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APPENDICES

Appendix A Density of Porous films

-Cell size: Small
-V added-small: 12.4138 cc
-V cell: 20.8798 cc
-Target Pressure: 17 psi
-Deviation Achieved: +/- 0.0219
-Maximum Runs: 20
-Number of Runs Averaged: 3

a) Flat PVDF films

Table A1 Show tabular Data Density analysis of PVDF films

RUN	VOLUME(cc)	DENSITY(g/cc)
1	0.9878	1.8433
2	1.0339	1.7611
3	1.0044	1.8127
4	1.0055	1.8107
5	1.0046	1.8124
6	1.0101	1.8026
7	1.0070	1.8080
8	1.0144	1.7949
9	1.0145	1.7948
10	1.0253	1.7758
11	1.0213	1.7827
12	1.0218	1.7819
13	1.0254	1.7756
14	1.0212	1.7829
15	1.0144	1.7948
16	1.0262	1.7743
17	1.0284	1.7743
18	1.0278	1.7703
19	1.0362	1.7571

20	1.0313	1.7654
Average	1.0408	1.7894

b) Porous PVDF films

Table A2 Show tabular Data Density analysis of porous PVDF films. (PVDF (10 %wt) and DMAc (90 %wt)

RUN	VOLUME(cc)	DENSITY(g/cc)
1	0.0798	1.1658
2	0.0815	1.1405
3	0.0830	1.1211
4	0.0883	1.0534
5	0.0879	1.0574
6	0.0873	1.0655
7	0.0905	1.0278
8	0.0909	1.0227
9	0.0922	1.0085
10	0.0930	1.0005
11	0.0923	1.0079
12	0.0948	0.9812
13	0.0925	1.0058
14	0.0960	0.9684
15	0.0969	0.9596
16	0.0954	0.9753
17	0.1005	0.9257
18	0.0990	0.9391
19	0.0977	0.9522
20	0.0978	0.9512
Average	0.0982	0.9475

Table A3 Show tabular Data Density analysis of porous PVDF films. (PVDF (20 %wt) and DMAc (80 %wt)

RUN	VOLUME(cc)	DENSITY(g/cc)
1	0.0933	1.1308
2	0.0875	1.2051
3	0.0945	1.1161
4	0.0975	1.0824
5	0.0959	1.1002
6	0.0973	1.0840
7	0.0993	1.0627
8	0.0993	1.0628
9	0.0996	1.0597
10	0.1002	1.0358
11	0.1019	1.0524
12	0.0980	1.0764
13	0.1011	1.0439
14	0.1045	1.0158
15	0.1039	1.0151
16	0.1039	1.0095
17	0.1053	1.0021
18	0.1055	1.0003
19	0.1074	0.9820
20	0.1063	0.9928
Average	0.1064	0.9917

Table A4 Show tabular Data Density analysis of porous PVDF films. (PVDF (30 %wt) and DMAc (70 %wt)

RUN	VOLUME(cc)	DENSITY(g/cc)
1	0.1660	1.1021
2	0.1602	1.1415
3	0.1640	1.1155
4	0.1607	1.1380
5	0.1602	1.1418
6	0.1660	1.1019
7	0.1657	1.1039
8	0.1623	1.1269
9	0.1640	1.1149
10	0.1651	1.1076
11	0.1657	1.1080
12	0.1623	1.1270
13	0.1640	1.1149
14	0.1650	1.1073
15	0.1660	1.1019
16	0.1601	1.1416
17	0.1642	1.1152
18	0.1610	1.1341
19	0.1658	1.1040
20	0.1622	1.1271
Average	0.1635	1.1188

Table A5 Show tabular Data Density analysis of porous PVDF films. (PVDF (10 %wt) and DMF (90 %wt)

RUN	VOLUME(cc)	DENSITY(g/cc)
1	0.1116	0.8618
2	0.1118	0.8605
3	0.1074	0.8961
4	0.1149	0.8375
5	0.1135	0.8475
6	0.1121	0.8582
7	0.1123	0.8570
8	0.1120	0.8572
9	0.1149	0.8371
10	0.1074	0.8961
11	0.1173	0.8958
12	0.1076	0.8968
13	0.1150	0.8380
14	0.1139	0.8479
15	0.1130	0.8592
16	0.1128	0.8577
17	0.1120	0.8572
18	0.1070	0.8962
19	0.1159	0.8390
20	0.1143	0.8483
Average	0.1124	0.8622

Table A6 Show tabular Data Density analysis of porous PVDF films. (PVDF (20 %wt) and DMF (80 %wt)

RUN	VOLUME(cc)	DENSITY(g/cc)
1	0.1187	0.9573
2	0.1206	0.9422
3	0.1233	0.9215
4	0.1216	0.9339
5	0.1209	0.9393
6	0.1185	0.9587
7	0.1219	0.9316
8	0.1226	0.9267
9	0.1239	0.9166
10	0.1264	0.8988
11	0.1233	0.9210
12	0.1212	0.9373
13	0.1255	0.9051
14	0.1222	0.9295
15	0.1229	0.9243
16	0.1255	0.9050
17	0.1200	0.9466
18	0.1221	0.9300
19	0.1213	0.9367
20	0.1234	0.9205
Average	0.1223	0.9290

Table A7 Show tabular Data Density analysis of porous PVDF films. (PVDF (30 %wt) and DMF (70 %wt)

RUN	VOLUME(cc)	DENSITY(g/cc)
1	0.0947	1.1983
2	0.0974	1.1778
3	0.0994	1.0583
4	0.1014	0.9770
5	0.0905	0.9487
6	0.0926	0.9580
7	0.1024	0.9945
8	0.1308	0.9363
9	0.1023	0.9504
10	0.1005	0.9668
11	0.1024	0.9496
12	0.1085	0.9490
13	0.0985	0.9961
14	0.0952	0.9865
15	0.0965	1.0206
16	0.0940	1.0172
17	0.0963	1.1339
18	0.0948	1.2094
19	0.0974	0.9982
20	0.0994	1.0747
Average	0.0997	1.0269

Table A8 Show tabular Data Density analysis of porous PVDF films. (PVDF (10 %wt) and TEP (90 %wt)

RUN	VOLUME(cc)	DENSITY(g/cc)
1	0.1266	0.6982
2	0.1284	0.6992
3	0.1302	0.6988
4	0.1313	0.7044
5	0.1315	0.7031
6	0.1334	0.7820
7	0.1293	0.7054
8	0.1327	0.7883
9	0.1321	0.6998
10	0.1298	0.6968
11	0.1300	0.7321
12	0.1267	0.6967
13	0.1321	0.7278
14	0.1296	0.7198
15	0.1334	0.7165
16	0.1265	0.7074
17	0.1367	0.7997
18	0.1289	0.6978
19	0.1356	0.7344
20	0.1290	0.6992
Average	0.1306	0.7204

Table A9 Show tabular Data Density analysis of porous PVDF films. (PVDF (20 %wt) and TEP (80 %wt)

RUN	VOLUME(cc)	DENSITY(g/cc)
1	0.1246	1.0268
2	0.1209	0.9982
3	0.1125	0.9078
4	0.1119	0.9082
5	0.1126	0.9077
6	0.1109	0.8801
7	0.1145	0.9141
8	0.1100	0.8709
9	0.1108	0.8875
10	0.1128	0.9789
11	0.1125	0.9775
12	0.1098	0.8856
13	0.1095	0.8876
14	0.1098	0.8857
15	0.1007	0.8450
16	0.1002	0.8234
17	0.0998	0.8173
18	0.0989	0.8045
19	0.1112	0.8553
20	0.1135	0.8867
Average	0.1107	0.8974

Table A10 Show tabular Data Density analysis of porous PVDF films. (PVDF (30 %wt) and TEP (70 %wt)

RUN	VOLUME(cc)	DENSITY(g/cc)
1	0.1376	1.0116
2	0.1368	1.0174
3	0.1333	1.0446
4	0.1337	1.0668
5	0.1305	1.0486
6	0.1328	1.0531
7	0.1330	1.0442
8	0.1322	1.0422
9	0.1333	1.0414
10	0.1336	1.0369
11	0.1330	1.0430
12	0.1342	1.0409
13	0.1335	1.0383
14	0.1337	1.0486
15	0.1341	1.0325
16	0.1327	1.0527
17	0.1348	1.0117
18	0.1364	1.0203
19	0.1376	1.0117
20	0.1398	1.0117
Average	0.1380	1.0090

Appendix B Porosity measurement of porous PVDF films

The porous PVDF films were immersed in iso-butanol around 24 hr then taken them out to remove iso-butanol on the surface before weighing and calculating the porosity.

Table B1 Data for pore diameter and porosity of porous PVDF films by using DMAc solvent (thickness 120 μm).

PVDF (wt%)	Sample No.	% Porosity
10	1	78.45
	2	76.98
	3	78.43
	4	78.98
	5	78.01
Average = 78.17		
15	1	70.80
	2	70.39
	3	70.56
	4	71.65
	5	70.12
Average = 70.04		
20	1	62.54
	2	61.07
	3	62.67
	4	62.07
	5	63.32
Average = 62.34		
25	1	55.43

	2	53.65
	3	54.89
	4	54.11
	5	51.24
Average = 53.84		
30	1	46.01
	2	44.86
	3	50.23
	4	46.57
	5	44.38
Average = 46.41		

Table B2 Data for pore diameter and porosity of porous PVDF films by using DMF with thickness 120 μm .

PVDF (wt%)	Sample No.	% Porosity
10	1	83.68
	2	83.97
	3	84.54
	4	84.02
	5	83.33
Average = 83.90		
15	1	70.12
	2	71.23
	3	70.22
	4	70.11
	5	69.78
Average = 70.29		
20	1	68.40

	2	67.98
	3	67.45
	4	68.05
	5	68.22
Average = 68.02		
25	1	62.53
	2	61.09
	3	63.31
	4	63.15
	5	61.13
Average = 62.24		
30	1	51.47
	2	49.27
	3	49.98
	4	50.45
	5	50.87
Average = 50.48		

Table B3 Data for pore diameter and porosity of porous PVDF films by using TEP with thickness 120 μm .

PVDF (wt%)	Sample No.	% Porosity
10	1	87.61
	2	88.23
	3	87.52
	4	86.42
	5	86.23
Average = 87.02		

15	1	78.12
	2	80.50
	3	79.67
	4	78.44
	5	78.31
	Average = 79.01	
20	1	73.48
	2	71.99
	3	72.23
	4	70.89
	5	66.73
	Average = 71.04	
25	1	60.53
	2	66.18
	3	62.13
	4	63.34
	5	63.55
	Average = 63.14	
30	1	59.66
	2	54.67
	3	55.26
	4	55.67
	5	54.09
	Average = 55.87	

Appendix C Differential Scanning Calorimetry - DSC

a) Non-stretching films

The melting temperature and crystallinity of porous PVDF were determined by DSC thermal analysis.

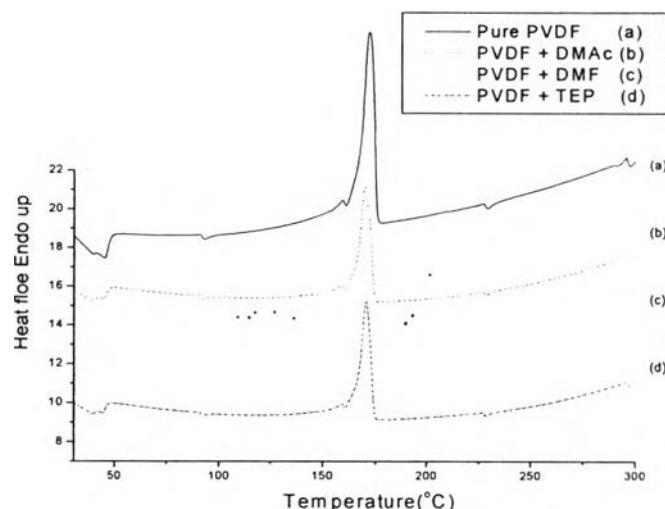


Figure C1 DSC thermograms of Porous PVDF Films in different solvent system
(a)DMAc, (b)DMF, and (c)TEP.

Table C1 Melting and crystalline behavior of flat film and porous films

PVDF Films	T_m (°C)		ΔH_m (J/g)	Crystallinity (%)
	Onset	Peak		
Pure PVDF	165.15	170.03	34.81	51.95
Porous PVDF by DMAc	165.60	169.70	38.86	58.00
Porous PVDF by DMF	166.03	170.89	37.81	56.43
Porous PVDF by TEP	166.36	170.35	35.22	52.50

(Reference: Heat of fusion (30°C to end of melting) 67 J/g)

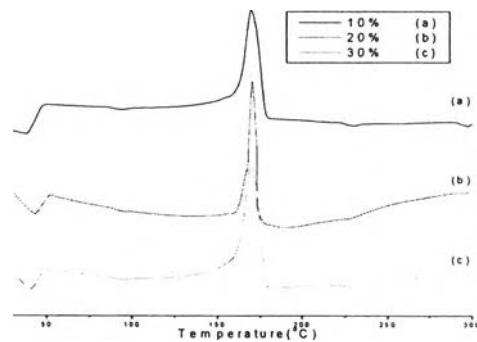


Figure C2 DSC thermograms of porous films with (b) 10, (c) 20 and (d) 30 (%wt) of PVDF by DMAc.

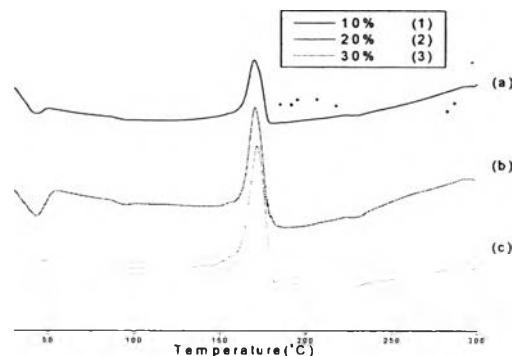


Figure C3 DSC thermograms of porous films with (b) 10, (c) 20 and (d) 30 (%wt) of PVDF by DMF.

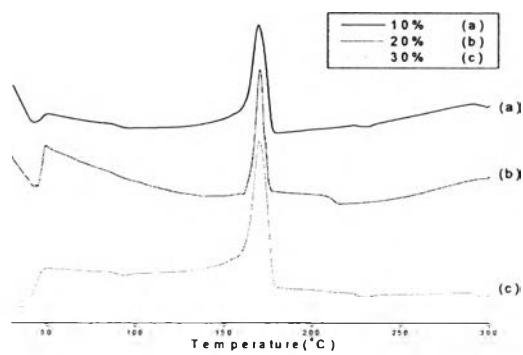


Figure C4 DSC thermograms of porous films with (b) 10, (c) 20 and (d) 30 (%wt) of PVDF by TEP.

Table C2 Melting and crystalline behavior of different porosity in PVDF films by DMAc

PVDF Films	T_m (°C)		ΔH_m (J/g)	Crystallinity (%)
	Onset	Peak		
Porous PVDF 10% by DMAc	165.48	168.98	37.69	56.25
Porous PVDF 20% by DMAc	165.60	169.70	38.86	58.00
Porous PVDF 30% by DMAc	165.50	169.44	38.79	57.89

(Reference: Heat of fusion (30°C to end of melting) 67 J/g)

Table C3 Melting and crystalline behavior of different porosity in PVDF films by DMF

PVDF Films	T_m (°C)		ΔH_m (J/g)	Crystallinity (%)
	Onset	Peak		
Porous PVDF 10% by DMF	165.23	170.87	37.63	56.16
Porous PVDF 20% by DMF	166.03	170.89	37.81	56.43
Porous PVDF 30% by DMF	165.95	171.72	38.00	56.71

(Reference: Heat of fusion (30°C to end of melting) 67 J/g)

Table C4 Melting and crystalline behavior of different porosity in PVDF films by TEP

PVDF Films	T_m (°C)		ΔH_m (J/g)	Crystallinity (%)
	Onset	Peak		
Porous PVDF 10% by TEP	164.68	169.87	34.98	52.20
Porous PVDF 20% by TEP	166.36	170.35	35.22	52.50
Porous PVDF 30% by TEP	166.05	170.87	35.02	52.26

(Reference: Heat of fusion (30°C to end of melting) 67

J/g)

b) Stretching films

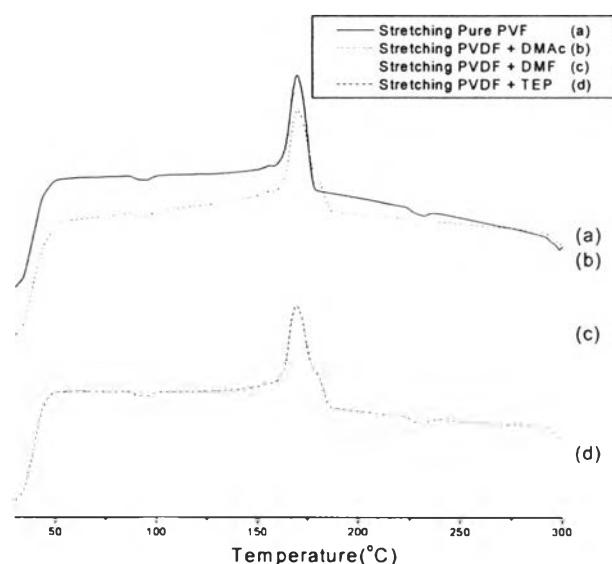


Figure C5 DSC thermograms of stretching porous PVDF Films in different solvent system (a)DMAc, (b)DMF, and (c)TEP.

Table C5 Melting and crystalline behavior of flat film and porous films which stretching at (1:1 ratio)

PVDF Eilms	T_m (°C)		ΔH_m (J/g)	Crystallinity (%)
	Onset	Peak		
Pure PVDF	166.11	171.37	40.06	59.79
Porous PVDF by DMAc	166.03	170.02	41.32	61.67
Porous PVDF by DMF	165.54	170.13	40.59	60.58
Porous PVDF by TEP	166.25	170.70	38.35	57.23

(Reference: Heat of fusion (30°C to end of melting) 67 J/g)

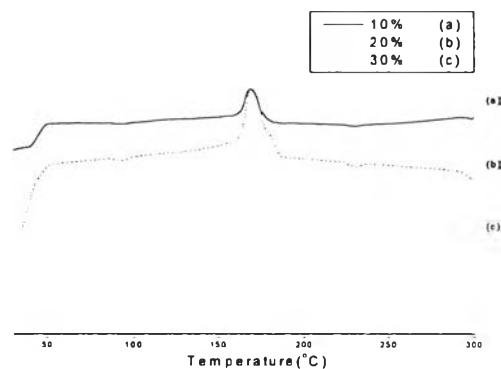


Figure C6 DSC thermograms of stretching porous films with (b) 10, (c) 20 and (d) 30 (%wt) of PVDF by DMAc.

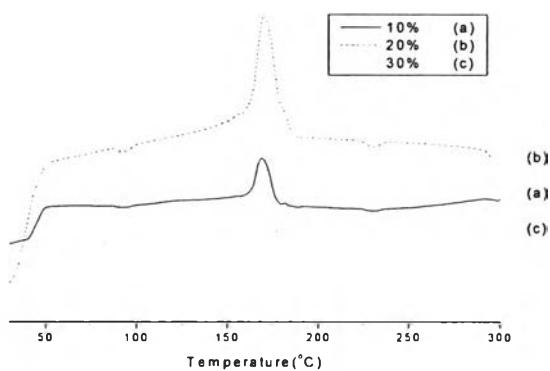


Figure C7 DSC thermograms of stretching porous films with (b) 10, (c) 20 and (d) 30 (%wt) of PVDF by DMF.

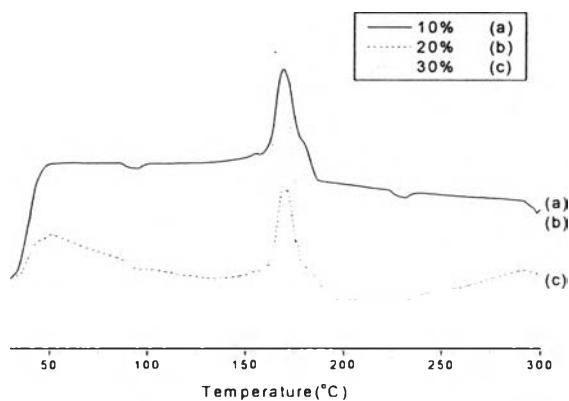


Figure C8 DSC thermograms of stretching porous films with (b) 10, (c) 20 and (d) 30 (%wt) of PVDF by TEP.

Table C6 Melting and crystalline behaviours of different porosity in stretching PVDF films by DMAc

PVDF Films	T_m (°C)		ΔH_m (J/g)	Crystallinity (%)
	Onset	Peak		
Porous PVDF 10% by DMAc	165.95	170.62	39.91	59.56
Porous PVDF 20% by DMAc	166.03	170.02	41.32	61.67
Porous PVDF 30% by DMAc	166.21	170.39	40.05	61.26

(Reference: Heat of fusion (30°C to end of melting) 67 J/g)

Table C7 Melting and crystalline behavior of different porosity in stretching PVDF films by DMF

PVDF Films	T_m (°C)		ΔH_m (J/g)	Crystallinity (%)
	Onset	Peak		
Porous PVDF 10% by DMF	165.91	170.03	39.98	59.67
Porous PVDF 20% by DMF	165.54	170.13	40.59	60.58
Porous PVDF 30% by DMF	166.06	170.37	40.27	60.11

(Reference: Heat of fusion (30°C to end of melting) 67 J/g)

Table C8 Melting and crystalline behavior of different porosity in stretching PVDF films by TEP

PVDF Films	T_m (°C)		ΔH_m (J/g)	Crystallinity (%)
	Onset	Peak		
Porous PVDF 10% by TEP	165.98	169.75	37.68	56.23
Porous PVDF 20% by TEP	166.25	170.70	38.35	57.23
Porous PVDF 30% by TEP	166.26	169.53	37.96	56.65

(Reference: Heat of fusion (30°C to end of melting) 67 J/g)

Appendix D FT-IR of PVDF films

a) Porous PVDF films (Non-stretching)

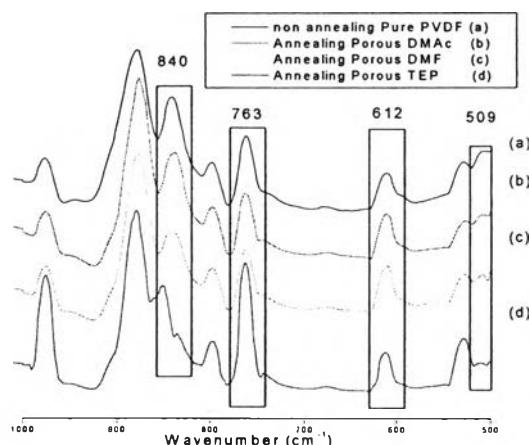


Figure D1 FT-IR spectra of (a) Pure PVDF and porous PVDF with (b) DMAc, (c) DMF and (d) TEP solution-crystallized.

Table D1 The variations of F(β) % of solution-crystallized PVDF system

Material	β -phase content, F(β) (%)
Pure PVDF	49.36
Porous PVDF + DMAc solution	52.43
Porous PVDF + DMF solution	50.80
Porous PVDF + TEP solution	45.21

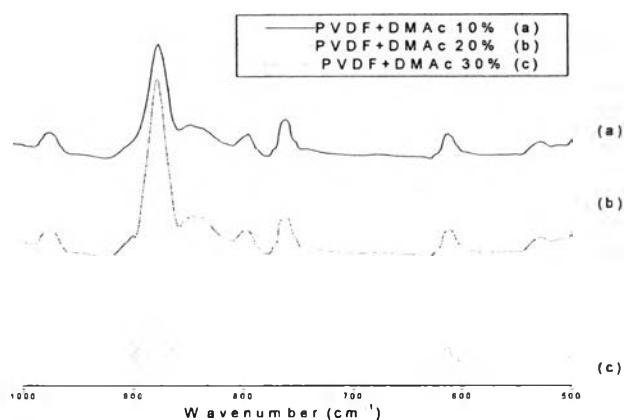


Figure D2 Infrared spectra of DMAc solution-crystallized porous PVDF films at different polymer concentration (a) 10, (b) 20, and (c) 30%.

Table D2. The F (β) % of PVDF and DMAc solution-crystallized films at different polymer concentrations.

Material	β -phase content, F (β) (%)
PVDF + DMAc 10 (%wt)	52.15
PVDF + DMAc 20 (%wt)	52.43
PVDF + DMAc 30 (%wt)	53.28

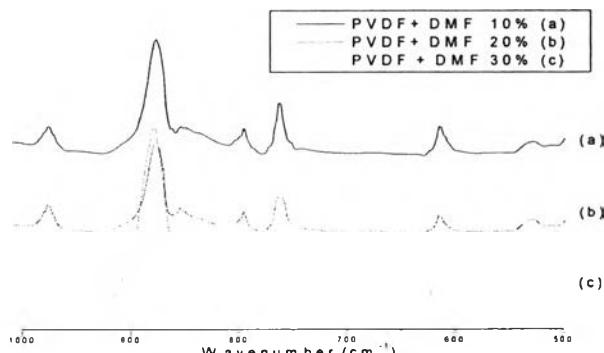


Figure D3 Infrared spectra of DMF solution-crystallized porous PVDF films at different polymer concentration (a) 10, (b) 20, and (c) 30%.

Table D3 The F (β) % of PVDF and DMF solution-crystallized films at different polymer concentrations.

Material	β -phase content, F (β) (%)
PVDF + DMF 10 (%wt)	50.66
PVDF + DMF 20 (%wt)	50.80
PVDF + DMF 30 (%wt)	51.76

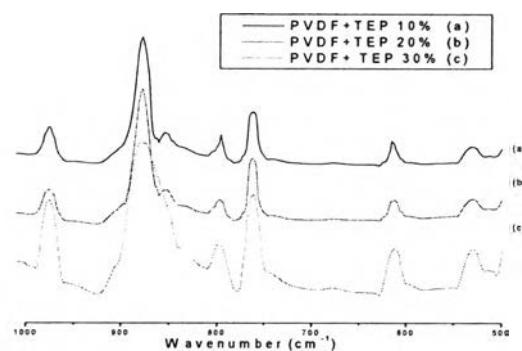


Figure D4 Infrared spectra of TEP solution-crystallized porous PVDF films at different polymer concentration (a) 10, (b) 20, and (c) 30%.

Table D4 The F (β) % of PVDF and TEP solution-crystallized films at different polymer concentrations.

Material	β -phase content, F (β) (%)
PVDF + TEP 10 (%wt)	45.13
PVDF + TEP 20 (%wt)	45.21
PVDF + TEP 30 (%wt)	47.54

b) Porous PVDF films (Stretching ratio 1:I)

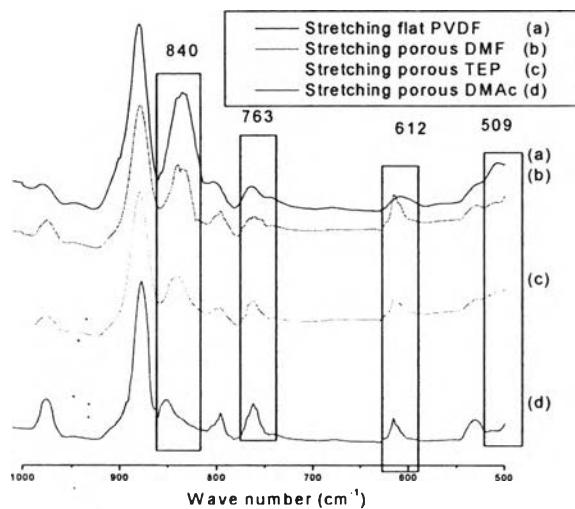


Figure D5 FT-IR spectra of stretching (a) flat PVDF and porous PVDF with (b) DMAc, (c) DMF and (d) TEP solution-crystallized.

Table D5 The variations of $F(\beta)\%$ of stretching PVDF films at solution-crystallized system.

Material	β -phase content, $F(\beta)$ (%)
Stretching flat PVDF	77.65
Porous PVDF + DMAc solution	62.96
Porous PVDF + DMF solution	60.71
Porous PVDF + TEP solution	58.44

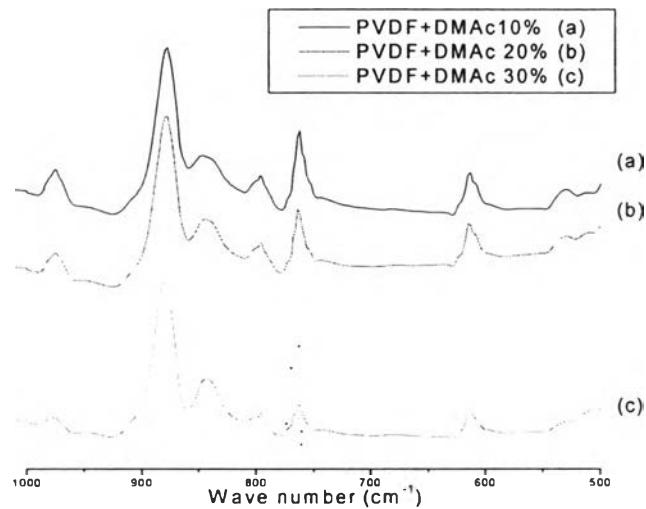


Figure D6 Infrared spectra of stretching DMAc solution-crystallized porous PVDF films at different polymer concentration (a) 10, (b) 20, and (c) 30%.

Table D6 The F (β) % of stretching PVDF and DMAc solution-crystallized films at different polymer concentration (1:1 ratio at constant drawn rate of 2.5 min/mm)

Material	β -phase content, F (β) (%)
PVDF + DMAc 10 (%wt)	61.44
PVDF + DMAc 20 (%wt)	62.96
PVDF + DMAc 30 (%wt)	62.07

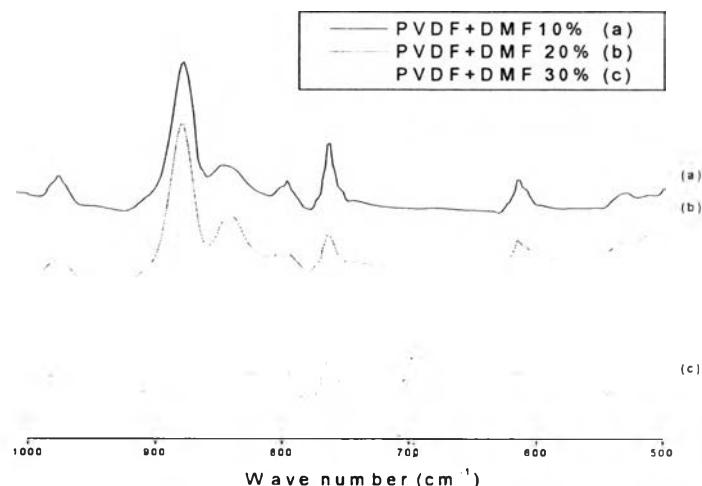


Figure D7 Infrared spectra of stretching DMF solution-crystallized porous PVDF films at different polymer concentration (a) 10, (b) 20, and (c) 30%.

Table D7 The F (β) % of stretching PVDF and DMF solution-crystallized films at different polymer concentration (1:1 ratio at constant drawn rate of 2.5 min/mm)

Material	β -phase content, F (β) (%)
PVDF + DMF 10 (%wt)	59.90
PVDF + DMF 20 (%wt)	60.71
PVDF + DMF 30 (%wt)	61.43

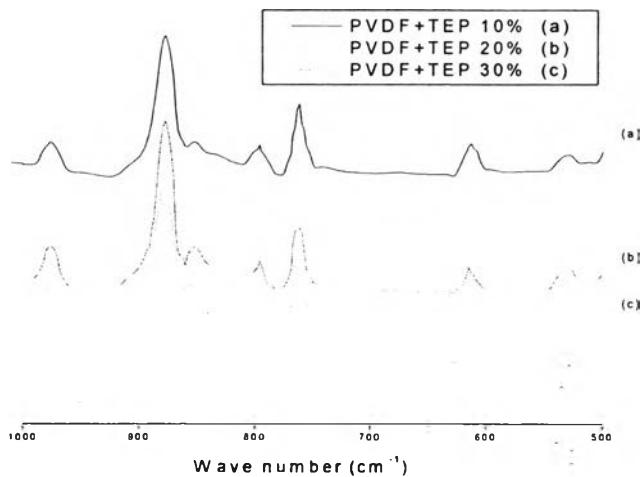


Figure D8 Infrared spectra of stretching TEP solution-crystallized porous PVDF films at different polymer concentration (a) 10, (b) 20, and (c) 30%.

Table D8 The F (β) % of stretching PVDF and TEP solution-crystallized films at different polymer concentration (1:1 ratio at constant drawn rate of 2.5 min/mm)

Material	β -phase content, F (β) (%)
PVDF + TEP 10 (%wt)	58.09
PVDF + TEP 20 (%wt)	58.44
PVDF + TEP 30 (%wt)	58.21

Appendix E Shape Parameter

The shape parameter of the ellipsoid is the inverse of the depolarization factor in the field direction; that is

$$\frac{1}{\eta} = \frac{a^2 c}{2} \int_0^\infty \frac{du}{(c^2 + u^2)^{3/2} (a^2 + u)} \quad (\text{E1})$$

where a and c are the axis lengths of the ellipsoid perpendicular and parallel to the applied field. The axis ratio (from 0.1-4.5) versus the shape parameter are plotted in Figure E1 (Liou and Chiou, 1998).

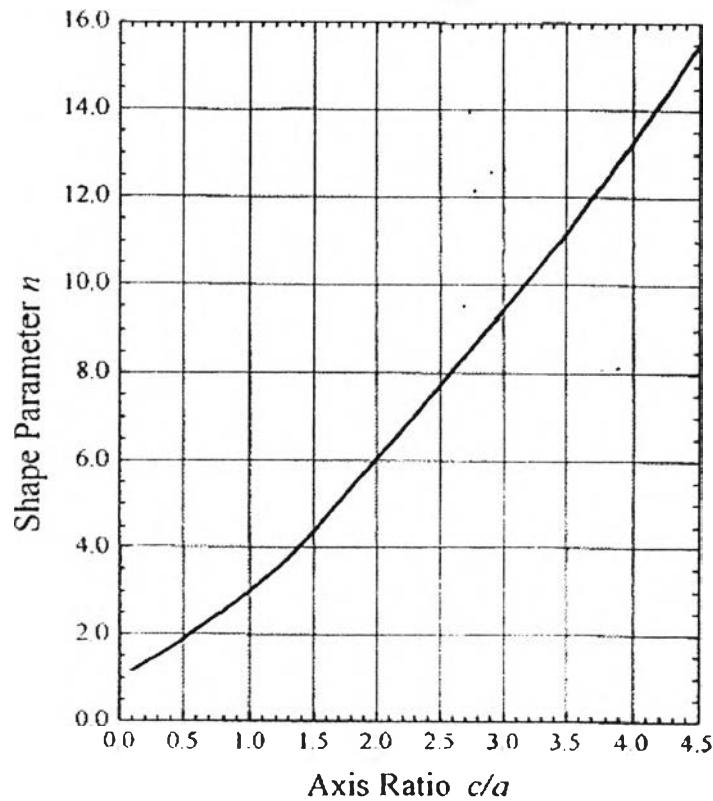


Figure E1 The axis ratio c/a of the ellipsoid versus the shape parameter η calculated from equation E1.

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Proceedings:

1. D. Suwansumpan, H. Manuspiya, P. Laoratanakul, and Amar S. Bhalla, (2008, April 6-10) Internal Bubble Shapes Effect on Dielectric Behaviors in PVDF Films. Proceeding of 235th American Chemical Society (ACS) Spring 2008 National Meeting & Exposition, New Orleans, LA USA.
2. D. Suwansumpan, H. Manuspiya, P. Laoratanakul, and Amar S. Bhalla, (2008, April 23-25) Piezoelectric Enhancement of PVDF Films by Induced Internal Bubble Shapes, Proceeding of International Conference on Smart Materials/Intelligent Materials and Nanotechnology and 2nd International Workshop on Functional Materiala and Nanomaterials, Chiangmai, Thailand.
3. D. Suwansumpan, H. Manuspiya, P. Laoratanakul, and Amar S. Bhalla, (2008, April 24) Piezoelectric Enhancement of PVDF Films by Induced Internal Bubble Shapes. Paper presented at the 14th PPC Symposium on Petroleum, Petrochems



and Polymers, Sasa Patasala Building, Chulalongkorn University, Bangkok, Thailand.

Presentations:

1. D. Suwansumpan, H. Manuspiya, P. Laoratanakul, and Amar S. Bhalla, (2008, April 8) Internal Bubble Shapes Effect on Dielectric Behaviors in PVDF Films. Poster presented at 235th American Chemical Society (ACS) Spring 2008 National Meeting & Exposition, New Orleans, LA USA.
2. D. Suwansumpan, H. Manuspiya, P. Laoratanakul, and Amar S. Bhalla, (2008, April 23) Piezoelectric Enhancement of PVDF Films by Induced Internal Bubble Shapes, Poster presented at International Conference on Smart Materials/Intelligent Materials and Nanotechnology and 2nd International Workshop on Functional Materiala and Nanomaterials, Chiangmai, Thailand.
3. D. Suwansumpan, H. Manuspiya, P. Laoratanakul, and Amar S. Bhalla, (2008, April 24) Piezoelectric Enhancement of PVDF Films by Induced Internal Bubble Shapes. Poster presented at the 14th PPC Symposium on Petroleum, Petrochems and Polymers, Sasa Patasala Building, Chulalongkorn University, Bangkok, Thailand.