

Study of the Mechanical and Electrical Properties of Carbon/Poly(vinylidene fluoride–tetrafluoroethylene–propylene) Films Crosslinked with Triethylenetetramine: Possible Application as Binder for Lithium-Ion Battery Electrodes

Zonghai Chen,¹ L. Christensen,² J. R. Dahn^{1,3}

¹Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 3J5, Canada

²3M Company, 3M Center, St. Paul, Minnesota 55144-1000

³Department of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia B3H 3J5, Canada

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ABSTRACT: The mechanical properties of poly(vinylidene fluoride–tetrafluoroethylene–propylene) (PVDF–TFE–P) were evaluated as a function of the degree of crosslinking. Both bisphenol and triethylenetetramine (TETA) were used as crosslinkers to improve the mechanical properties of PVDF–TFE–P and carbon black–filled PVDF–TFE–P. Bisphenol was incorporated into the polymer by the manufacturer and crosslinking was achieved through additions of MgO and CaO followed by heating. Although bisphenol crosslinking improves the mechanical properties, further crosslinking was needed to obtain good extensibility under repeated deformation of carbon black/PVDF–TFE–P composites. By incorporating small amounts of 1,4-diazabicyclo[2.2.2]octane and CaO,

additions of TETA added more crosslinks in PVDF–TFE–P, leading to improved mechanical and electrical properties. The crosslinked polymer does not become brittle in typical solvents used in lithium battery electrolytes, so we believe that this highly extensible binder system may be useful for electrode materials that show large volume changes during charge–discharge cycling. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2949–2957, 2004

Key words: crosslinking; electrical properties; lithium-ion batteries; mechanical properties; poly(vinylidene fluoride–tetrafluoroethylene–propylene) (PVDF–TFE–P)

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is widely used as the polymeric binder in the electrodes of lithium-ion cells because of its electrochemical and chemical stability and because of its acceptable adhesion to particles of electrode materials and to current collectors.^{1,2} However, we believe PVDF is unsuitable for applications involving electrodes prepared from powders of alloy electrode materials,^{3–7} which can have up to 250% volumetric changes during charge/discharge cycling.⁴ One reason is that commonly used PVDF has very poor extensibility. It can be cyclically deformed only with very small strains, for example, strains less than 10%.⁸ PVDF works well as a binder for electrodes made of commonly used materials, such as mesocarbon microbeads (MCMB) and LiCoO₂ where volumet-

ric changes of 10% are the maximum. However, we believe that such a binder cannot tolerate the huge volumetric changes of high capacity tin or silicon-based anode materials. The poor extensibility will result in the breaking of binder strands and an increase in the contact resistance between electrode particles and to the current collector. Eventually, we believe that poor binder extensibility leads to electrically isolated electrode particles and hence to electrode failure.

Fluorinated polymers, including poly(vinylidene fluoride–hexafluoropropylene) (PVDF–HFP), can sometimes be readily swollen, gelled, or dissolved by non-aqueous liquid electrolytes used in lithium-ion batteries.^{9–11} Swelling or dissolving can cause the adhesion of electrode materials to the current collector to deteriorate. Furthermore, the viscous flow of polymer chains under applied stress is inevitable for linear polymers.¹² This can also lead to the breaking of binder strands and loss of electrical contact between electrode materials and current collectors. Crosslinked polymers with excellent extensibility and rebound may overcome the shortcomings of PVDF-based binders.

Crosslinking is a commonly used and effective way to improve the mechanical properties of polymers.^{8,13–16} It is well known that triethylenetetramine (TETA) can be

Correspondence to: J. Dahn (jeffdahn@dal.ca).

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used to crosslink VDF-containing fluorinated polymers. PVDF is chemically stable at room temperature, and it is difficult to react with other chemicals to form unsaturated $-\text{CH}=\text{CF}-$ bonds that can act as active sites for crosslinking with TETA. With the addition of HFP to the PVDF chain, the VDF monomer in the chain can easily react with a base and to yield unsaturated $-\text{CH}=\text{CF}-$ bonds that act as sites for crosslinking with TETA. Another bonus is that the extensibility of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) is much better than that of PVDF.⁸ By introducing crosslinks, the extensibility of the polymer can be further improved, the degree of swelling in nonaqueous solvents can be reduced, and the viscous flow under stress can be greatly suppressed.

PVDF-HFP polymers can absorb a relatively large amount of nonaqueous electrolyte. On the other hand, polypropylene absorbs none, presumably because polypropylene is nonpolar and the solvents are polar. Additions of propylene to fluoroelastomers should reduce swelling during exposure to nonaqueous electrolytes. Therefore, a commercially available terpolymer, poly(vinylidene fluoride-tetrafluoroethylene-propylene) (PVDF-TFE-P) was chosen for careful evaluation in this work. We used a combination of 1,4-diazabicyclo[2.2.2]octane (DABCO), CaO, and TETA to induce significant crosslinks in PVDF-TFE-P. The mechanical properties of crosslinked PVDF-TFE-P and the mechanical and electrical properties of crosslinked carbon black-filled PVDF-TFE-P composites were studied and are reported here.

EXPERIMENTAL

A PVDF-TFE-P polymer (BRE-7131X, 60% fluorine; Dyneon Co., Oakdale, MN) was used in this study. The details of the polymer (relative monomer content, molecular weight) were not made available to us.

One crosslinking recipe involved the use of TETA (Aldrich, Milwaukee, WI) and the other relied on the bisphenol incorporated within the as-supplied polymer. In the TETA method, the polymer was completely dissolved in methyl ethyl ketone (MEK; Aldrich) and mixed with Super-S carbon black (SS; MMM Carbon, Brussels, Belgium) if desired. Then, a measured amount of chemical additives, including CaO (Fisher Scientific, Pittsburgh, PA), 1,4-diazabicyclo[2.2.2]octane (DABCO; Aldrich) and triethylenetetramine (TETA; Aldrich), were added. The final mixture was coated on a piece of Teflon release film (3M Co., St. Paul, MN) using a notch bar spreader with a gap of 0.4 mm and then dried in air overnight. The typical thickness of resulting freestanding films was about 0.06 mm. The amount of chemical additives and SS in the films are reported in units of parts per hundred polymer by mass (pph).

Some bisphenol was already incorporated in the as-supplied BRE-7131X polymer. Just as recom-

TABLE I
Crosslinking Recipes for the PVDF-TFE-P Polymer and Carbon-Filled PVDF-TFE-P Composite^a

Material	Heating	TETA
PVDF-TFE-P	100	100
Super-S carbon black	0 or 25	0 or 25
MgO (Maglite Y)	6	0
CaO	2	4
DABCO	0	3
TETA	0	X

^a Quantities of additives are given in parts per hundred by mass (pph). For TETA, X ranged from 0 to 5.

mended by the supplier, BRE-7131X can be crosslinked by heating with MgO (Maglite Y; C. P. Hall Co., Bedford Park, IL) and CaO. As above, the BRE-7131X polymer was dissolved in MEK and the additives mixed with the solution. Films were cast as above and dried in air, then heated under a flow of argon in a tube furnace. Based on the results to be shown below, the degree of crosslinking introduced by this method is quite low. The recipes for both the bisphenol and TETA crosslinking methods are listed in Table I. In the TETA-based crosslinking recipe, X represents the content of TETA ranging from 0 to 5 pph. When the heating recipe was used, the samples were heated in argon at 110°C after the samples were dried in air overnight.

A homemade stress-strain and resistivity tester⁸ was used to measure the mechanical and electrical properties of binder films simultaneously with a strain rate of $\pm 0.01 \text{ min}^{-1}$. A slow strain rate was adopted to mimic the expansion and contraction of Sn- or Si-based electrode particles during a 3-h charge or discharge in lithium-ion batteries.

To evaluate the swelling of the crosslinked polymer films, the films were immersed in a mixed solvent of ethylene carbonate/diethyl carbonate (EC/DEC, 1 : 2 by volume; Mitsubishi Chemical Co., Tokyo, Japan) for 24 h. The mass of the film before and after soaking was used to determine the percentage weight uptake of the films. Normally, the typical mass of sample used for the soaking test was about 0.2 g.

RESULTS AND DISCUSSION

Effect of chemical additives in both recipes

The polymer used, BRE-7131X, already incorporated some bisphenol, one of the crosslinkers for fluorinated elastomers. As recommended by the supplier, the polymer can be crosslinked by heating with additions of CaO and MgO. The reaction mechanisms can be summarized as follows. A base such as MgO or CaO dehydrofluorinates the fluoroelastomer backbone as given by eqs. (1) and (2). The VDF unit reacts with the

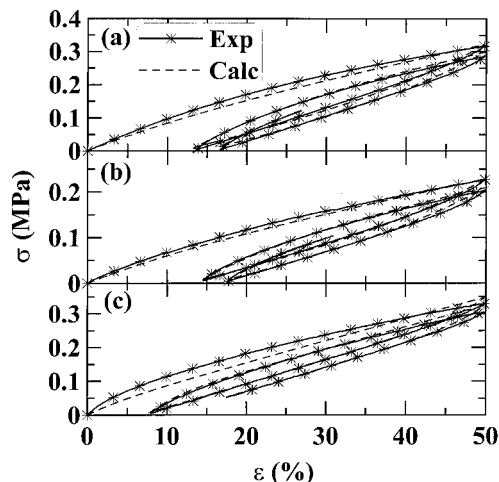


Figure 1 Stress-strain curves of cured PVDF-TFE-P (110°C for 24 h) showing the effect of the additives MgO and CaO: (a) 6 pph MgO and 2 pph CaO; (b) 8 pph MgO; (c) 8 pph CaO. The data are the symbols and the solid lines are calculated stress-strain behavior using the linear model and the parameters in Table II.

base to form an active site, unsaturated $-\text{CH}=\text{CF}-$. After that, a bifunctional molecule, such as bisphenol, is added to the backbone to provide crosslinking [eq. (3)].

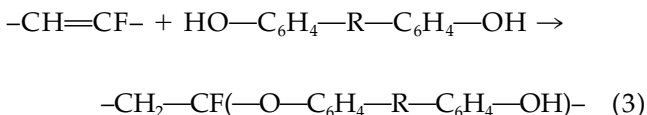
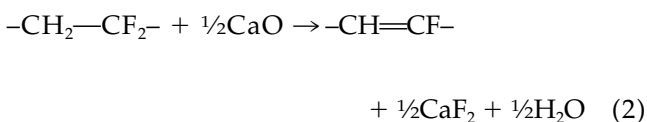
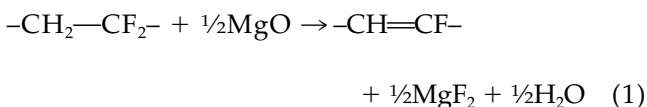


Figure 1 shows the stress-strain curves of bisphenol-crosslinked PVDF-TFE-P films that were prepared with different contents of MgO and CaO. These films were all heat treated at 110°C for 24 h. The true stress is plotted in Figure 1, that is, the force divided by the strain-dependent cross-sectional area of the film. The cross-sectional area as a function of strain was calculated assuming that the volume of the polymer remained constant during strain, as is common.¹² The experimental curves were also fitted with the linear model, schematically shown in Figure 2.^{8,12} The best-fit parameters for the spring constants K_1 and K_2 and the dashpot viscosities K_{d1} and K_{d2} are listed in

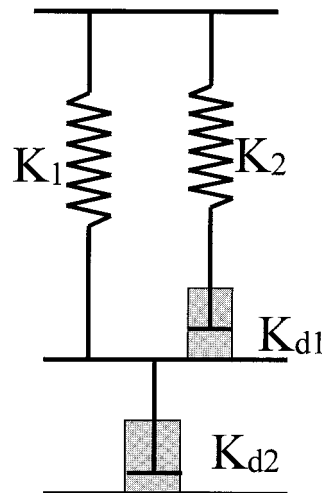


Figure 2 Schematic of the linear model used to describe the mechanical properties of polymer films. K_1 and K_2 are the spring constants in the model and K_{d1} and K_{d2} are constants to characterize the viscosity of the dashpots in the model.

Table II. Only small differences between the samples heated with only MgO, only CaO, and with both can be seen from both Figure 1 and the fitted parameters in Table II.

The sample with 8 pph CaO [Fig. 1(c)] has slightly better mechanical properties than those of the other samples. It has the largest spring constant K_1 , the largest dashpot viscosity K_{d2} , and rebounds closest to its original length when the stress is removed. Hence, CaO was chosen as the inorganic base for the new crosslinking recipe with TETA. However, the degree of crosslinking needs to be improved because the values of K_1 and K_{d2} are still quite small. Although the sample with the manufacturer's recommended ratio of 2 pph CaO and 6 pph MgO was not the best one, films made using the recommended recipe were used for comparison to the TETA-crosslinked films hereafter.

The amount of crosslinking can be increased by two methods. Both MgO and CaO have dual roles in the reactions: they both act as a base to dehydrofluorinate the backbone and as a reagent to consume the byproduct

TABLE II
Best-Fit Parameters of the Linear Model (Fig. 2) to the Data Shown in Figures 1 and 3

Method	K_1 (MPa)	K_2 (MPa)	K_{d1} (10^2 MPa S ⁻¹)	K_{d2} (10^4 MPa S ⁻¹)
Heating (Fig. 1)				
(a)	0.59	0.39	2.9	2.1
(b)	0.42	0.28	2.2	1.3
(c)	0.69	0.51	1.2	2.6
TETA (Fig. 3)				
(a)	1.23	0.28	2.4	9.8
(b)	0.33	0.36	3.1	1.0
(c)	0.54	0.28	2.6	3.4

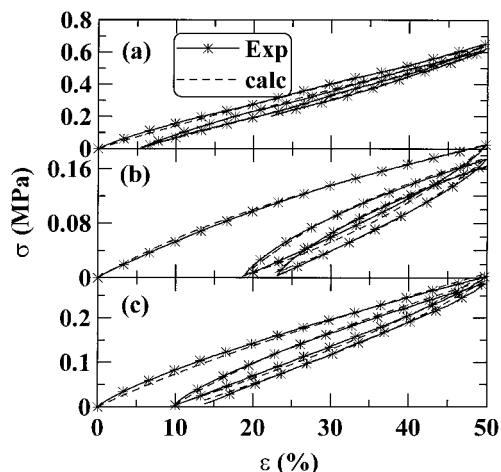
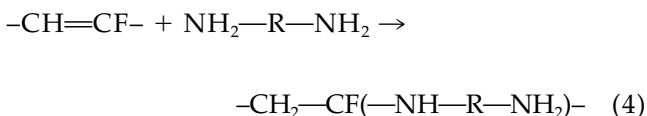


Figure 3 Stress-strain curves of TETA crosslinked PVDF-TFE-P showing the effect of DABCO and CaO: (a) 5 pph TETA + 3 pph DABCO + 4 pph CaO; (b) 5 pph TETA + 5 pph DABCO; (c) 5 pph TETA + 5 pph CaO. The data are the symbols and the solid lines are calculated stress-strain behavior using the linear model and the parameters in Table II.

HF. A stronger base, such as DABCO, will form more unsaturated active sites. In addition, the content of the crosslinker bisphenol is set by the amount added by the manufacturer to the initial as-received polymer. Another crosslinking molecule, TETA, can be added to increase the density of crosslinks. The crosslinking reaction involving TETA is given by eq. (4), where the group R is $-C_2H_4-NH-C_2H_4-NH-C_2H_4-$.



Another advantage of TETA is that it can be used to crosslink the polymer at room temperature.

Figure 3 shows the cyclic stress-strain curves of TETA (5 pph) crosslinked PVDF-TFE-P with different additives. Figure 3(a) shows results for a film cast with TETA, DABCO, and CaO. Figure 3(b) and (c) show the results a film cast with TETA and DABCO [Fig. 3(b)] and for a film cast with TETA and CaO [Fig. 3(c)]. The results in Figure 3 show that the film is much stiffer, but still very elastic, when both DABCO and CaO are used. Both a strong base, like DABCO, and CaO must be included to achieve good mechanical properties. The linear model was used to fit the stress-strain curves in Figure 3, and the best-fit parameters are listed in Table II. Compared to films crosslinked by the heating recipe (shown in Fig. 1 and Table I), both K_1 and K_{d2} increased significantly for the film crosslinked with TETA, DABCO, and CaO [Fig. 3(a)]. K_1 increased from 0.59 to 1.23 MPa, and K_{d2} increased from 2.1 to 9.8 MPa S⁻¹. The sample described by Figure 3(a)

rebounded to 1.06 times its original length when the stress was removed, significantly better than the samples prepared by the heating recipe.

Mechanical properties of crosslinked PVDF-TFE-P films

Figure 4 shows stress-strain curves for the bisphenol-crosslinked PVDF-TFE-P films as a function of heat treatment conditions. The strength of the polymer film increases with the heating time at 110°C, presumably attributable to an increased density of crosslinks. As expected, the crosslinking reaction is faster at higher temperature (180°C). The sample cured at 110°C for 24 h has almost the same mechanical properties as those of the sample cured at 180°C for 3 h. To avoid possible thermal degradation of the samples, the lower temperature (110°C) was adopted for the heating recipe in the experiments described below.

In Figure 4 the slope of the stress-strain curves for the bisphenol-crosslinked samples decreases as the strain increases near 50% strain. The decrease of the slope is caused by viscous flow in the uncrosslinked and lightly crosslinked samples. For the uncrosslinked sample, the viscous flow is so significant that eventually the film breaks near 100% strain. In the high strain region, the slope of the stress-strain curve increases with strain. This phenomenon is called non-Gaussian behavior, which can be described by the theory of James and Guth.^{12,17} However, this theory does not fit the data in Figure 4 because of the obvious viscous flow.

Figure 5 shows the stress-strain curves of the TETA-crosslinked PVDF-TFE-P films. Both viscous flow and non-Gaussian behavior can be seen in the curves. By simply comparing the scale of Figures 4 and 5, one can easily see that the samples prepared using the TETA

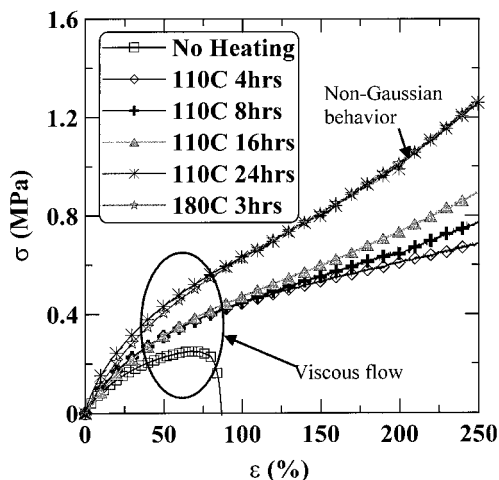


Figure 4 Stress-strain curves of cured PVDF-TFE-P (curing conditions listed in the inset) with strains up to 250%.

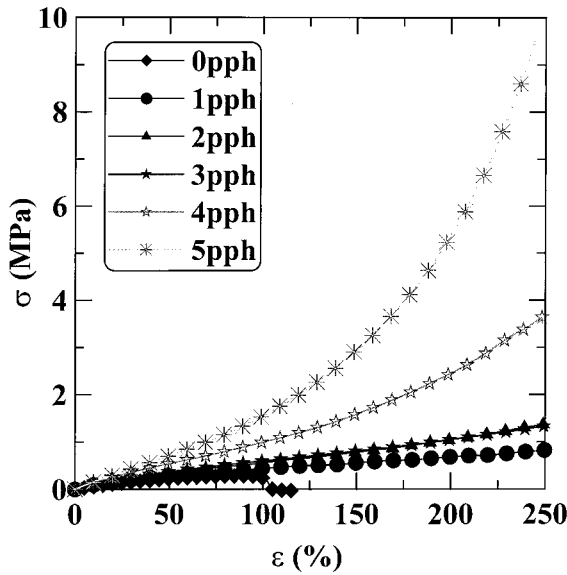


Figure 5 Stress-strain curves of TETA crosslinked PVDF-TFE-P with strains up to 250%. The amount of TETA added to each sample is indicated in the legend.

recipe are more crosslinked than the samples prepared by the heating recipe. When 4 or 5 pph TETA was added, viscous flow was almost eliminated by the crosslinks. Hence, these two samples can be fitted with eqs. (5) and (6) derived by Guth and James¹⁷ and discussed by Ward [eq. (3.27) in Ward and Hadley¹²]:

$$f = \frac{NkT}{3} n^{1/2} \left[L^{-1} \left(\frac{\lambda}{n^{1/2}} \right) - \lambda^{-3/2} L^{-1} \left(\frac{1}{\lambda^{1/2} n^{1/2}} \right) \right] \quad (5)$$

$$\sigma = f\lambda \quad (6)$$

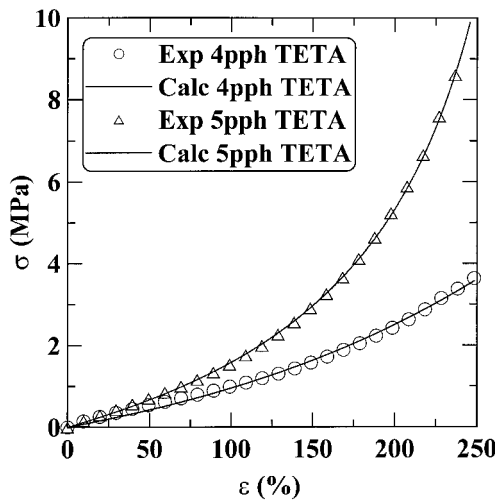


Figure 6 Stress-strain curves of TETA crosslinked PVDF-TFE-P with strains up to 250%. The solid lines are calculations using eqs. (5) and (6) with the parameters listed in Table III.

TABLE III
Best-Fit Parameters of Equation (5) to the Data in Figure 6 for the Highly Crosslinked PVDF-TFE-P Films

TETA content (pph)	NkT (MPa)	n	χ^2
4	0.086	57	3.77
5	0.126	18	1.11

where f is the nominal stress, σ is the true stress, N is the number of freely jointed chains per unit volume, n is the number of chain links between successive crosslinks, λ is the elongation ratio, and $L^{-1}(\cdot)$ is the inverse Langevin function.

Figure 6 shows that eqs. (5) and (6) can fit the experiments well for a suitable choice of parameters, listed in Table III. The fitted parameters clearly indicate the impact of TETA on the degree of crosslinking. That is, N increases and n decreases with TETA content, as expected.

Figures 7 and 8 show the stress-strain curves of bisphenol and TETA-crosslinked PVDF-TFE-P films, respectively, under cyclic deformation to 50% strain. Both figures show that the mechanical properties are improved by increasing the degree of crosslinking. The stiffness of the polymer film increases as the crosslinking increases. As the degree of crosslinking increases, the film rebounds closer to its original length when the stress is removed. However, the TETA-crosslinked films have much better mechanical properties than those of the films crosslinked with the heating recipe. When 5 pph TETA was added, the stress at 50% strain was 0.66 MPa, and the film rebounded to 5% strain when the stress was removed.

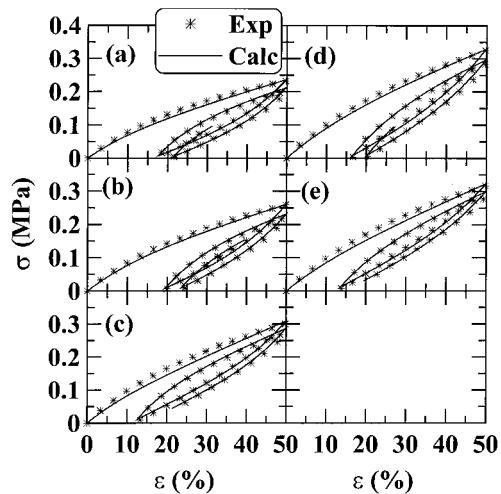


Figure 7 Cyclic stress-strain curves of bisphenol crosslinked PVDF-TFE-P films at 110°C for (a) 0 h; (b) 4 h; (c) 8 h; (d) 16 h; and (e) 24 h. The data are the symbols and the solid lines are calculated stress-strain behavior using the linear model and the parameters in Table IV.

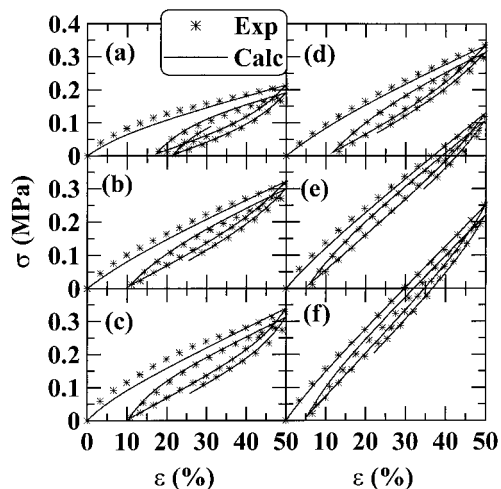


Figure 8 Cyclic stress-strain curves of TETA crosslinked PVDF-TFE-P films with different TETA contents: (a) 0 pph; (b) 1 pph; (c) 2 pph; (d) 3 pph; (e) 4 pph; and (f) 5 pph. The data are the symbols and the solid lines are calculated stress-strain behavior using the linear model and the parameters in Table V.

For the bisphenol-crosslinked sample (heated for 24 h at 110°C), the stress at 50% strain was only about 0.32 MPa and the film rebounded to 12% strain.

To determine the effect of crosslinking, the cyclic deformation curves were fitted with the linear model. The calculated curves are also shown in Figures 7 and 8. Tables IV and V list the best-fit parameters of the linear model and Figure 9 shows how the parameters K_1 and K_{d2} vary with heating time (for the bisphenol crosslinking method) and with TETA content. Crosslinking with TETA at levels of 4 or 5 pph causes a rapid increase in the film stiffness and viscosity, leading to improved mechanical properties.

Exposure of the crosslinked PVDF-TFE-P films to organic solvents used in lithium-ion batteries

Solvents based on linear carbonates (like DEC) and cyclic carbonates (like EC) are commonly used in the electrolytes of lithium-ion batteries.¹⁸ To facilitate the transport of lithium ions through polymer binder

TABLE IV
Best-Fit Parameters of the Linear Model (Fig. 2) to the Stress-Strain Curves of Bisphenol Crosslinked PVDF-TFE-P Films (Fig. 7)

Time (h)	K_1 (MPa)	K_2 (MPa)	K_{d1} (10^2 MPa S ⁻¹)	K_{d2} (10^4 MPa S ⁻¹)
0	0.44	0.42	2.6	0.89
4	0.46	0.46	3.6	0.98
8	0.58	0.47	3.0	1.8
16	0.58	0.41	2.2	1.9
24	0.59	0.39	2.9	2.1

TABLE V
Best-Fit Parameters of the Linear Model (Fig. 2) to the Stress-Strain Curves of TETA Crosslinked PVDF-TFE-P (Fig. 8)

TETA (pph)	K_1 (MPa)	K_2 (MPa)	K_{d1} (10^2 MPa S ⁻¹)	K_{d2} (10^4 MPa S ⁻¹)
0	0.41	0.46	2.1	0.74
1	0.62	0.32	1.9	2.1
2	0.66	0.57	2.0	1.9
3	0.71	0.34	2.8	2.8
4	1.0	0.34	1.5	6.8
5	1.3	0.44	1.5	7.9

films on the surface of electrode particles, it is useful for the binder to uptake some electrolyte, to impart ionic conductivity to the binder layer. On the other hand, excessive electrolyte uptake will degrade the mechanical properties of the binder. Therefore, it is important to be able to control the amount of swelling of the binder in the liquid electrolyte.

The crosslinked polymer samples were immersed in the EC/DEC (1 : 2 by volume) mixed solvent for 24 h, and then the change of weight, which was caused by the uptake of the solvent, was recorded. Figure 10 shows the fractional weight change of the crosslinked PVDF-TFE-P films as a function of the amount of crosslinking. For both sets of polymers, the amount of solvent absorbed decreases with increased crosslinking. The uncrosslinked film absorbs 140% solvent by weight, whereas the film crosslinked with 5 pph TETA absorbs 47% solvent by weight. The amount of solvent absorbed can be controlled by the amount of crosslinking. The polymer films remained elastic after solvent uptake.

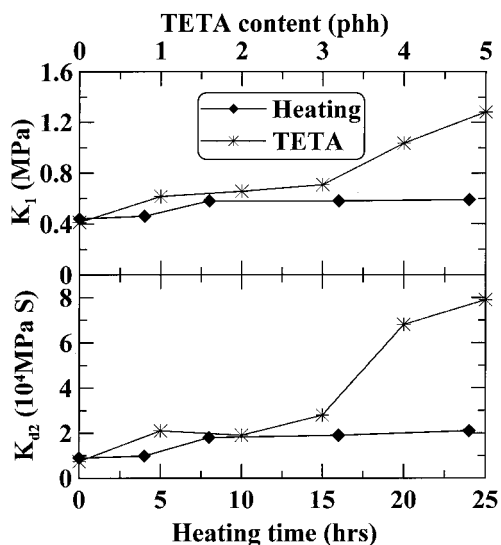


Figure 9 Comparison of the best-fit parameters of the linear model to the data in Figures 7 and 8. (◆) heating recipe; (*) TETA-based recipe.

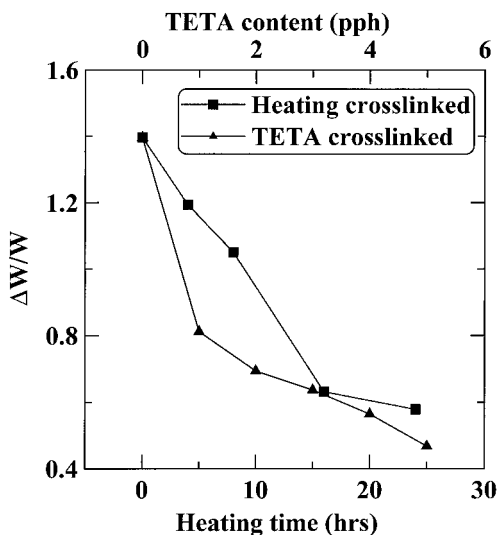


Figure 10 Fractional increase in weight of crosslinked PVDF-TFE-P exposed to EC/DEC solvent for 24 h: (■) heating recipe; (▲) TETA recipe.

Mechanical and electrical properties of crosslinked PVDF-TFE-P/carbon black composites

It is our opinion that the mechanical and electrical properties of electrode films (which contain active solids, carbon black, and polymer binder) under large-strain cyclic deformation must be stable. The mechanical and electrical properties must not degrade with increasing number of deformations for the electrodes to display good capacity retention with charge-discharge cycle number. To gain some appreciation of the effect of solids loading on the mechanical and electrical properties of crosslinked PVDF-TFE-P films, we decided to load the polymer films to the level of 25

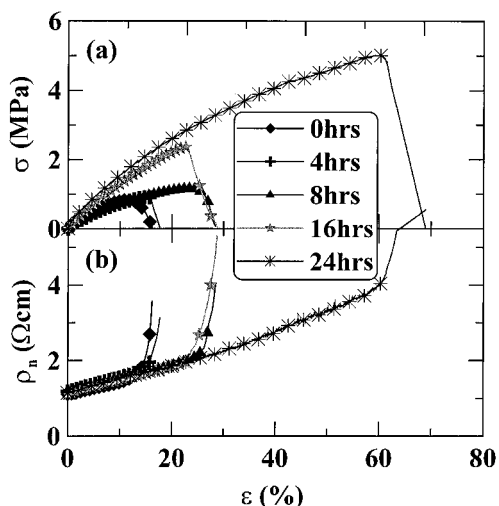


Figure 11 (a) Stress-strain and (b) nominal resistivity-strain curves of the bisphenol crosslinked (110°C, 24 h) carbon-filled PVDF-TFE-P composites (25 pph carbon).

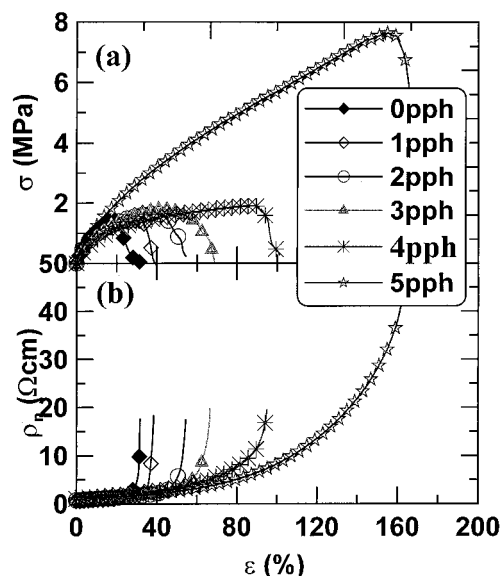


Figure 12 (a) Stress-strain and (b) nominal resistivity-strain curves of the TETA crosslinked carbon-filled PVDF-TFE-P composites (25 pph carbon).

pph with Super-S (SS) carbon black. It is well known that the addition of carbon black will decrease the elasticity of the polymers while improving the electrical conductivity. In this section, SS-filled PVDF-TFE-P films with different amounts of crosslinking and different crosslinking recipes are compared in terms of mechanical and electrical properties.

Figures 11(a) and 12(a) show the stress-strain curves of SS-filled polymer films as a function of the relative amount of crosslinking for films crosslinked by the heating method and the TETA method, respectively. The breaking point of the polymers was se-

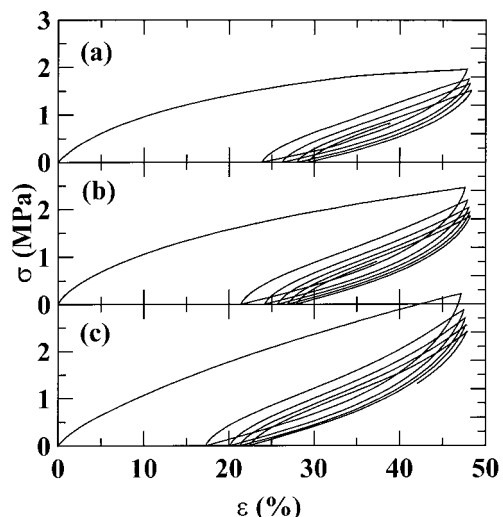


Figure 13 Cyclic stress-strain curves of the TETA crosslinked carbon-filled PVDF-TFE-P composites: (a) 3 pph TETA; (b) 4 pph TETA; and (c) 5 pph TETA.

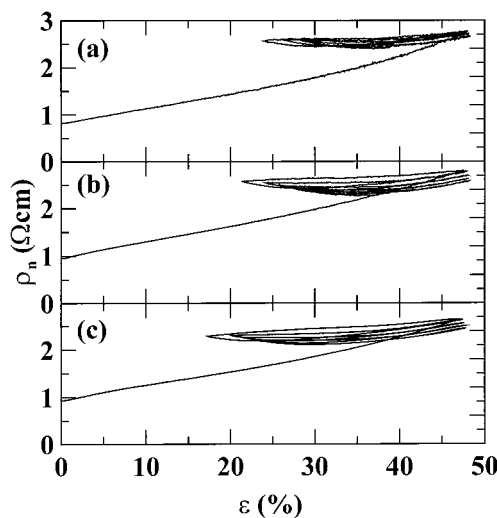


Figure 14 Cyclic nominal resistivity-strain curves of the TETA crosslinked carbon-filled PVDF-TFE-P composites: (a) 3 pph TETA; (b) 4 pph TETA; and (c) 5 pph TETA.

verely degraded by the addition of SS. The film crosslinked with bisphenol (110°C for 24 h) can be strained to only 60% before breaking, and the film crosslinked with 4 pph TETA can be extended by 100%. The maximum elongation of the film with 5 pph TETA is about 160%. In both figures, the improvement of mechanical properties with crosslinking is clear. The maximum elongation before break increases with the amount of crosslinking, and the TETA crosslinking method apparently gives a higher degree of crosslinking than the bisphenol crosslinking method.

Figures 11(b) and 12(b) show the nominal resistivity-strain curves of SS-filled films as a function of the relative amount of crosslinking. The nominal resistivity is defined as the film resistance times the original cross-sectional area of the unstretched film divided by the length of film between the measurement points. The nominal resistivity ρ_n increases with strain for both crosslinking methods. However, the nominal resistivity-strain curves for polymer/carbon films with different amounts of crosslinking degree almost overlap. No significant impact of crosslinking on the resistivity was found.

Figure 13 shows the cyclic stress-strain curves of carbon-filled polymer films crosslinked with TETA. Only samples containing more than 3 pph TETA can be stretched to 50% strain without breaking and only results for these samples are shown. As the TETA content increases, the maximum stress increases and the film rebounds closer to its original length when the stress is removed. However, no striking improvement of mechanical properties with TETA content can be seen. Figure 14 shows the nominal resistivity-strain curves measured for the same films during the deformations shown in Figure 13. No obvious difference can be seen in the

resistivity-strain behavior as a function of TETA content. The nominal resistivity rises from about 1 Ω cm and is stable at about 2.5 Ω cm during cyclic deformation. The addition of TETA improves the mechanical properties of the carbon/PVDF-TFE-P system, whereas the electrical properties are basically unaffected by the addition of the crosslinks.

CONCLUSIONS

The mechanical properties of poly(vinylidene fluoride-tetrafluoroethylene-propylene) (PVDF-TFE-P) were evaluated as a function of the degree of crosslinking. Both bisphenol and triethylenetetramine (TETA) were used as crosslinkers to improve the mechanical properties of PVDF-TFE-P and carbon black-filled PVDF-TFE-P. Bisphenol was incorporated into the polymer by the manufacturer and crosslinking was achieved through additions of MgO and CaO followed by heating.

Although bisphenol crosslinking improves the mechanical properties, further crosslinking using the TETA recipe was needed to obtain good extensibility under repeated deformation of carbon black/PVDF-TFE-P composites.

The addition of crosslinks was shown to have little or no effect on electrical properties of carbon black-filled PVDF-TFE-P films. Therefore, we believe that electrical properties of a particular electrode formulation using the TETA recipe will remain unaffected, whereas the mechanical properties are tuned by changing the amount of crosslinking. Furthermore, the crosslinked polymer does not become brittle in typical solvents used in lithium battery electrolytes, so we believe that this highly extensible binder system may be useful for electrode materials that show large volume changes during charge-discharge cycling.

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