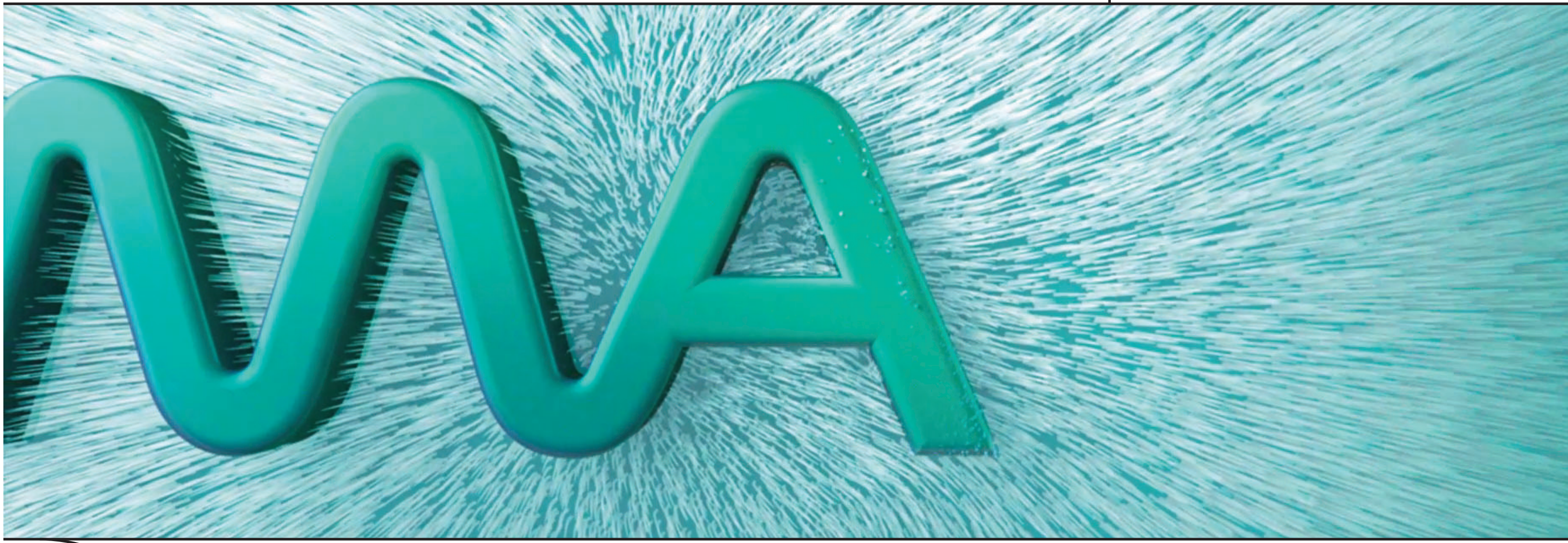
ARKEMA

KYNAR®

RADIATION CROSSLINKING OF KYNAR® PVDF RESINS TECHNICAL BRIEF

Contents



1.0 Introduction to Crosslinked Kynar® PVDF Resins 3

2.0 Crosslink Efficiency 4

3.0 Radiation Sources and Mechanisms 5

4.0 Kynar® PVDF Grades for Irradiation 6

5.0 Crosslink Promoters 7

6.0 Use of Crosslink Promoters 8

7.0 Effect of E-beam Processing on PVDF Properties 9

  7.1 Gel Formation 9

  7.2 Color 9

  7.3 Tensile Strength at Break 9

  7.4 Tensile Strength at Yield 10

  7.5 Tensile Strain at Break 10

  7.6 Flexural Modulus 11

  7.8 Crystallinity and Melting Point 11

References 12

Introduction to Cross-linked Kynar® PVDF Resins

Kynar® PVDF (Polyvinylidene fluoride) resins can be efficiently cross-linked by ionizing irradiation with electron beam (e-beam) being the most commonly used method. The main purpose of crosslinking is to create a linked polymer network that extends the useful temperature range of the PVDF polymer above the melting point. The development of a cross-linked network causes polymer insolubility and dimensional stability at temperatures up to and above the crystalline melting point. Other benefits of crosslinking include improved resistance to creep at elevated temperatures, cut through resistance and abrasion resistance.

In addition, e-beam crosslinking allows for the manufacture of heat shrink tubing. Once a PVDF tube is cross-linked, it can be expanded to a larger ID, and when heated later above the melting point, the tube shrinks back to its original unexpanded dimensions. The presence of the crosslink network creates "memory" that allows the material to revert to its original form once re-melted.

It is important to note that not all polymers can be cross-linked by e-beam irradiation. For many polymers, chain scission is the dominant reaction under e-beam. For such polymers, the result of e-beam exposure is a reduction in molecular weight leading to unacceptable property loses. Only polymers that crosslink preferentially over chain scission exhibit improved physical properties after e-beam exposure. Kynar® PVDF resins crosslink preferentially versus chain scission resulting in property improvements. The following favorable property changes can be expected after e-beam crosslinking Kynar® PVDF resins:

- Gel Content: Gel content and polymer insolubility increases with e-beam dose
- Flexural Modulus: Flexural Modulus will slightly increase up to 20 mrads of e-beam irradiation. The Flexural Modulus will decrease at higher irradiation doses.
- Tensile Stress (Yield): Tensile Stress at yield will exhibit a slight to moderate increase with increasing e-beam dose.
- Tensile Stress (Break): Tensile Stress at break will exhibit a slight to moderate increase with e-beam dose.
- Penetration and Creep Resistance: Penetration and Creep Resistance at elevated temperatures increase significantly with e-beam dose.
- Heat Distortion Temperature: Heat Distortion temperature will increase with e-beam dose.

It should be pointed out that not all properties "improve" with e-beam crosslinking. After e-beam crosslinking PVDF resins, the following property changes can also be expected:

- Melting Point: The melting point will decrease with e-beam dose.
- Tensile Strain (break): The Tensile Strain at break will decrease with e-beam dose.
- Notch Impact Strength: The Notch Impact Strength will decrease with e-beam dose.
- Color and Yellowness Index: The PVDF resins will yellow and darken at higher levels of e-beam dose.
- Weldability: The PVDF resin will no longer be weldable after e-beam crosslinking.

2.0 Crosslink Efficiency

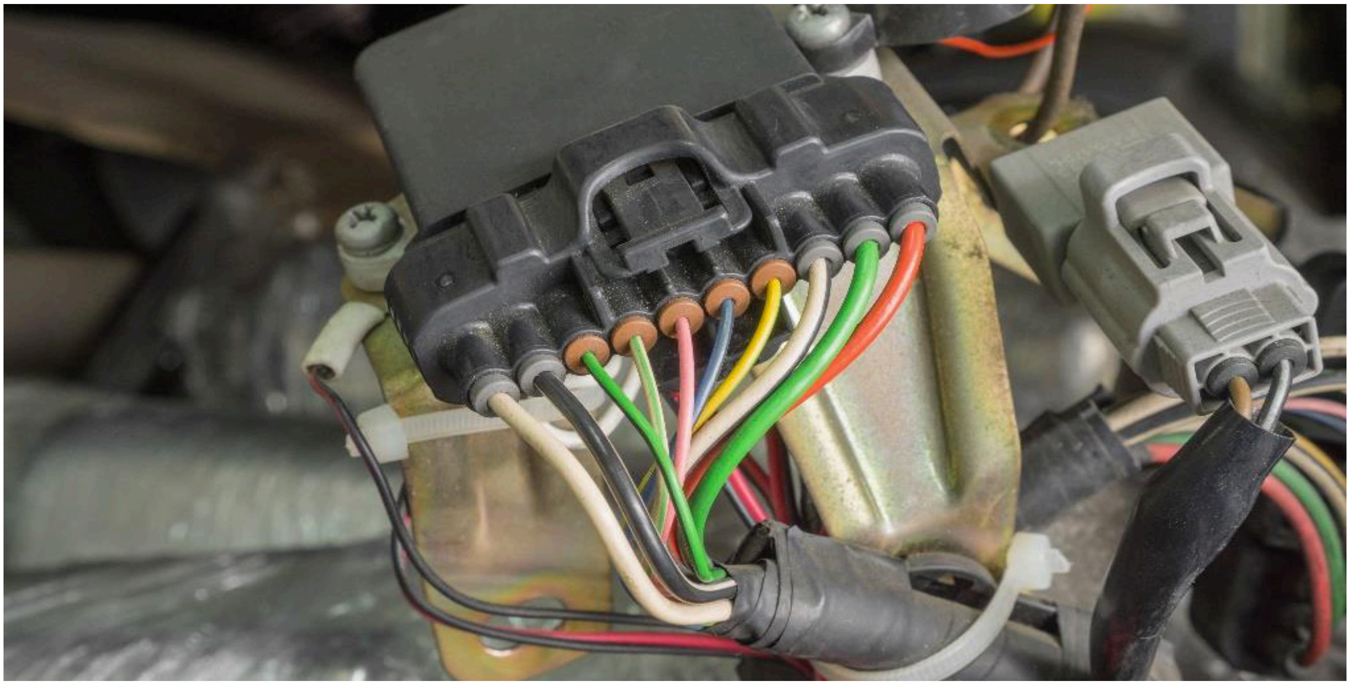
Crosslink efficiency can be described by the amount of irradiation exposure needed to achieve some desired property. A resin that crosslinks efficiently requires less e-beam exposure which by itself can improve final properties. In many cases, the desired property is simply the lack of flow at elevated temperatures (above the resins melting point). For heat shrink tubing, it would be to create a thermoset like structure to retain memory after expansion. Independent of need, the act of crosslinking converts the resin from a thermoplastic to a thermoset resin.

One way to measure crosslink efficiency is accomplished by performing solvent extraction to separate the insoluble fraction (created by crosslinking) from the soluble fraction. The percent crosslinking can then be described as the percent insoluble fraction. As a rule of thumb, a 70 to 80% insoluble fraction is considered sufficiently cross-linked for many applications.

In industry, another means of assessing crosslinking is by performing resin creep tests. In a typical creep test, the resin is exposed to elevated temperature under load, and strain is reported as a function of time. The material is considered sufficiently cross-linked if the amount of strain is maintained below some defined level.

Another way to measure crosslinking is by examining effects of e-beam exposure on rheological properties i.e. resistance to flow. As crosslink density increases, a predictable viscosity shift can be observed when performing a rheological experiment. The higher the viscosity shift, the higher the number of crosslinks generated.

A PVDF copolymer that forms higher numbers of crosslinks for any given amount of e-beam exposure is said to have better crosslinking efficiency. As an example, if two PVDF copolymers have similar starting viscosities, and after e-beam exposure, one of the resins has a higher viscosity, the higher viscosity resin is said to have a higher crosslinking efficiency. In a quantitative example, if these same two PVDF copolymers are exposed to different levels of irradiation, and one of the PVDF resins requires half the e-beam dosage to achieve a similar viscosity shift, then the PVDF resin crosslinked with the lower dose can be described as having twice the crosslink efficiency.



Kynar® PVDF resins used in high performance cable applications are known to crosslink very efficiently. Please contact your Arkema sales representative for proper grade selection.

3.0 Radiation Sources and Mechanisms

Generally, two types of radiation sources can be used to crosslink PVDF resins:

- Gamma radiation: High-energy electromagnetic radiation (wavelength 10^{-4} to 10^{-2} nm).
- Beta radiation (e-beam): Radiation produced by an electron beam accelerator (wavelength 10^{-3} to 10^{-1} nm).

Gamma irradiation is a high-energy electromagnetic irradiation produced from radioactive sources such as Cobalt-60 and Cesium-137. Gamma irradiation requires a nuclear source, which limits industrial uses due to stringent control of radiation sources. Its main advantage is with enhanced penetration depth, which can exceed one meter. Beta irradiation (e-beam) is produced using an electron beam accelerator. In many applications, e-beam irradiation is preferred because it is easier to employ in industrial environments. The primary disadvantage of e-beam irradiation is its limited penetration depth, which does not exceed more than a few millimeters.

During e-beam crosslinking, the irradiation energy leads to the formation of free radicals along the polymer chain. A crosslink then forms when free radicals contained on adjacent chains combine to form a link. The reaction mechanism of ionizing irradiation in PVDF is dominated by crosslinking reactions. Unfavorable reactions such as chain scission or depolymerization either do not occur, or occur at very low levels in Kynar® PVDF resins. In other words, PVDF resins are effectively cross-linked because the crosslinking reaction is favored over chain scission. The basic mechanism responsible for crosslinking is depicted in Figure 1.

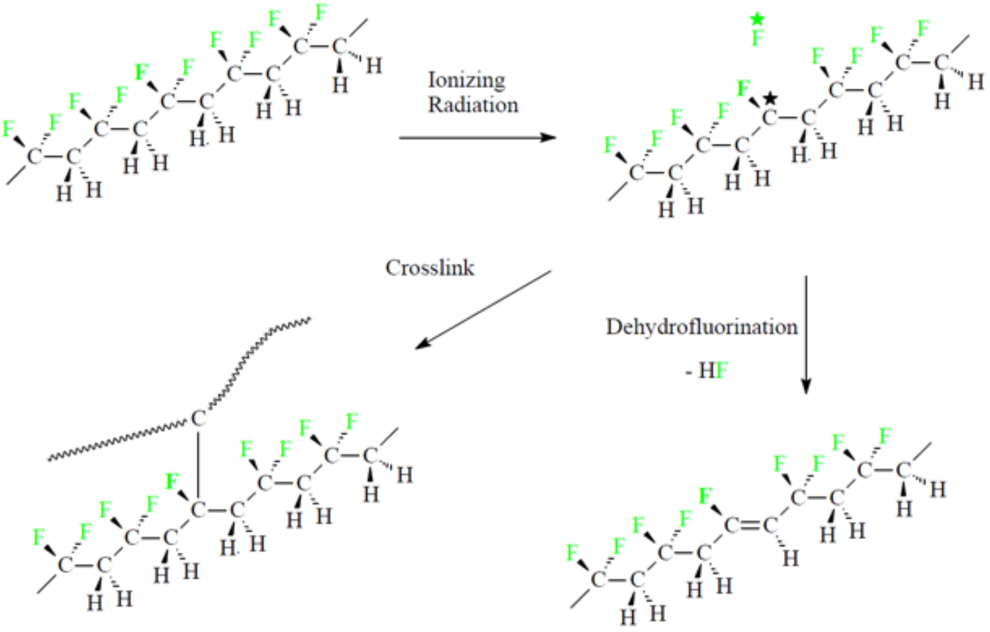


Figure 1. Reaction scheme of PVDF under ionizing irradiation

Irradiation doses are commonly expressed in kilograys (kGy), with one Gray equaling one J energy absorbed per kg of product. Another commonly used unit of measure for irradiation dose is the megarad (Mrad) with one Mrad equivalent to 10 kGy of irradiation.

In PVDF resins, the e-beam crosslinking process causes dehydrofluorination with the formation of hydrogen fluoride. As the irradiation dose increases, so does the dehydrofluorination reaction, which leads to color generation (yellowness and darkening). At very high doses (in excess of 150 Mrads), the dehydrofluorination reaction can lead to more significant property changes. Due to the creation of hydrogen fluoride, safety measures such as appropriate ventilation are needed when e-beam crosslinking Kynar® PVDF resins. It should be noted that Kynar® PVDF resins have been tested and used successfully in nuclear environments with "high" levels of radiation exposure in excess of 1000 mrads.

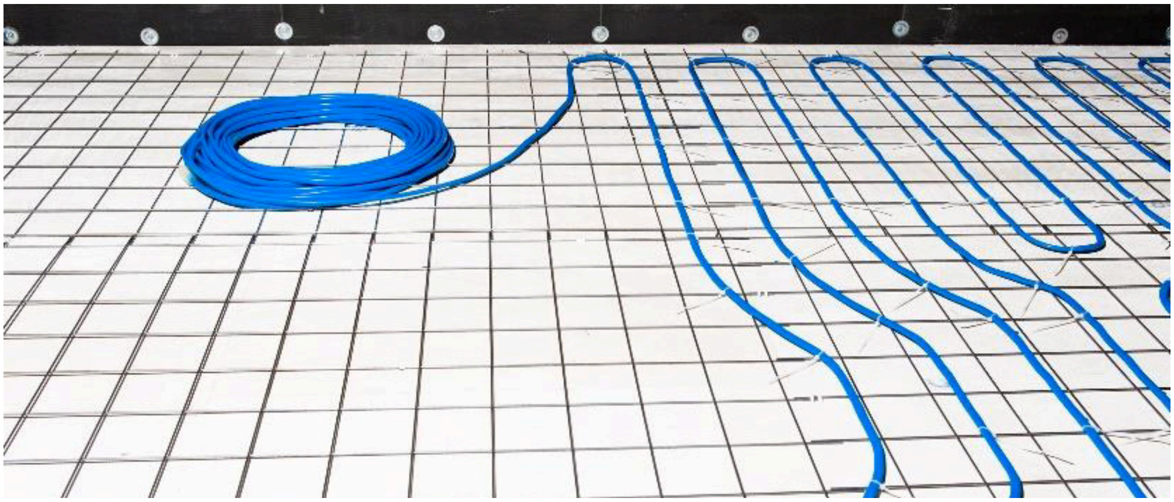
4.0 Kynar® PVDF Grades for Irradiation

The relative effects of irradiation on physical properties, both favorable and unfavorable, can be influenced by the PVDF grade selected. Although all Kynar® PVDF resins can be crosslinked, as a general rule, higher molecular weight grades (and non-plenum) are normally selected for applications requiring e-beam crosslinking. Higher molecular weight resins require less crosslinks to form a large polymer network, and as a result, require less e-beam exposure to achieve desired properties. In addition to higher molecular weight, the addition of comonomers such as Hexafluoropropylene (HFP) also increase crosslink formation from e-beam exposure. The presence of comonomers increase the amorphous content of the polymer, which then improves "crosslinkability" (since crosslinking occurs predominantly in the amorphous phase). Consequently, several high viscosity Kynar Flex® copolymers are preferred for purposes of crosslinking and include the following Kynar Flex® PVDF grades.

KYNAR FLEX® GRADE	TYPICAL PROPERTIES			
	Flexural Modulus (kpsi)	Tensile Strength @ Break (psi)	Tensile Elongation @ Break	Melting Point (°C)
Kynar Flex® 2850-00	165	5700	40	157
Kynar Flex® 3120-50	95	4000	200	165
Kynar Flex® 3030-50	44	2100	>300	168
Kynar Flex® 2800-00	88	4000	250	143
Kynar Flex® 2750-01	48	2500	>300	134

In addition, if a PVDF homopolymer is required, the high viscosity homopolymer Kynar® 460 grade (ASTM D3222, Type I, Grade 1) is the preferred PVDF homopolymer resin for crosslinking purposes and provides performance properties similar to Kynar Flex® 2850-00 resin.

For efficient crosslinking, doses between 50 and 200 kGy (5 to 20 Mrads) are typically enough for most wire and cable applications. Crosslinking doses in the range of 200 to 400 kGy (20 to 40 Mrads) may be suitable for thicker walled products.



5.0 Crosslink Promoters

At times, moderate to high irradiation levels are required to achieve desired properties. When higher irradiation doses are used, certain negative consequences can occur including loss of useful physical, mechanical and/or thermal properties. Some property loss at high irradiation doses is attributed to chain scission resulting in a molecular weight reduction. In addition, higher irradiation levels can disrupt the polymer's crystalline structure resulting in a reduction in crystallinity, and causing a downward shift in enthalpy and melting point. The combination of chain scission and lower melting point can reduce strength and stiffness properties. Lowering the irradiation dose to minimize such negative effects from e-beam exposure is sometimes needed.

The crosslinking efficiency is significantly enhanced by the addition of a coagent (also referred to as a crosslink promoter). The addition of a crosslink promoter allows for higher levels of crosslinking at lower levels of e-beam exposure. Crosslink promoters are therefore often added to improve crosslink efficiency. In most cases, the addition of a crosslink promoter allows the effective dose to be reduced significantly, and in so doing, helps to improve physical properties (and reduce negative property changes). The ability to lower the effective e-beam dose for effective crosslinking is considered useful for improving overall performance.

Typically, crosslink promoters used to improve PVDF resin crosslinking are multifunctional and comprised of either small molecules (or oligomers) containing unsaturated pendant groups (multiple vinyl groups). Vinyl groups are very reactive with free radicals and combine readily to form crosslinks along the PVDF polymer chain.

Crosslink promoters available to improve crosslink efficiency are sometimes classified as either a Type I or Type II coagent. A Type I coagents (typically not used to crosslink PVDF resins) are polar molecule of low molecular weight and used to improve both the reaction rate as well as the degree of cure. Acrylate and Methacrylate oligomers make up a large portion of Type 1 coagents available. A Type II coagent (normally selected to crosslink PVDF resins) are typically less reactive than a Type I coagent and sometimes comprised of higher molecular weight oligomers. Unlike Type I coagents, Type II coagents are used to improve the degree of cure without affecting the rate of cure. An example of Type II coagents is described in Figure 3.

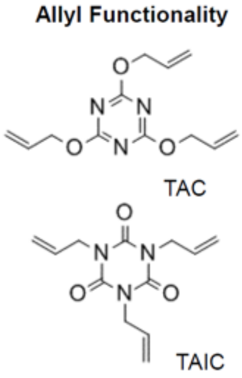


Figure 3. Type II Coagent

6.0 Use of Crosslink Promoters

Parallel Plate experiments are useful for evaluating the effects of e-beam exposure on polymer crosslinking by measuring viscosity changes. As one would expect, a polymer's viscosity will increase as e-beam exposure and amount of crosslinking increases. A typical Parallel Plate test would involve an oscillatory frequency sweep at shear rates from 0.01 to 500 rad/s at 230°C, and with the strain amplitudes maintained within the linear viscoelastic region so as not to damage the crosslink network during the test.

In the following example, parallel plate experiments were performed on Kynar Superflex® 2500-20 resin samples exposed to 0, 3 and 6 Mrads e-beam irradiation. The shear profile for the unexposed sample (0 Mrads) displays a "more" Newtonian response in the low shear region, and after exposure to e-beam irradiation, noticeable changes can be observed. First, the viscosity curves shift upward (to higher viscosities), and second, the rheological response becomes less Newtonian and more thixotropic. In other words, as the number of crosslinks increase, viscosity increases with the resin behaving more like a "networked" polymer. The effect of e-beam irradiation on complex viscosity can be viewed in Figure 4.

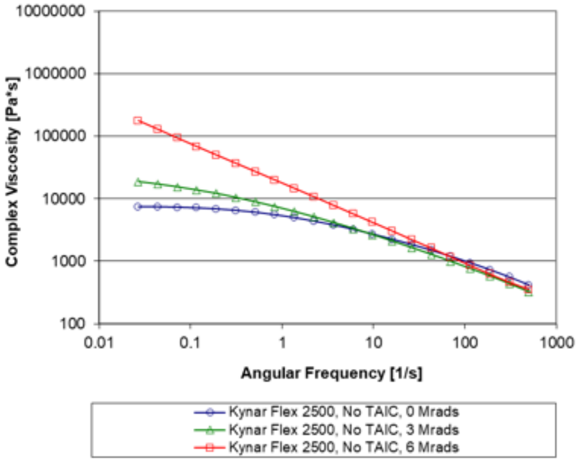


Figure 4. Effect of crosslinking on Viscosity, Kynar Flex® 2500-20

The Parallel Plate experiment was also used to demonstrate how crosslink efficiency can be improved by adding a crosslink promoter such as TAIC. In this example, two samples of Kynar Superflex® 2500-20 resin are prepared, one with TAIC and the other without. After exposing both samples to 6 Mrads of irradiation, we observe a more significant viscosity shift for the sample containing TAIC. The results from Parallel Plate testing can be viewed in Figure 5.

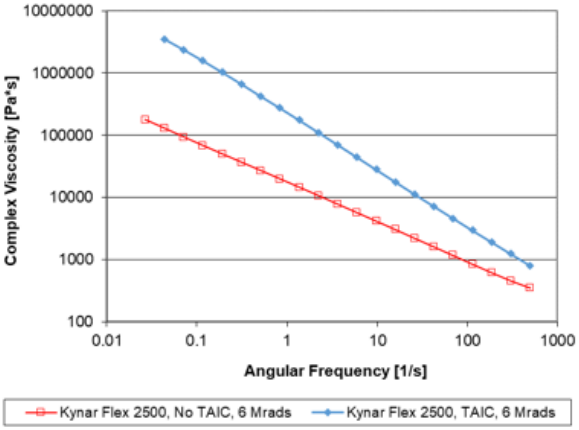


Figure 5. Effect of Crosslink Promoter on Crosslinking

The parallel plate experiment also yielded similar trends for the Kynar Flex® 3120-50 resin with complex viscosity increasing as e-beam exposure increased. Parallel plate rheometry overlay for Kynar Flex® 3120-50 resin can be found in Figure 6.

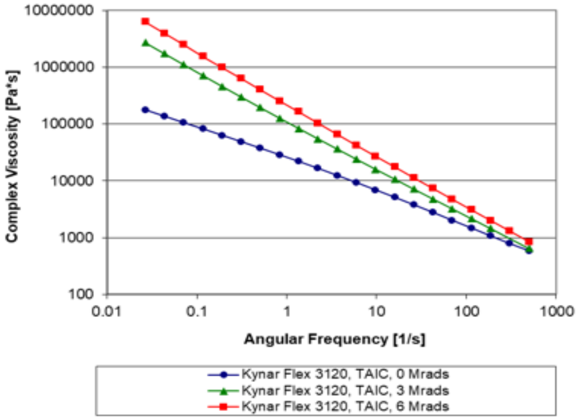


Figure 6. Effect of crosslinking on Viscosity, Kynar Flex® 3120-50

A typical Parallel Plate test would involve an oscillatory frequency sweep at shear rates from 0.01 to 500 rad/s at 230°C, and with the strain amplitudes maintained within the linear viscoelastic region so as not to damage the crosslink network during the test.

7.0 Effect of E-beam Processing on PVDF Properties

The effect of e-beam crosslinking on Kynar® PVDF properties is covered in this next section. For all examples, the e-beam exposures discussed were facilitated by the use of an e-beam accelerator. All tables shown in this section are based on internal testing performed by Arkema.

7.1 Gel Formation

The degree of crosslinking is directly related to the percent gel or insoluble resin content with the percent gel measured by performing solvent extraction testing. Solvent extraction is performed using a solvent such as dimethyl acetamide (DMAC) or triethyl phosphate (TEP) at elevated temperature with the goal of removing the soluble fraction (uncrosslinked) from the insoluble fraction (cross-linked). After extracting the soluble fraction, what remains is the cross-linked insoluble fraction. The insoluble fraction is then dried in an explosion proof oven to remove any remaining residual solvent. The weight percent insoluble fraction (% gel) is then calculated using weight measurements taken before and after solvent extraction.

We learn that gel content increases with irradiation dose, and relatively high gel contents are obtained for all Kynar® PVDF resins exposed to 10 Mrads e-beam irradiation. In addition to increasing gel content with irradiation dose, we also find the gel content increasing as copolymer content increases. As an example, we observe the low copolymer containing grade Kynar Flex® 2850 resin, in general, having less percent gel compared with the medium copolymer containing grade Kynar Flex® 2800 resin. The Kynar Flex® 2800 resin has a higher gel content (higher crosslinking) simply because it has a higher copolymer content and less crystallinity. The percent gel formation as a function of irradiation dose can be found in Figure 7.

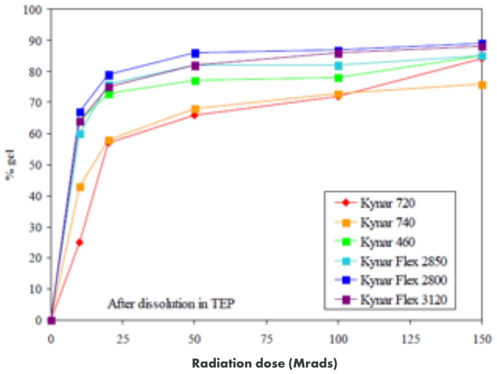


Figure 7. Irradiation Dose and Gel Formation

7.2 Color

PVDF resins will darken when exposed to e-beam irradiation, and this is often the first property change noticed. Kynar® homopolymers such as Kynar® 740 PVDF tend to show "first" signs of yellowing near 30 kGy (3 Mrad) and become darker and "brownish" in appearance at 50 kGy (5 Mrad). Kynar Flex® copolymers will also darken with e-beam irradiation, but they tend to be more resistant to color change compared to the homopolymers. For most Kynar Flex® copolymers, the first signs of yellowing occurs closer to 100 kGy (10 Mrad). As can be observed in the following figure displaying color as a function of irradiation dose, we learn that on average, PVDF copolymers require twice the e-beam dose to achieve the same color shift compared to PVDF homopolymers. A summary of these results can be found in Figure 8.

In addition to PVDF resins darkening after e-beam exposure, post-thermal color stability is also affected by e-beam exposure. What this means is that after PVDF resins are e-beam crosslinked, if later exposed to elevated temperatures, higher color shifts can be expected. This effect becomes more prevalent as e-beam dose increases. The addition of a coagent such as TAIC can improve the post-thermal color stability of PVDF resins.

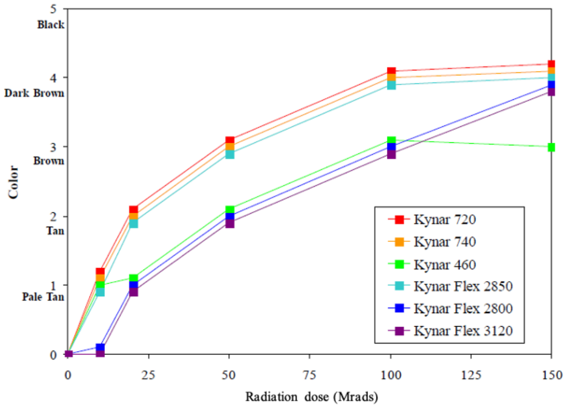


Figure 8. Irradiation Dose and Color Change

7.3 Tensile Strength at Break

In general, the tensile strength at break for Kynar Flex® PVDF resins is only marginally affected by e-beam exposure. As a general trend, the tensile strength at break for both homopolymers and copolymers tends to increase with ebeam dose, but as mentioned, the change is relatively small. In the range of 10 to 20 Mrads e-beam irradiation, we can observe some changes in Tensile strength at break with some PVDF grades showing increasing properties while others showing decreasing properties. The same is true at radiation doses of 50 Mrads. At 100 Mrads, the general trend is a slight increase in Tensile strength at break, and at 150 Mrads, this property tends to be more similar to the starting properties of their respective grade. A summary of these results can be found in Figure 9.

Elongational properties tends to be effected to a greater extent from Irradiation then strength properties (see ¶7.5)

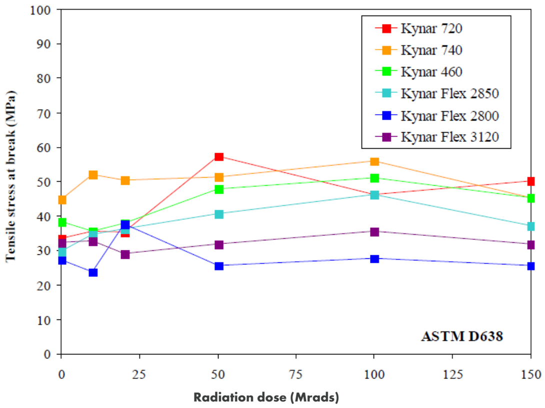


Figure 9. Irradiation Dose and Tensile Stress at Break

7.4 Tensile Strength at Yield

The tensile strength at yield of all grades increased with irradiation dose to a maximum at 20 to 50 Mrads due to crosslinking. The yield point was lost at 100 Mrads for all grades except Kynar® 740, which lost the yield point at 50 Mrads. Loss of the yield point in crosslinked PVDF resins is related to a reduction of elongational properties (see¶7.5). As a general note, the tensile strength at yield of PVDF homopolymers is considerably higher than that of the PVDF copolymers, and this is primarily due to higher crystallinity (of the homopolymers). A summary of the Tensile Yield strength as a function of irradiation dose can be found in Figure 10.

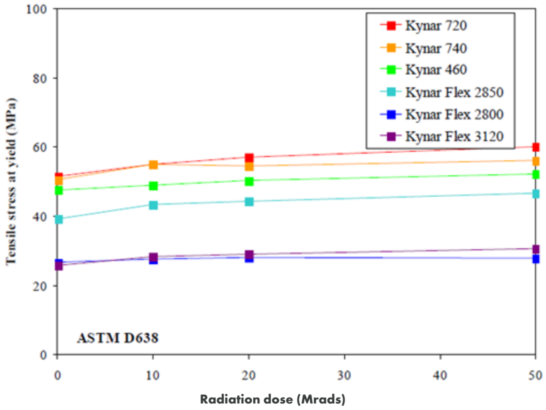


Figure 10. Irradiation Dose and Tensile Stress at Yield

As a general comment, the stress at yield increases by 10 percent on average with an irradiation dose of 10 to 20 Mrads, and continues to increase at higher doses. Above 50 Mrads, minimal yield type behavior is observed for most PVDF grades.

7.5 Tensile Strain at Break

The tensile strain at break for PVDF resins typically decreases with increasing e-beam irradiation dosage. PVDF copolymers in general show higher loss of tensile strength at break compared to the homopolymers. More specifically, PVDF copolymer grades normally having high elongational properties tend to show the greatest loss of elongational properties. To explain why, the presence of crosslinks prevents ductile deformation of the resin, and simply reduces its ability to be cold drawn. One way to describe this change is that PVDF copolymers having high initial elongation at break properties will exhibit properties more similar to homopolymers after ebeam exposure. A noteable exception is Kynar Flex® 3120-50 resin which retains a higher level of break strain compared to other PVDF copolymer grades. A summary of the Tensile Yield strength as a function of irradiation dose can be found in Figure 11.

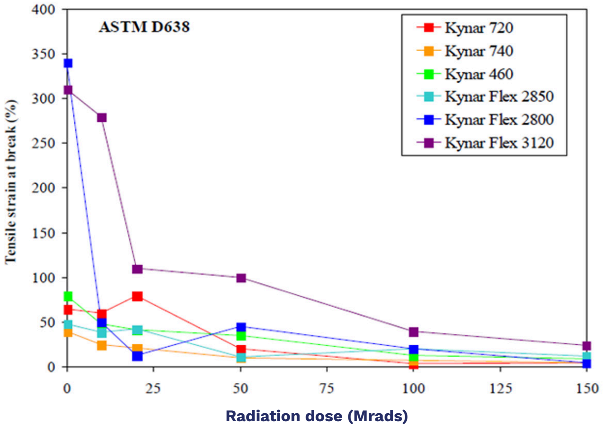


Figure 11. Radiation Dose and Tensile Stress at Break

A reduction in the strain at break is expected and directly attributed to the presence of crosslinks. The highest strain at break was found with the copolymers compared to the PVDF homopolymers. The Kynar Flex® 3120-50 resin retained the highest elongation after irradiation with 100% elongation at 50 Mrads.

It should be noted that in more recent studies, it was found that the strain at break was much less affected when irradiation doseage was maintained below 10 Mrads. As an example, for several Kynar Flex® resins, the strain at break was mostly unchanged after 6 Mrads irradiation exposure. The highest reduction of break strain reported for any PVDF copolymer after 6 Mrads irradiation was 35 to 40 percent. The study also confirmed that the addition of a crosslink promoter further reduces strain at break due to higher levels of crosslink formation.

7.6 Flexural Modulus

The flexural modulus moderately increases at lower e-beam irradiation levels up to about 10 to 20 Mrads. This increase was most evident in the PVDF homopolymer Kynar® 740 resin, and less evident in the PVDF copolymers. The increase in flexural modulus is directly related to the formation of crosslinks. Above 20 Mrads, the flexural modulus decreased as irradiation levels further increased. This drop in flexural modulus is attributed to a drop in crystallinity associated with the irradiation process (see ¶7.7). The data also suggests that Kynar Flex® copolymer grades having higher levels of copolymer may not display any increase in flexural modulus at all with irradiation dose and will simply "soften" as e-beam dosage is increased. A summary of the Flexural Modulus as a function of irradiation dose can be found in Figure 12.

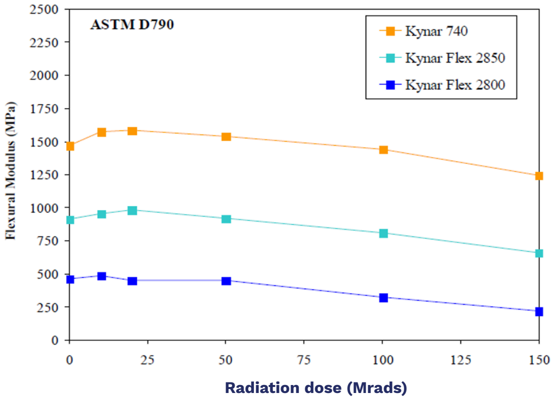


Figure 12. Radiation Dose and Flexural Modulus

It is worth noting that "flexibility" is beneficial for many wire and cable applications, and lower flexural modulus means improved flexibility. In the case of Kynar Flex® copolymers, the softer more flexible grades are expected to retain much of the desired flexibility after ebeam exposure.

7.7 Thermal Stability

A steady decrease of melting temperature and heat of fusion is observed with increasing irradiation dose. The drop in melting point is due to disruption of the crystalline structure associated with e-beam exposure. The changes to the crystalline structure are also responsible for lowering of Flexural Modulus (see ¶7.6). The drop in melting point temperature is relatively low at radiation doses below 20 Mrads. For most applications, the melting point drop should be no more than 1 or 2 degrees after irradiation. A summary of the melting point as a function of irradiation dose can be found in the following Table.

PVDF GRADE	**DSC MELTING POINT (°C), 2ND HEAT**			
	0 Mrads	10 Mrads	20 Mrads	50 Mrads
Kynar® 720	169	167	165	159
Kynar® 740	169	168	165	161
Kynar® 460	158	158	156	150
Kynar Flex® 2850	156	155	153	146
Kynar Flex® 2800	143	141	138	130

Conclusion

E-beam irradiated Kynar Flex® PVDF resins have been used to produce high temperature wire and cables as well as heat shrink tubing for many decades. These products find use in a variety of applications found in the commercial sector, industry and military. Proper selection of any Kynar Flex® PVDF grade should take into account factors such as desired end-use properties, other physical property changes (associated with crosslinking), and crosslinking efficiency. Higher viscosity PVDF grades such as Kynar Flex® 2800-00 resin are normally selected due to their improved crosslinking efficiency. Further improvements with crosslinking efficiency can be gained by the addition of a crosslink promoter, and also by the selection of softer grades. The use of a thermal stabilizer is often included when a crosslink promoter is included.

The primary goal of crosslinking is to create a thermoset like structure that improves high temperature properties, creates memory and prevents creep. More specifically, crosslinking allows the Kynar Flex® PVDF resin to be used above its melting point, and also to function as a heat shrink tubing. As an example, crosslinked Kynar Flex® 3120-50 resin, which has a melting point of 165°C, can be used in cable applications requiring a 175°C rating or higher. Softer grades such as Kynar Flex® 3030-50 resin are preferred when even higher temperature ratings are needed, or at times when a blended composition is needed to achieve tailored properties.

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