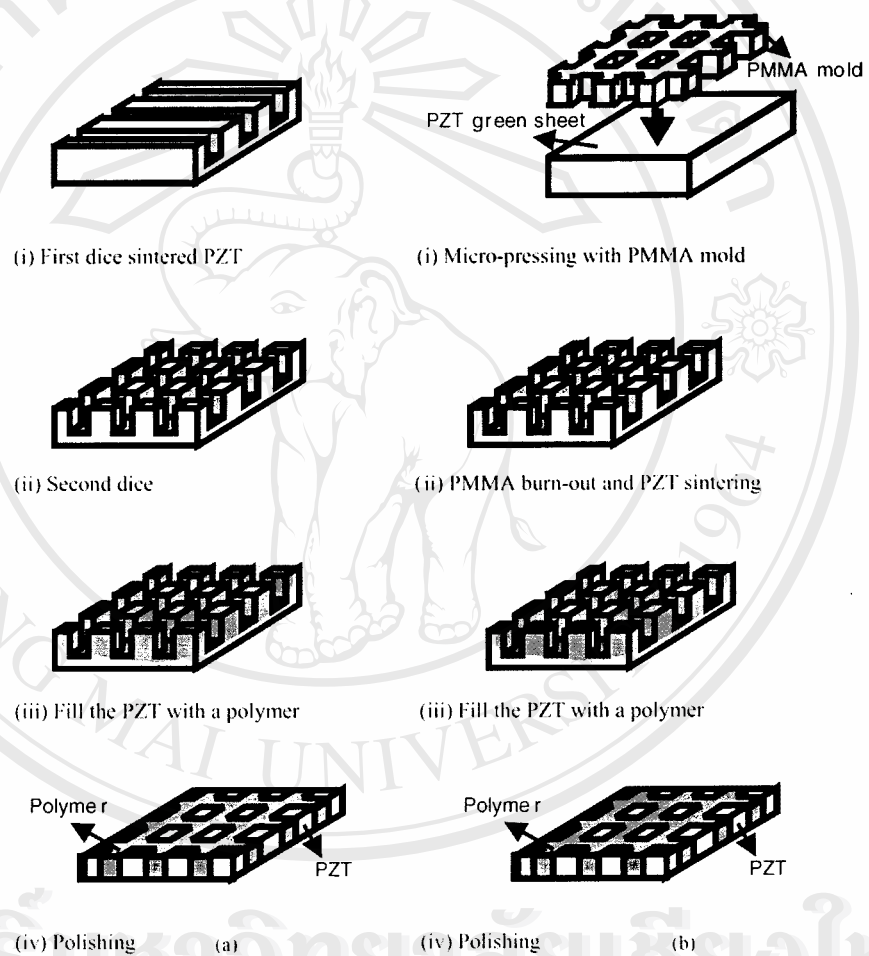


Figure 5 Schematic fabrication procedure of 1-3 PZT/polymer composite by (a) dicing and (b) micro-pressing method.

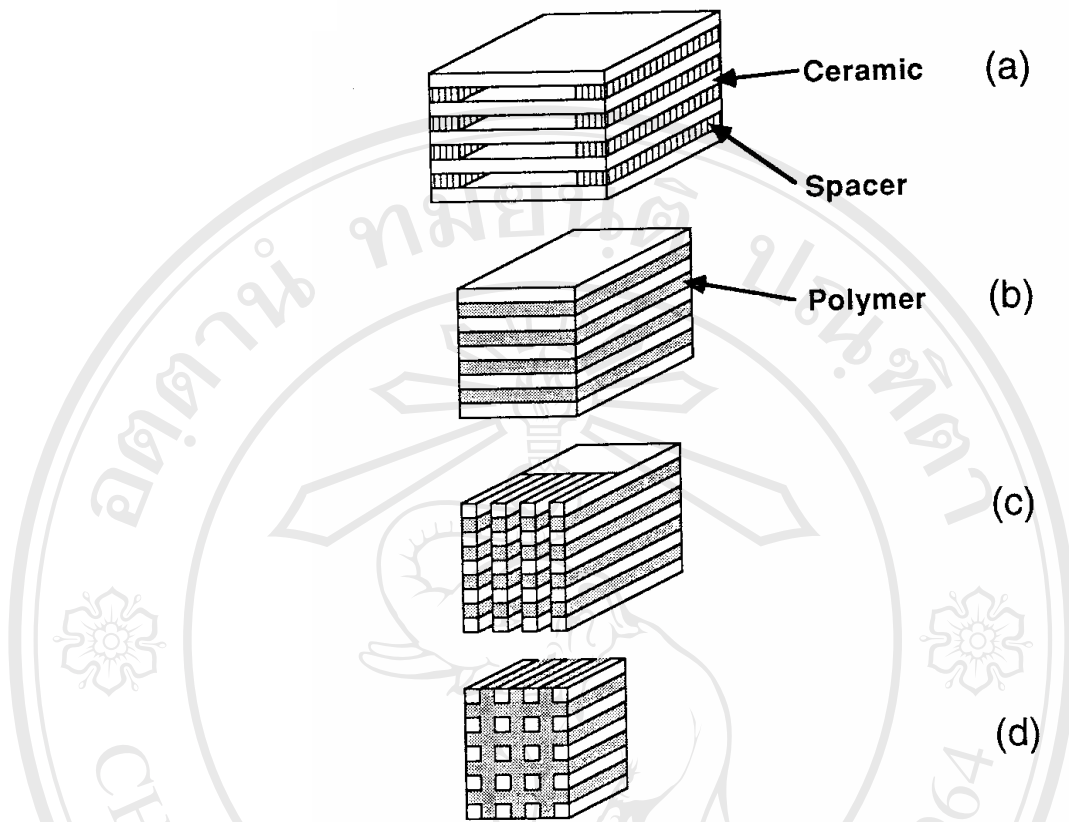


Figure 6 Schematic of forming tape cast composite structures: (a) stacked tape separated by spacers, (b) polymer stack with spacers removed (2-2 laminated composite), (c) diced stack, and (d) polymer-filled diced stack (1-3 rod composite).

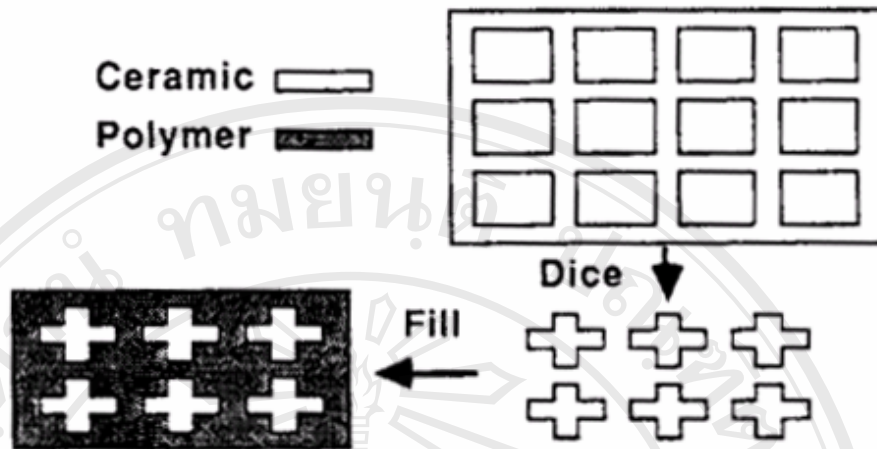


Figure 7 Schematic of diced honey comb composite.

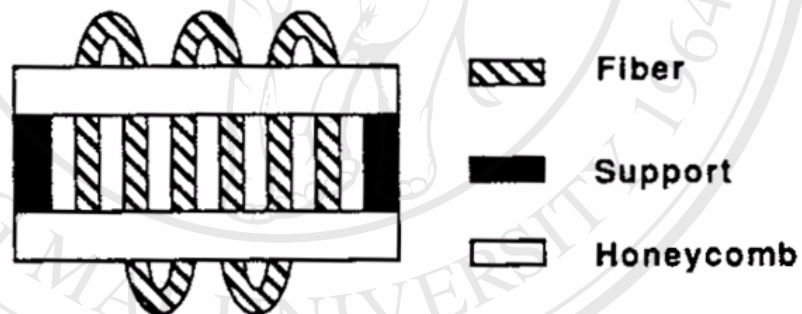


Figure 8 Schematic of woven PZT composite.

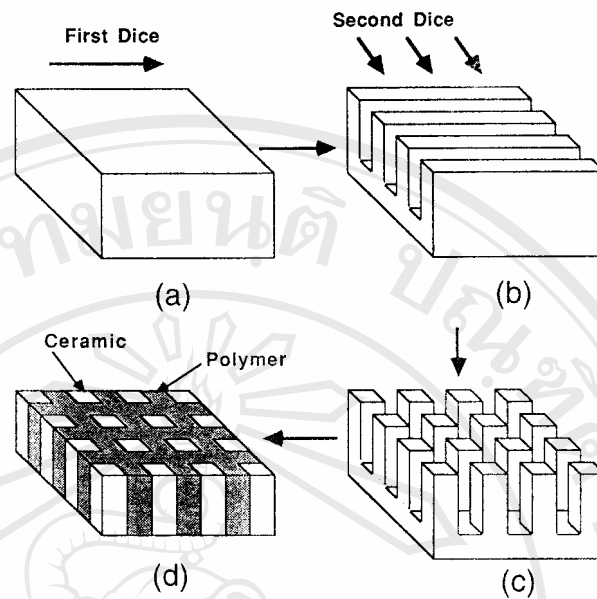


Figure 9 Dice-and-fill method of forming piezoelectric ceramic/polymer composites: (a) ceramic block prior to first cut, (b) after first cut (2-2 connectivity), (c) after second cut, and (d) final composite (1-3 connectivity).

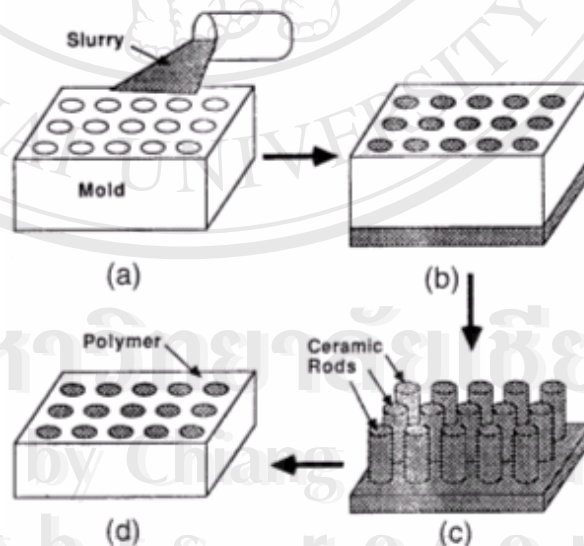


Figure 10 Lost-mold method of forming 1-3 piezoelectric ceramic/polymer composites: (a) fill mold with slip, (b) full mold before heat treatment, (c) after heat treatment and (d) completed composite.



APPENDIX B

EDX RESULTS

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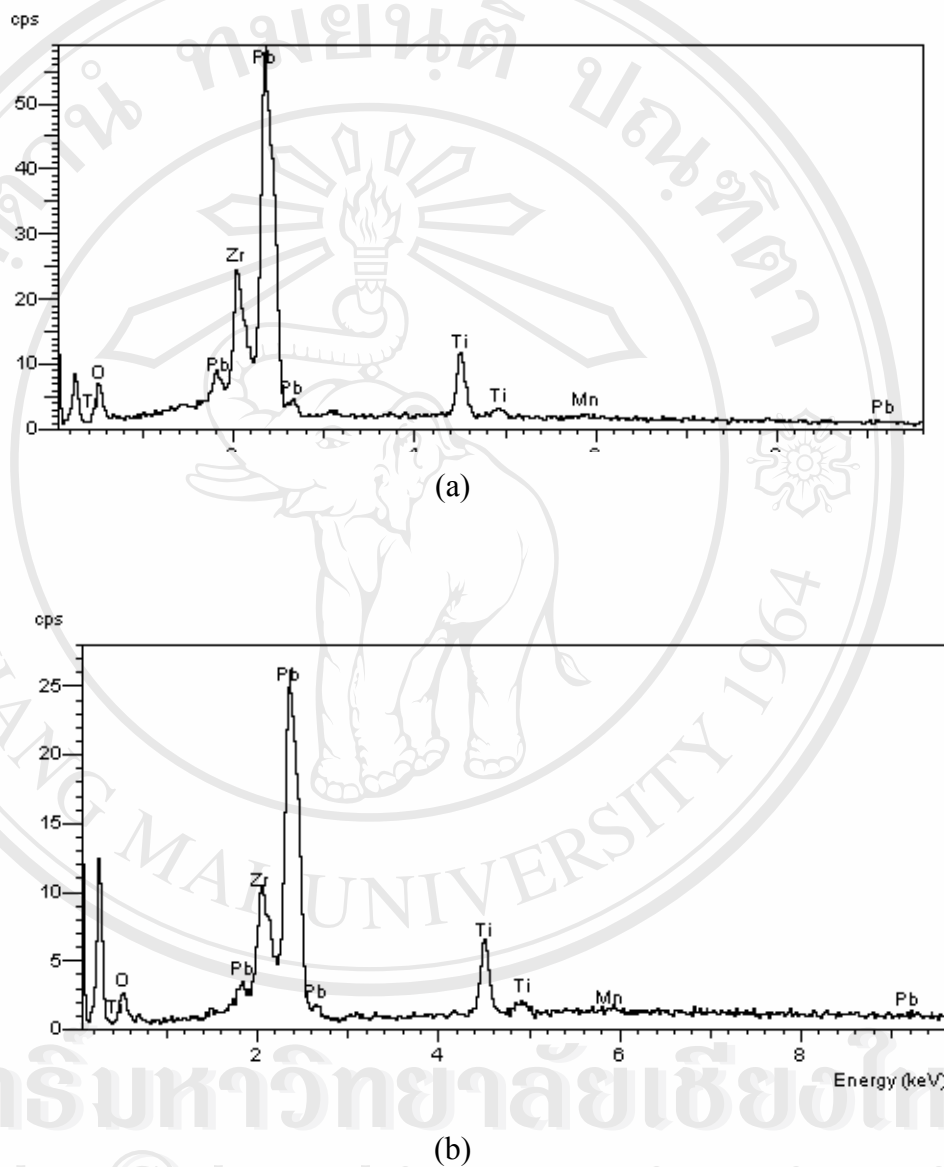


Figure 11 EDS of PZT sample in different area.



APPENDIX C

SEM AND TEM

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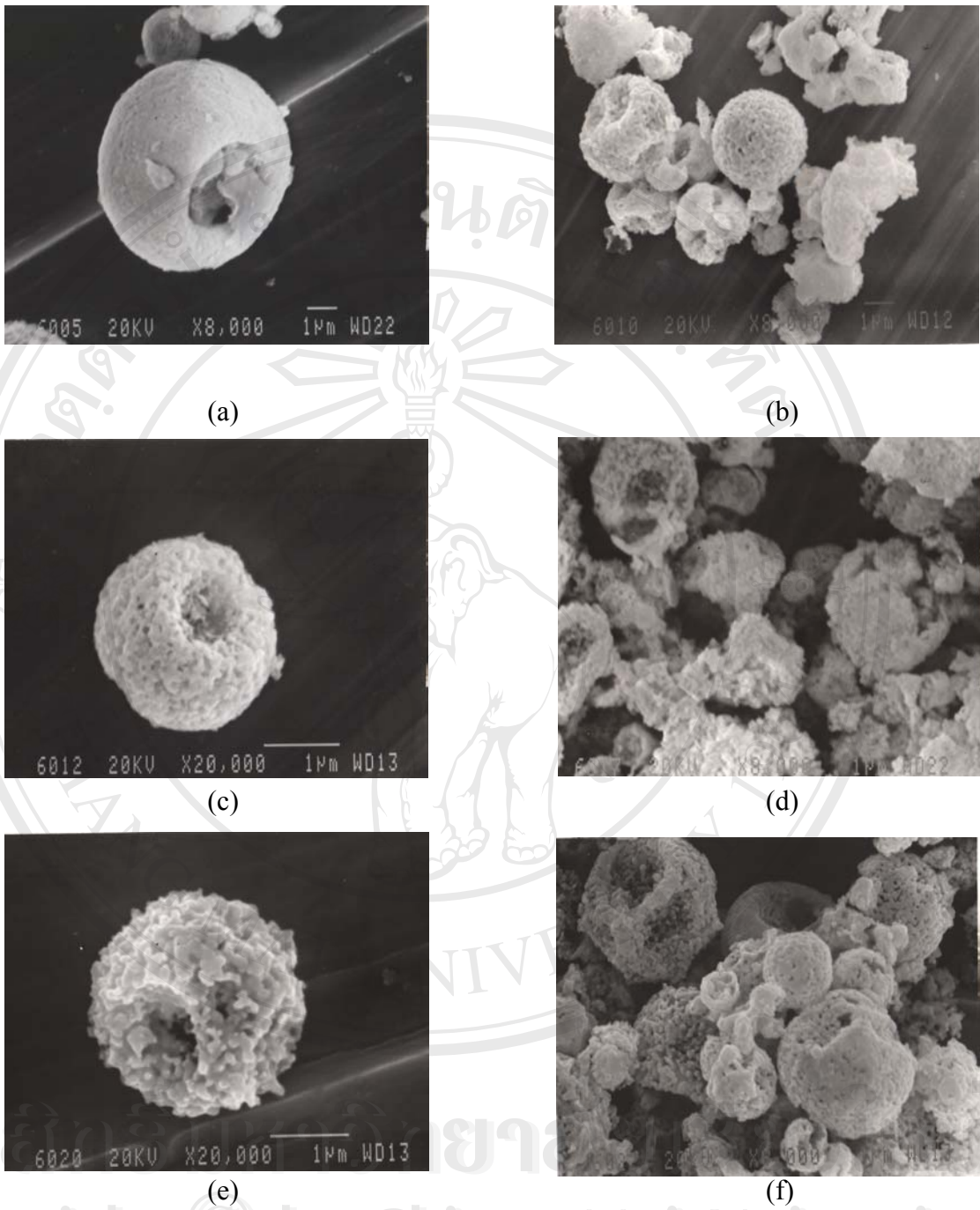


Figure 12 SEM micrographs of PZT sprayed granules calcined at (a) 500 °C (b) 600 °C (c) 625 °C (d) 650 °C (e) 675 °C and (f) 700 °C.

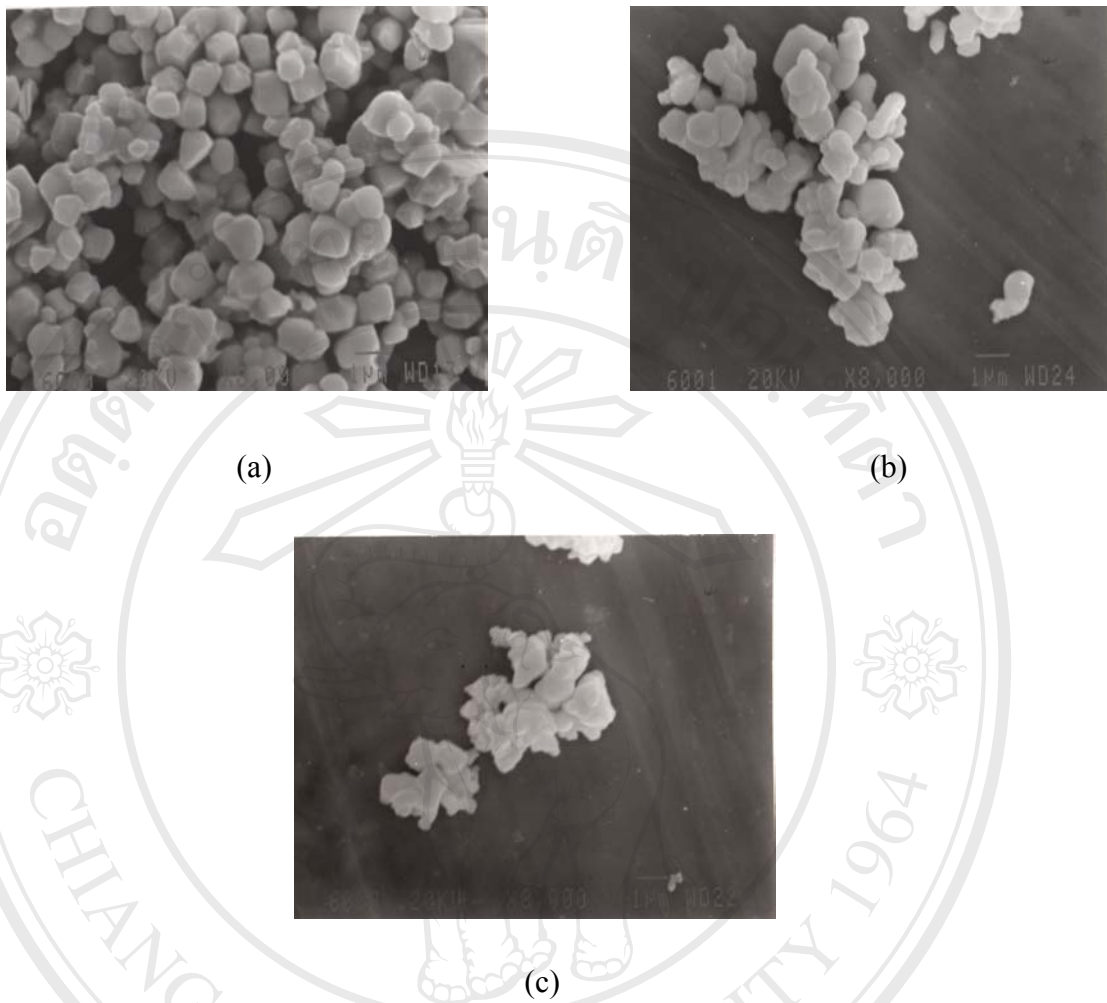


Figure 13 SEM micrographs of PZT sprayed powder (a), mixed oxide powder (b) and PZT commercial powder 40/40 calcined at 800 °C.

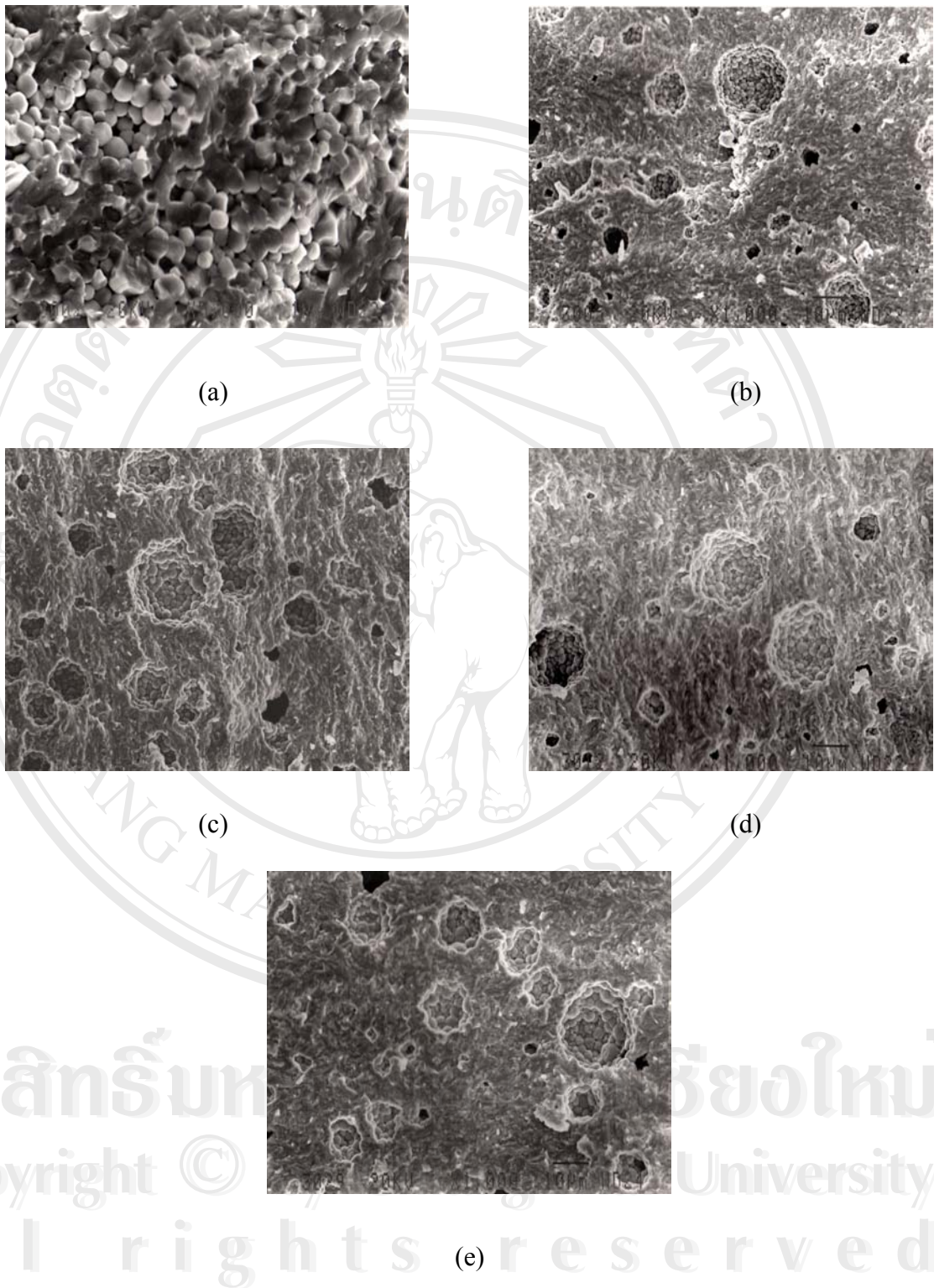
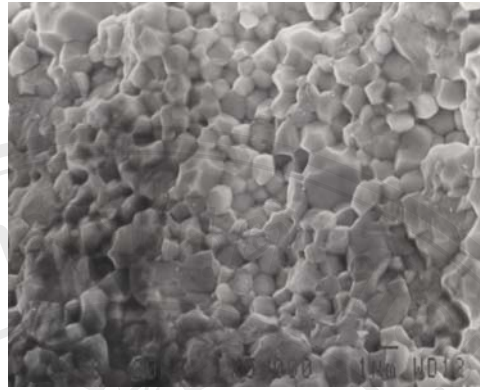
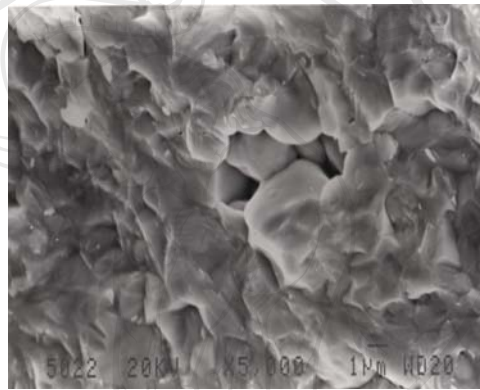


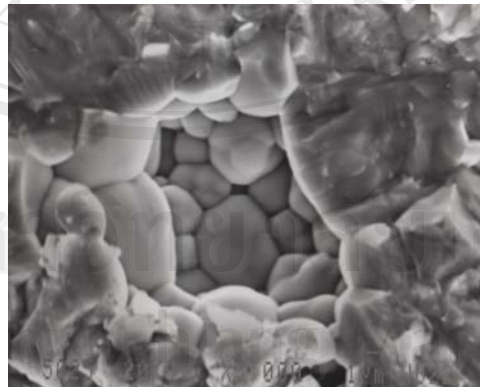
Figure 14 SEM micrographs of PZT sample (spray+mixed) sintered at (a) 1000 °C (b) 1100 °C (c) 1200 °C (d) 1230 °C and (e) 1250 °C.



(a)



(b)



(c)

Figure 15 SEM micrographs of undoped PZT made from sprayed powder sintered at (a) 1000 °C (b) 1100 °C (c) 1200 °C

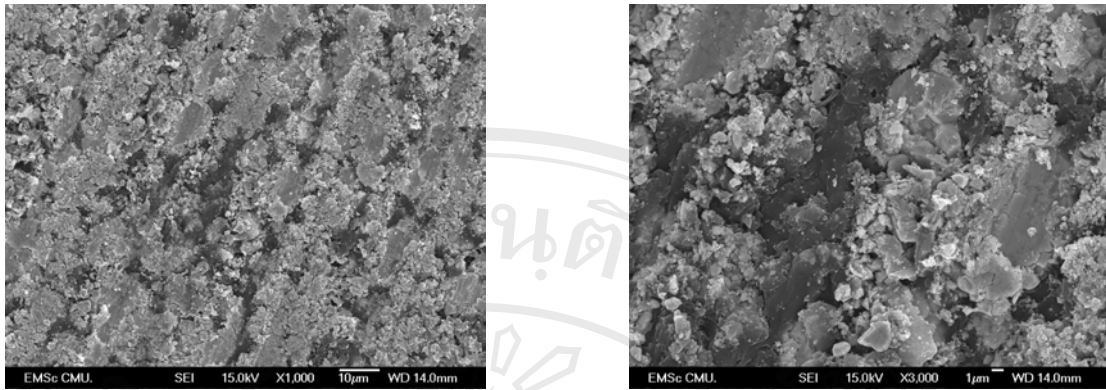


Figure 16 SEM of 0-3 composite of mixed oxide PZT/epoxy resin

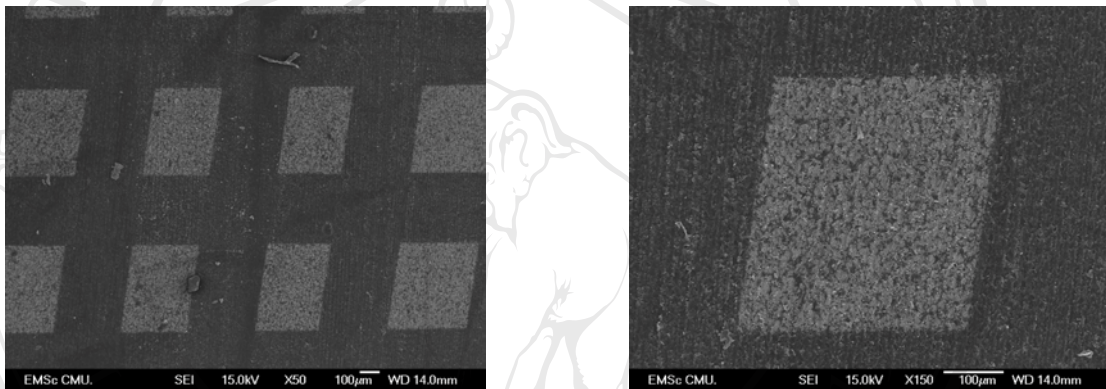


Figure 17 SEM of 1-3 composite of mixed oxide PZT/epoxy resin

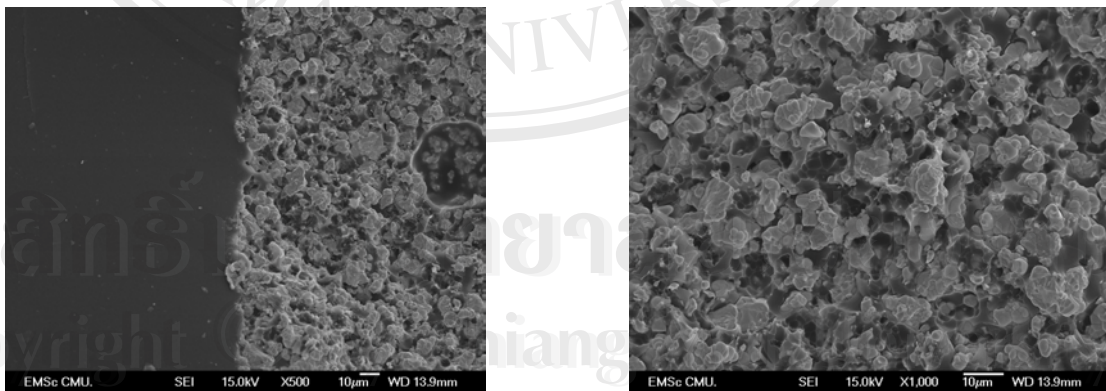


Figure 18 SEM of cross section of combination 0-3 and 1-3 composite of mixed oxide PZT/epoxy resin

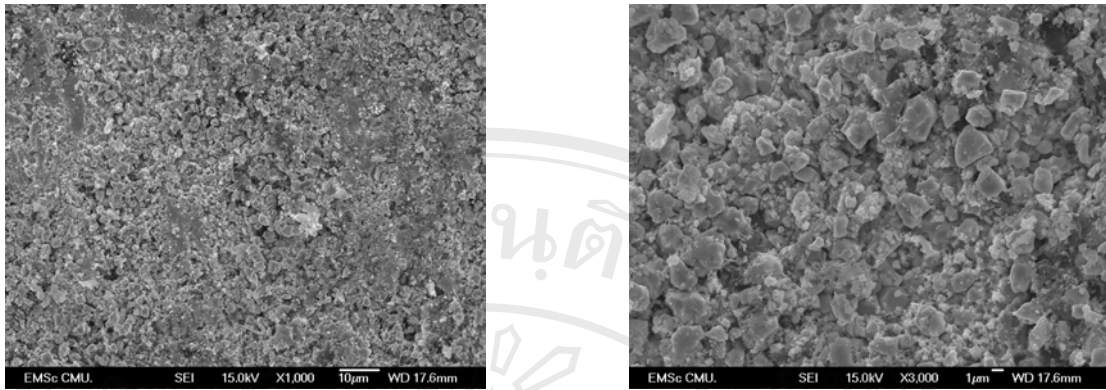


Figure 19 SEM of 0-3 composite of mixed oxide PZT(Nd)/epoxy resin

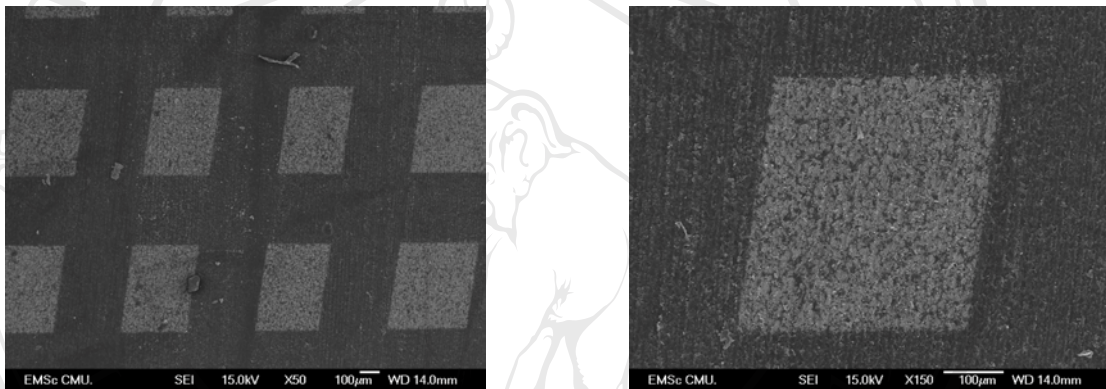


Figure 20 SEM of 1-3 composite of mixed oxide PZT(Nd)/epoxy resin

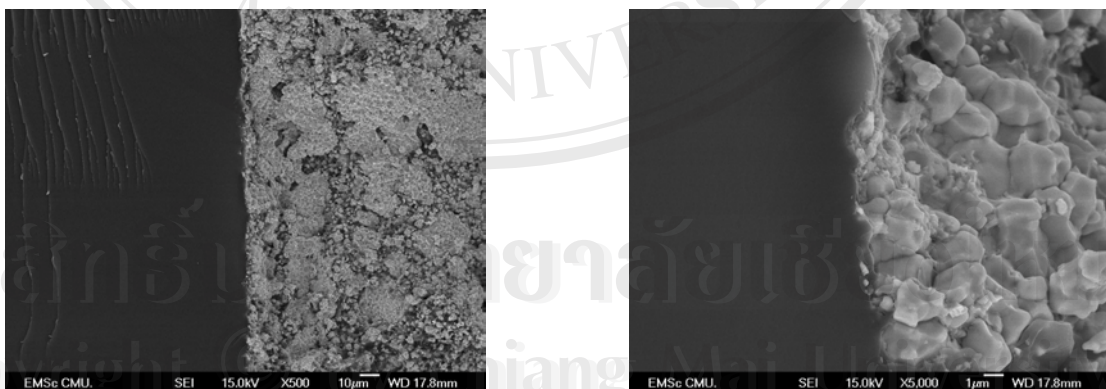


Figure 21 SEM of cross section of combination 0-3 and 1-3 composite of mixed oxide PZT(Nd)/epoxy resin

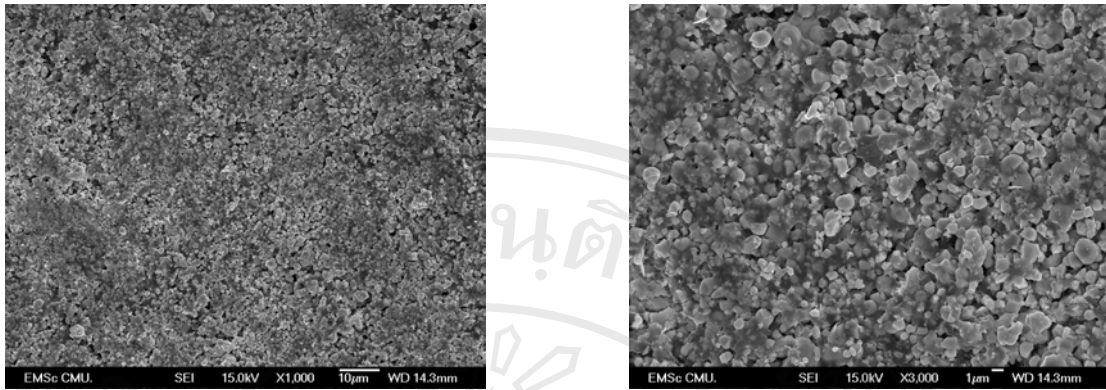


Figure 22 SEM of 0-3 composite of PZT(4040)/epoxy resin

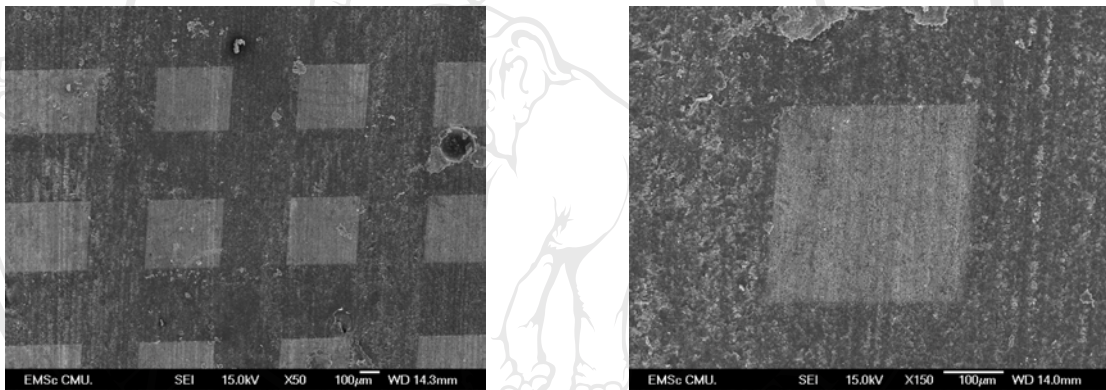


Figure 23 SEM of 1-3 composite of PZT(4040)/epoxy resin

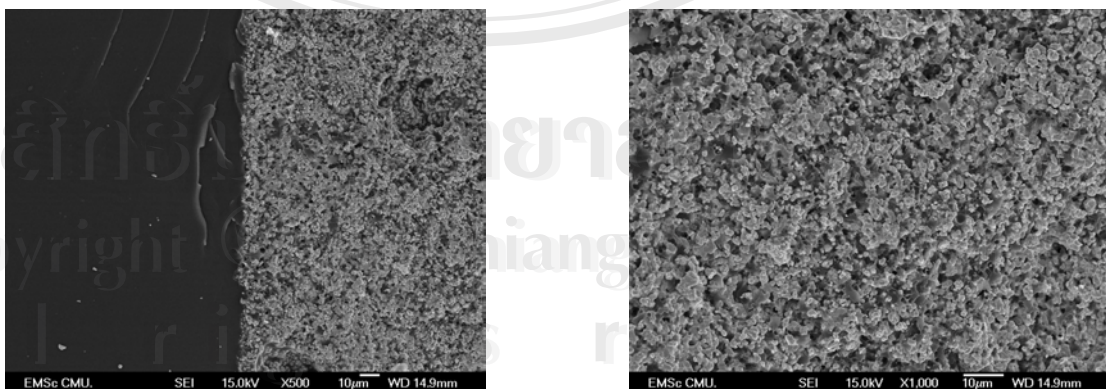


Figure 24 SEM of cross section of combination 0-3 and 1-3 composite of PZT(4040)/epoxy resin

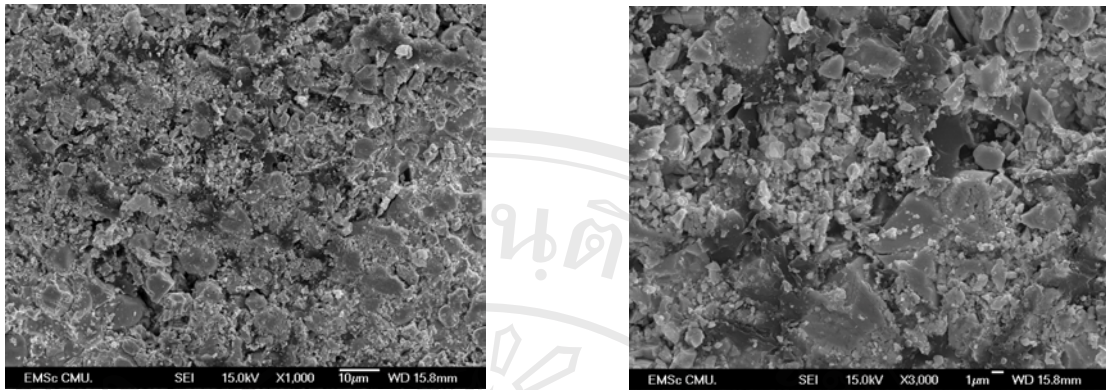


Figure 25 SEM of 0-3 composite of spray dried powder/epoxy resin

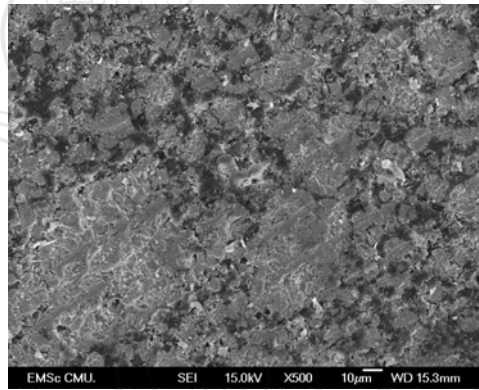


Figure 26 SEM of 1-3 composite of spray dried powder/epoxy resin

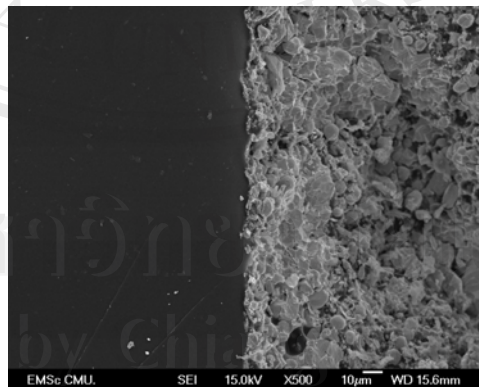


Figure 27 SEM of cross section of combination 0-3 and 1-3 composite of spray dried PZT powder /epoxy resin

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Conferences and Publications

National Conference:

1. W. Thamjaree, N. Vittayakorn, G. Rujijanagul, S. Ananta and T. Tunkasiri, Preparation of 0-3 Carbon/HDPE Composites, The First Thailand Materials Science and Technology Conference, Bangkok, 2000.
2. T. Tunkasiri and W. Thamjaree, Effect of Calcining Temperature to Physical Properties of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, The Second Thailand Materials Science and Technology Conference, Bangkok, 2002.
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4. W. Thamjaree and T. Tunkasiri, Preparation of PZT Powder Using the Spray Drying Technique, RGJ-Ph.D. Congress III, Chonburi, 2002, 84.
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8. W. Thamjaree, W. Nhuapeng and T. Tunkasiri, Preparation of Hybrid Composites Between PZT and Epoxy Resin, STT30, Bangkok, 2004.
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2. W. Thamjaree, L.D. Yu, K. Pengpat and T. Tunkasiri, Preparation and Characterization of High-Purity PZT Powders and Ceramics Made by Spray Drying Technique, Electroceramics XI, Cherbourg, France, 2004.
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1. W. Thamjaree, W. Nhuapeng and T. Tunkasiri, Analysis of X-ray Diffraction Line Profiles of Lead Zirconate Titanate Using the Fourier Method, *Ferro. Lett.* **31:1-5** (2004) 79-85.
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