

KYNAR® POLYVINYLIDENE FLUORIDE RESINS FOR BATTERIES

KYNAR® and KYNAR FLEX® polyvinylidene fluoride (PVDF) based resins are highly stable polymers that offer an exceptional balance of performance properties. As the world's leading producer of PVDF, Arkema Inc. has over forty years experience in coating, film, and polymer technologies. From the beginnings of lithium technology, we have worked closely with battery scientists to help design batteries with higher charge density.

KYNAR® and KYNAR FLEX® PVDF resins are excellent polymers for use in both lithium-ion polymeric batteries and in lithium batteries containing a liquid electrolyte. While KYNAR FLEX® PVDF is used in the construction of the polymer matrix of lithium-ion polymer batteries, both battery designs utilize KYNAR® and KYNAR FLEX® PVDF resins in electrode construction.

The polymeric binder used in the anode and cathode of lithium-ion liquid or polymer cells plays a critical role in the cell performance. KYNAR® and KYNAR FLEX® PVDF resins yield unmatched performance compared to other polymeric binders due to the following:

- exceptional purity
- high electrochemical, thermal, and chemical stability
- ease of processing
- excellent adherence within electrodes

KYNAR® and KYNAR FLEX® PVDF resins are exceptionally pure and free of any additives or ionic impurities that can interfere with electrochemical reactions. They are widely used in semi-conductor and pharmaceutical piping applications requiring extremely low extractables.

Produced via an emulsion polymerization which yields a finer powder particle than a suspension polymerization process, KYNAR® and KYNAR FLEX® PVDF powder resins dissolve with comparative ease in the solvents shown on Tables 4 and 5.

Several battery-grade polymers optimized for specific battery technologies are available. KYNAR® HSV and KYNAR® ADX are new grades designed for battery applications. KYNAR® HSV is a high molecular weight resin that provides improved adhesion with reduced loading as a binder in battery applications. KYNAR® ADX is a functionalized PVDF that blends well with other KYNAR® PVDF grades to offer strong adhesion on various substrates. Additionally, water-borne Kynar® binders are available upon request.



Table 1: General Properties of KYNAR® PVDF Battery Grade Resins

	Melt Viscosity (kilopoise)	Melting Point (°C)	Homopolymer	Copolymer	Functionalized homopolymer
KYNAR® 301F	29-33	155-165	●		
KYNAR® 761	23-29	165-172	●		
KYNAR® HSV	33-55	158-170	●		
KYNAR® ADX		165-172			●
KYNAR FLEX® 2801	23-27	140-145		●	
KYNAR POWERFLEX® LBG	34-38	148-155		●	

KYNAR® HSV 900 PRODUCT HIGHLIGHTS

Advantages in lithium-ion battery application

- emulsion resin powder provides improved productivity due to quicker dissolution versus suspension grade resins
- improved electrode adhesion due to higher molecular weight
- high molecular weight allows lower amount of binder to be used in electrodes

SWELLING PROPERTIES

Uniform and consistent swelling is a fundamental property for KYNAR® PVDF homopolymers and copolymers in a battery system. A solvent-swollen polymer acts as a permeable membrane that allows the passage of ions, but prevents electrical contact between the anode and the cathode. The degree of swelling must be predictable within high tolerances. This is particularly true in battery systems that use a polymer gel as the separator. If the polymer absorbs too much solvent, the increased volume may cause the anode/cathode lamination to fail. If the polymer absorbs too little solvent, the film may exhibit lower conductivity.

Tables 2 and 3 show the swelling percentages observed for battery grades of KYNAR® PVDF. Note that the ternary solvent blend of DMC/DEC/EC is a stronger swelling agent than either DMC or DEC alone. Note also the effect of hexafluoropropylene (HFP) content and lower crystallinity on solubility and swelling as exhibited in the Kynar Flex®

copolymer resins. At higher temperatures in DMC, the homopolymers retain their physical strength, while some HFP copolymers do not. In pure DEC, all polymers retained their physical structure. Thermally reversible gelation occurs as the crystallites or aggregates of the polymer reform in the solution.

Table 2: Solvent Uptake at 30°C (%)

Grade	Dimethylcarbonate (DMC)	Diethylcarbonate (DEC)	25:25:50 Blend DMC/DEC/EC
KYNAR® HSV 900	20	9	20
KYNAR® 761	14	7	18
KYNAR® 301F	16	9	–
KYNAR POWERFLEX® LBG-1	22	3	33
KYNAR FLEX® 2801	60	21	–

Table 3: Solvent Uptake at 60°C (%)

Grade	Dimethylcarbonate (DMC)	Diethylcarbonate (DEC)	25:25:50 Blend DMC/DEC/EC
KYNAR® HSV 900	35	14	30
KYNAR® 761	24	10	27
KYNAR® 301F	30	13	–
KYNAR POWERFLEX® LBG-1	36	16	Dissolved
KYNAR FLEX® 2801	Dissolved	45	–

SOLUTION VISCOSITY

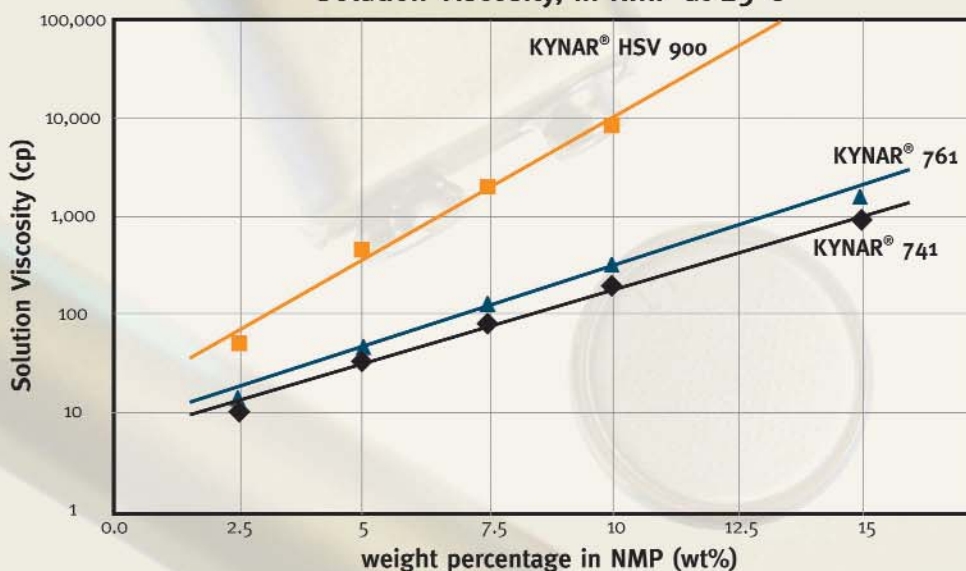
The behavior of polymeric chains in solution is highly dependent on the nature of the polymer and the solvent. This behavior could range between a compact swollen coil in a poor solvent to an extended chain freely rotating in a good solvent.

Dissolution of the polymer is a multi-step process in which the solvent first diffuses into the amorphous region creating a swollen polymer mass.

In the second, but less thermodynamically favored step, the solvent penetrates the crystalline region resulting in total dissolution. The second step is aided by increasing the solvent temperature.

In the chart to the right, KYNAR® HSV 900 exhibits the highest solution viscosity because it has the highest molecular weight.

Solution Viscosity, in NMP at 25°C



SOLUBILITY OF KYNAR® PVDF

KYNAR® PVDF resins have solubility properties suitable for battery production processes. Generally, KYNAR® resins are not soluble in aliphatic hydrocarbons, aromatic hydrocarbons, chlorinated solvents, alcohols, acids, halogens and basic solutions. KYNAR Flex® PVDF copolymer resins tend to be slightly more soluble than the KYNAR® PVDF homopolymer resins due to the lower crystallinity.

Table 4: Solvents^a

Solvent	Boiling Point (°C)	Flash Point (°C)
Dimethyl Formamide(DMF)	153	67
Dimethyl Acetamide ^b (DMAC)	166	70
Tetramethyl Urea	177	65
Dimethyl Sulfoxide(DMSO)	189	35
Triethyl Phosphate	215	116
N-Methyl-2-Pyrrolidone ^b (NMP)	202	95

^a Solvent will dissolve at least 5-10% KYNAR® resin at ambient temperature.

^b Most commonly used solvents.

Table 5: Latent^c Solvents

Solvent	Boiling Point (°C)	Flash Point (°C)
Acetone	56	-18
Tetrahydrofuran	65	-17
Methyl Ethyl Ketone	80	-6
Methyl Isobutyl Ketone	118	23
Glycol Ethers ^d	118	40
Glycol Ether Esters ^d	120	30
n-Butyl Acetate	135	24
Cyclohexanone	157	54
Diacetone Alcohol	167	61
Diisobutyl Ketone	169	49
Ethyl Acetoacetate	180	84
Butyrolactone	204	98
Isophorone	215	96
Carbitol Acetate	217	110
Propylene Carbonate	242	132
Glyceryl Triacetate	258	146
Dimethyl Phthalate	280	149

^c As a rule, latent solvents do not dissolve or substantially swell KYNAR® homopolymer resin at room temperature; they solvate KYNAR® resin at elevated temperatures, but on cooling, KYNAR® resin crystallizes (e.g. precipitates from the solute).

^d Based on ethylene glycol, diethylene glycol and propylene glycol.

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The name Arkema reflects the principles of strength, balance, movement and vitality, as illustrated by the symbol of the arch and the graphics of the logo. In the center of the name, the syllable KEM clearly indicates our activity in the chemical industry and our pride in being in a business that is at the heart of life.



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