Piezo-electric PVdF film

Precision Acoustics Ltd is pleased to be able to supply a range of piezo-polymeric materials. The Piezo-electric PVdF film can be used to fabricate a wide variety of sensors and actuators. This application note provides a selection of useful information that may aid the construction of devices incorporating piezo-electric PVDF. This application note should be considered in conjunction with the relevant Technical Data Sheet supplied with the product.

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Version history

Version	Date	Description
1.0		Document created

1 STRUCTURE OF PVDF

The following is a condensed review of PVDF morphology and an excellent review paper has been published [1] and is recommended to the reader

PVDF is formed by polymerising Vinylidenefluoride (VDF) (CF_2-CH_2). The resulting polymer forms long chain molecules (typically >2000 repeat units. Study of the crystalline structure of PVDF reveals 5 unique crystal forms (chain conformations), labelled α through to ε . The most common of these forms is the α phase, which is the form found when raw PVDF is processed from melt, or solvent cast from acetone. Within α phase crystals, all chain formations are TGTG’ conformation described above, with adjacent chains lying anti-parallel. This results in no net dipole within the crystals, and hence α phase is non-polar. Closely related to α phase is δ phase. Both consist of the same chain conformations, but in δ phase the chains are parallel and thus the dipole moments align. This form is polar, but the overall dipole moment is relatively low. The γ and ε phases correspond to the δ and α phases, but with the chains of confirmation T_3GT_3G' form rather than TGTG’ form.

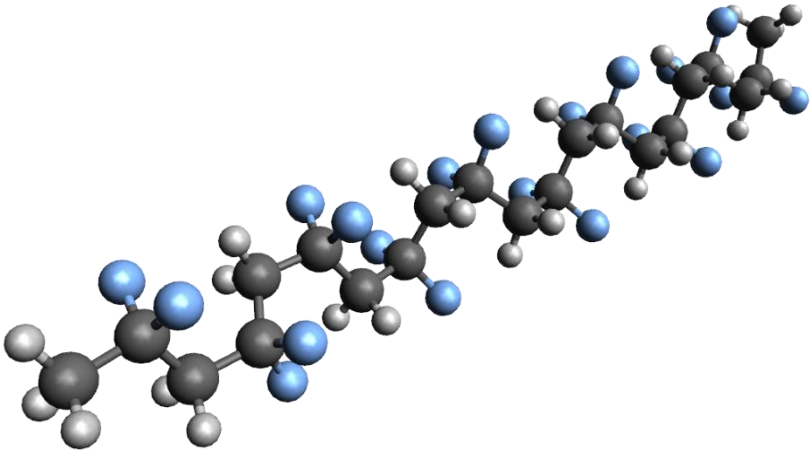


Figure 1 – Ball and stick model of alpha phase PVdF

Last of all is the β phase. This is particularly important since it consists of all chains in all transform (the strongest dipole chain conformation) with adjacent chains lying with their dipoles all aligned. As is to be expected, this form is highly polar, and is the form required for useable piezoelectric activity. It is important to note at this stage that appropriate processing can alter the particular phase of PVDF. This will be discussed in more detail in section 2. Of these conformations, α phase has the closest packing whilst β phase is the most open packed.

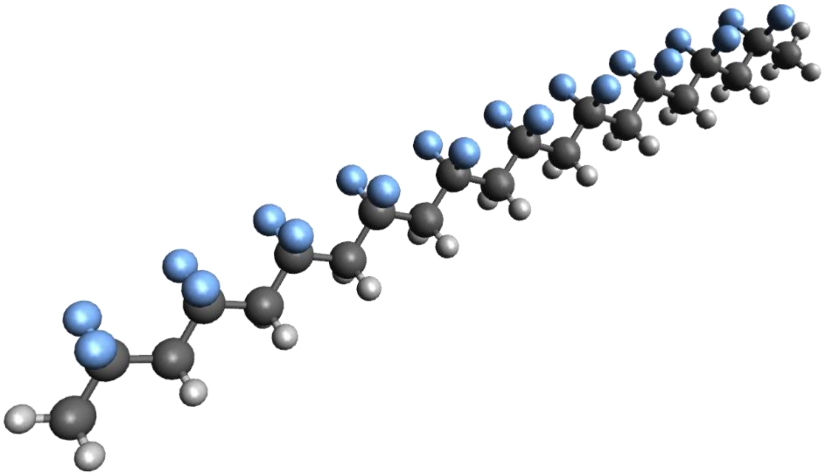


Figure 2 – Ball and stick model of beta phase PVdF

However, chain conformation is not the only factor. PVDF (along with a number of other polymers) is a semicrystalline polymer, consisting of both amorphous and crystalline phases. Polymer chain alignment within the amorphous phase is entirely random, but polymer chains pack neatly together within the crystals that can be found distributed throughout the amorphous phase. Instinctively, an amorphous polymer with a significant dipole moment should be able to be polarised, by heating it above its glass transition, applying an electric field, and allowing it to cool before removing the field. This ensures that the dipole moment of each is aligned in a similar direction. However as already mentioned, the polymer chains within the amorphous region are randomly aligned and this serves to dramatically reduce the overall polarisation. In contrast, if the polarisation exists within the crystalline phase, then application of the poling process above allows orientation of the crystals (as opposed to individual polymer chains), and the resulting polarisation is far more significant.

2 FILM ORIENTATION

2.1 GENERAL COMMENTS

As discussed in section 1, the largest dipole moment, and hence maximum piezo-activity is obtained from β phase film, whereas the majority of film produced is α phase. Consequently, a means of converting film of one phase to another is highly desirable. Recalling that α phase has much closer packing than β phase, it seems intuitive that a means of reducing the packing density along the polymer chain should cause a phase transformation from α to β phase. This is indeed the case, and film is routinely stretched to initiate the required phase transformation.

Film can either be stretched in one (uni-axial) or two (bi-axial) directions. The naming convention for the axes is illustrated in, and is as follows:

- Direction 1 (machine direction): the axis tangential to the surface of a wind-on roller
- Direction 2 (transverse direction): the axis parallel to the surface of the wind-on roller.
- Thickness Direction: the axis normal to the surface of the windup roller

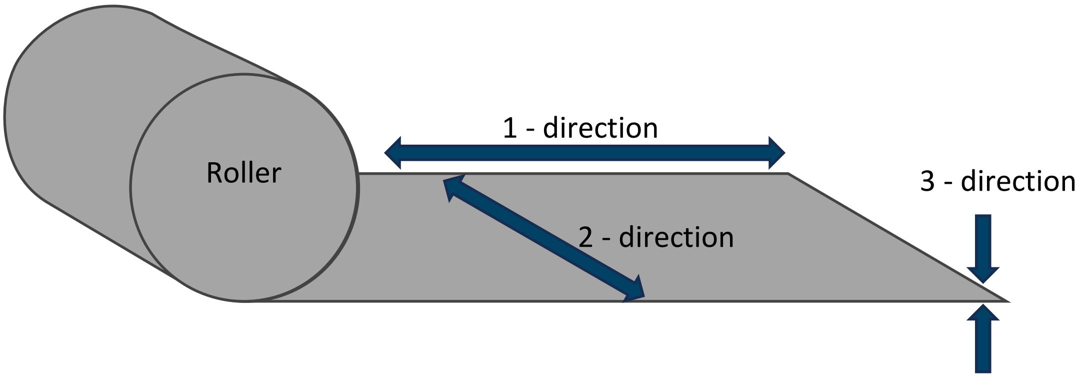


Figure 3 - Naming convention for directional identifiers of PVDF film

Since poling is normally conducted across the thickness of the film, we thereby obtain the nomenclature for identifying piezo-coefficients.

- d_{31} measure of the charge generated across the thickness (poling direction) when subject to stress in the machine direction (the classical length expander)
- d_{32} measure of the charge generated across the thickness (poling direction) when subject to stress in the transverse direction
- d_{33} measure of the charge generated across the thickness (poling direction) when subject to stress in the thickness direction (the classical thickness expander)

Uni-axial stretching causes dominant piezo-activity in the direction of stretching, at the expense of piezo-activity in the non-stretched direction. Bi-axial stretching is less anisotropic. Thus,

$$d_{31} \text{ (bi-axial)} \approx d_{32} \text{ (bi-axial)} ; \quad d_{31} \text{ (uni-axial)} \approx 6.0 \text{ x } d_{32} \text{ (uni-axial)}.$$

3 CHEMICAL RESISTANCE

3.1 KNOWN SOLVENTS

Abbreviation	Description
	Acetone
DMAc	Dimethylacetamide
DMF	Dimethylformamide
DMSO	Dimethylsulphoxide
HMPA	Hexamethylphosphoramide
MEK	Methyl thyl ketone
NMP	N-methyl-2-pyrrolidinone
TEP	Triethylphosphate
TMP	Trimethyl phosphate
TMU	Tetramethylurea

3.2 GENERAL

KEY TO TABLE		
	+	*resistant*
	+/o	*resistant to conditionally resistant*
	o	*conditionally resistant*
	o/–	*conditionally resistant to not resistant*
	–	*not resistant*

Medium	Concentration [%]	Temperature [°C]	Term	Resistance
Acetaldehyde	technically pure	23	7 days	-
Acetic acid	50	≤125	7 days	+
Acetic acid	50	≤150	7 days	o
Acetic acid	100	23	7 days	+
Allyl chloride		≤100	7 days	+
Ammonium hydroxide	30	≤150	7 days	+
Ammonium sulphate	50	≤150	7 days	+
Amyl acetate	technically pure	≤ 50	7 days	+
Amyl alcohol	technically pure	≤150	7 days	+
Aniline	technically pure	≤ 40	7 days	+
Benzaldehyde		23	7 days	-
Benzene	technically pure	23	7 days	+
Benzene	technically pure	50	7 days	o
Benzine regular		≤135	7 days	+
Benzine/benzene mixture		≤135	7 days	+
Benzoic acid	saturated	≤125	7 days	+
Borax	50	≤150	7 days	+
Brake fluid		≤ 60	7 days	+
Bromine		≤100	7 days	+
Butane		23	7 days	+
Butanol		≤ 75	7 days	+
Butanol		≤125	7 days	+
Calcium hydroxide		≤135		+
Calcium hypochlorite		≤ 95		+
Carbon dioxide	100	≤135	7 days	+
Carbon disulphide	100	23	7 days	+
Carbon tetrachloride	technically pure	≤150	7 days	+
Chlorine, gas		≤100	7 days	+
Chlorine, gas		≤125	7 days	o
Chlorine, liquid		≤ 95	7 days	+
Chlorobenzene		≤ 50	7 days	+
Chlorobenzene		≤ 75	7 days	o
Chloroform	technically pure	≤ 50	7 days	+
Chromic acid	≤ 40	≤ 80		+
Chromic acid	50	≤ 50		+
Citric acid	50	≤150	7 days	+
Copper sulphate	50	≤150	7 days	+
Cyclohexane		≤150	7 days	+

Cyclohexanol		≤ 65		+
Cyclohexanone		23		-
Decahydronaphthalene	technically pure	≤100	7 days	+
Detergents	ready-to-use	100	7 days	+
Diethylether		23	7 days	+
Dioxane		23		-
Ethanol	96 (Vol.)	≤100	7 days	+
Ethyl acetate	technically pure	23	7 days	+
Ethyl acetate	technically pure	50		-
Ethylene glycol		≤150	7 days	+
Formaldehyde	37	≤ 50	7 days	+
Formic acid	98	≤ 75	7 days	+
Freon® F 12	100	≤100	7 days	+
fruit juices	technically pure	≤100	7 days	+
Glycerin		≤125	7 days	+
Glycerin		≤150		o
Heptane		≤150	7 days	+
Hydrochloric acid	37	≤150	7 days	+
Hydrofluoric acid	40	≤100	7 days	+
Hydrofluoric acid	70	≤ 75	7 days	+
Hydrofluoric acid	100	≤ 50	7 days	+
Hydrogen peroxide	50	≤100	7 days	+
Hydrogen sulphide		≤100	7 days	+
Iron-III chloride	50	≤150	7 days	+
Lactic acid	50	23	7 days	+
Lactic acid	50	≤ 50	7 days	o
Magnesium chloride	50	≤150	7 days	+
Methanol	technically pure	≤ 75	7 days	+
Methanol	technically pure	≤100		o
Methyl isobutyl ketone		23		-
Milk		≤ 75	7 days	+
Motor oil		≤135	7 days	+
Nitric acid	30	≤125	7 days	+
Nitric acid	30	≤150	7 days	o
Nitric acid	65	≤ 60	7 days	+
Nitric acid	65	≤100		o
Nitric acid	98	23		-
Nitrobenzene		23	7 days	+
Nutrient fat		≤100	7 days	+
Paraffin oil		≤120	7 days	+
Perchloroethylene		≤ 50	7 days	+
Perchloroethylene		≤ 75	7 days	o
Petroleum		≤135		+
Phenol	100	≤ 50	7 days	+
Phenol	10	≤ 75	7 days	+
Phenol	10	≤100		o
Potassium dichromate	50	≤150	7 days	+

Potassium hydroxide	50	≤100	7 days	+
Potassium hydroxide	50	≤125		o
Potassium nitrate	50	≤150	7 days	+
Potassium permanganate	50	≤150	7 days	+
Propane		≤150	7 days	+
Propanol		≤ 50	7 days	+
Salad oil		≤120	7 days	+
Silicone oil		≤125	7 days	+
Sodium chlorite	50	≤150	7 days	+
Sodium hydrogen carbonate	50	≤150	7 days	+
Sodium hydroxide	45	≤100	7 days	+
Sodium hydroxide	45	≤125		o
Sodium hydroxide	60	≤ 75	7 days	+
Sodium hydroxide	60	100		-
Sodium thiosulfate	50	≤150	7 days	+
Sulphur dioxide		≤ 80	7 days	+
Sulphuric acid	50	≤150	7 days	+
Sulphuric acid	80	≤125	7 days	+
Sulphuric acid	93	≤ 75	7 days	+
Sulphuric acid	98	≤ 50	7 days	+
Toluene	technically pure	≤ 75	7 days	+
Toluene	technically pure	≤100	7 days	o
Trichloroethylene	technically pure	≤ 50	7 days	+
Trichloroethylene	technically pure	≤ 75	7 days	o
Water		≤150	7 days	+
Xylene	100	≤100	7 days	+
Zinc chloride	50	≤150	7 days	+

4 TIPS FOR USE OF PVDF

4.1 GENERAL INFORMATION

- PVdF is pre-shrunk prior to the deposition of electrodes and further "shrinking" is not required
- To bond PVdF to a substrate use a low viscosity epoxy or nitrile contact adhesive. In either case make sure sufficient pressure is applied during cure.
- To cut PVdF use a sharp scalpel

4.2 ATTACHING ELECTRODES TO PVDF

Electrodes can be attached to PVdF in one of two ways:

- conducting adhesive
- mechanical contact.

Soldering to PVdF film is NOT an option for two reasons:

- The heat of the soldering iron is likely to melt the film,
- long before it melts the film the heat will have caused permanent and irreversible damage to the piezo-electric nature of the film. Exposure to temperatures above 80deg C will start to irreversibly degrade the performance of PVdF

To make a connection to the metallised PVdF consider the use of:

- Adhesive connection using silver loaded epoxy
- Mechanical connection via a clamp, crimp or fold connection

4.2.1 Conductive-adhesive methods

There is a wide range of commercially available conduct adhesives, most of which are based upon an epoxy that has been loaded with conductive particulates, with the intention of getting a continuous electrical pathway across adjacent, touching, particulates. Often these adhesives are very heavily loaded with either silver or carbon powders, leading to very low resistances when cured. Unfortunately, the adhesive strength of these products is often poor (many of the standard conductive epoxies available from RS or Farnell fall into this category). However, the chemical company Henkel make a range of very good conductive adhesives that both bond well and have low resistance; particular recommendations are Henkel Loctite Abelstik 56C and 64C (also known as Hysol Eccobond 56C and 64C) for silver and carbon loaded epoxies respectively.

An alternative solution is to form a temporary bond between wire and PVdF film with a cyano-acrylate (Superglue) adhesive and then use silver loaded paint (RS own brand is just fine) over the ends of the wire on the film to make an electrical connection. Once the paint is dry, check the connection with a resistance meter and then re-enforce the connection by applying a small quantity of standard two-part clear non-conductive epoxy over the connection.

4.2.2 Mechanical contact methods

The other major means of obtaining an electrical contact to PVdF film is to bring the film and the end of the electrode wire into contact and maintaining them there with some form of pressure. This could be accomplished by clamping or crimping an electrode onto the film, or by a lip arrangement as shown in Figure 4. In this particular example the mechanical contact is established between the Metal Casing and the Electrode on the surface of the PVdF sample. The Backing is then pressed onto the rear surface of the PVdF ensuring it is in contact with the metal casing and once in place the backing can be fixed in place by means of a quick setting adhesive.

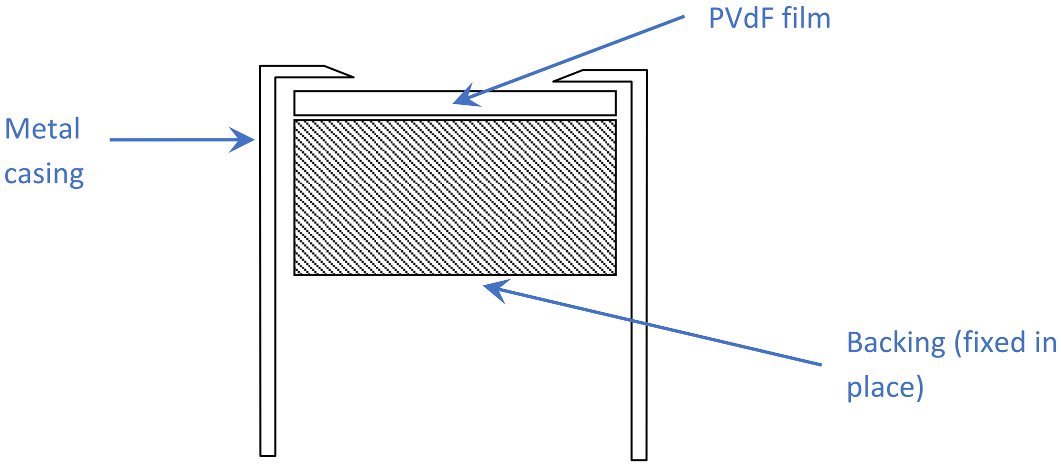


Figure 4 - Mechanical fixing of a PVdF active element

5 SPECIFICS FOR BI-MORPH CONFIGURATION

5.1 ELECTRODE ATTACHMENT

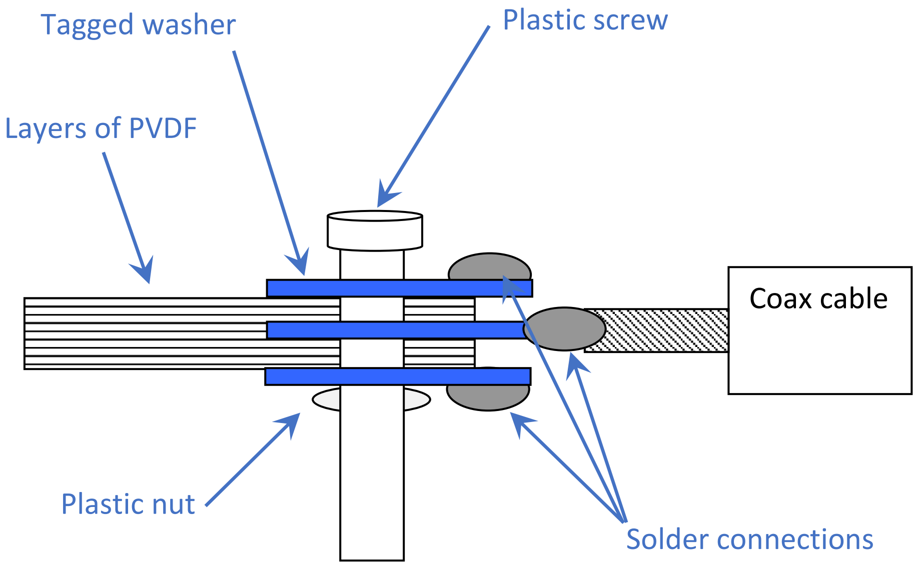
This should be a combination of both of conductive adhesive and mechanical methods.

5.2 ITEMS REQUIRED

- a small length of co-axial wire
- three tagged washers
- small plastic screw with mating nut

5.3 METHOD

- Slightly separate a small area of the lamination of the bi-morph along one edge.
- Strip 2 cm of the sheathing away from the co-ax and the braid separated into two portions
- Twist each portion so that two electrodes are formed from the braid of the co-ax.
- Finally strip back 1cm of the core insulator from the co-ax to expose the central core, to leave a total of three electrode leads (one live, two ground).
- Solder the leads onto the tags of the washers as shown in the diagram below. It is important to note that the solder connections are on the outer surfaces of the two braid electrodes.



- Slide the centre washer in between the layers of the PVdF laminate with the two washers from the braid electrodes going to the outer surfaces of the Bi-Morph
- Make a small hole through laminate such that the plastic screw can be passed all the way though the washers AND the individual sides of the bi-morph.
- Insert the plastic screw and secure with the plastic nut. This ensures a mechanical contact between the three washes and their respective electrodes (two on the outer surfaces, and one on both inner surfaces). The electrodes on the outer surface can then be reinforced with conductive adhesive (taking care not to allow any to seep through the hole in the laminate and therefore shorting inner and outer electrodes).
- Trim and tidy the connections as necessary.
- Further reinforcement of the joint with non-conductive epoxy can be made as required.

6 PRODUCT SUPPORT

6.1 DISCLAIMER

All information is based on results gained from experience and tests and is believed to be accurate but is given without acceptance of liability for loss or damage attributable to reliance thereon as conditions of use lie outside the control of Precision Acoustics Ltd.

7 CONTACT DETAILS

Address	Precision Acoustics Ltd, Hampton Farm Business Park, Higher Bockhampton, Dorchester, Dorset, DT2 8QH
Tel	+44 (0)1305 264669
Commercial matters	office@acoustics.co.uk
Technical matters	technical@acoustics.co.uk

PA terms & conditions are available at *https://www.acoustics.co.uk/company/terms-and-conditions/*

8 REFERENCES

[1] G. M. Sessler, “Piezoelectricity in polyvinylidenefluoride,” *J. Acoust. Soc. Am,* vol. 70 (6), pp. 1596-1608, 1981.