

PVDF/CB Composites Prepared by Novel Solvent Casting Method for Low Voltage PTC Temperature Regulation Applications

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ABSTRACT: A novel solvent casting preparation technique utilizing three variants of poly(vinylidene fluoride) (PVDF) to achieve a thermal cut off and a self regulation effect at a low applied voltage is reported in this study. The positive temperature coefficient (PTC) composites were prepared by dissolving PVDF in 1-methyl-2-pyrrolidone (NMP) solvent, blending with Vulcan[®] XC72 carbon black (CB) filler, crosslinking with vinyl trimethoxysilane (VTMOS) and quenching in water. All composites displayed a highly macrovoidal structure that promoted a PTC effect when subjected to a thermal expansion effect via an electrical current. Subsequently

the current was cut off and self regulation behavior was exhibited. Kynar[®] 761A PVDF resulted in the strongest PTC effect, and displayed temperature regulation at around 100°C which may be attributed to the highly semi crystalline nature and the larger molecular weight of this polymer in comparison with the other PVDF composites studied. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3673–3678, 2011

Key words: positive temperature coefficient; poly(vinylidene fluoride); composites; crosslinking; thermal properties

INTRODUCTION

Polymers can be combined with a conducting filler to create composites that retain the expansive properties of the polymer while enabling the flow of electricity. Poly(vinylidene fluoride) (PVDF) is a lightweight polymer that possesses easy conformability, flexibility, and robustness with remarkable piezoelectric properties¹ and a higher operating temperature than high density polyethylene.² PVDF is used in the wire and cable industry as a secondary insulator due to its high fire resistance and low smoke emission characteristics,³ but has only been partially investigated as a conductive polymer composite with a positive temperature coefficient (PTC) effect.^{4,5}

Previous studies into the PTC effect of PVDF have shown the dependence of crystallization history,⁶ powdered carbon black (CB) concentration,⁷ composite morphology,⁸ and CB diffusion and agglomeration⁹ on PTC intensity. Most recently carbon nanotubes have been used as conductive filler for polymers yielding positive results.^{10–12} However these investigations along with the majority of others involve high temperature polymer/CB dry melt mixing. This study differs because the PVDF is dissolved in a solvent to form a

highly viscous liquid polymer dope before CB is added. Once the PVDF/CB blend becomes homogeneous it is crosslinked (XL), casted, and quenched. This novel technique has resulted in different expansive and conductive behavior of the composite due to the formation of an altered semi crystalline polymer structure.

It is known that the addition of a crosslinking agent such as silane or peroxide causes the elimination of the negative temperature coefficient (NTC) effect present in semi crystalline polymers lined with CB.^{13,14} When combined with heat treatment a PTC effect is encouraged, leading to the inversion of the temperature/resistance relationship. The PTC effect occurs due to the thermal expansion of the polymer arising from the melting of crystalline regions within the polymer structure. Polymer expansion leads to a greater separation of CB particles within the composite structure, leading to an increase in resistance.¹⁵ A high resistance causes the flow of current to stop, initiating a self regulation effect that prohibits temperature increases above the cut off point.

Some more commonly used air filtration devices such as packed beds or adsorbent granules need to undergo heat regeneration once exhausted to be reused. Currently this can be achieved by heating metal plates located within these beds or passing heated air through the bed. During such an operation the process vessels, piping, and other ancillary equipment also get heated while the adsorbent bed

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TABLE I
Composition of Composite Before Quenching

Chemical	Weight (%)
PVDF 760/761/761A	18.02
NMP	72.07
CB	5.40
Dibutyltin dilaurate	0.01
VTMOS	4.50

reaches the correct regeneration temperature. An alternative method offered by utilizing the technique proposed in this article is to use structured adsorbent materials covered in a 1- to 2-mm coating of the PVDF/CB composite. As electricity is directly applied to this conductive coating and the coating itself is so thin, the heat would transfer into the adsorbent material leading to regeneration at a faster rate with less energy wasted. The cut off property arising from thermal expansion of the PVDF also reduces energy as no more energy than is required to expand the polymer is used before cutting out.

The objective of this article is to demonstrate that XL PVDF/CB solution can successfully be cast into a form that is mechanically stable, able to conduct electricity, and can initiate a thermal cut off in low voltage scenarios. In this study the composites will be analyzed to determine the extent of reproducibility of the thermal cut off temperature and subsequent stabilization of the PTC effect using this novel technique.

EXPERIMENTAL

Materials

Three varieties of PVDF supplied by Arkema: "Kynar[®] 760" ($M_W = 440,000$), "Kynar[®] 761" ($M_W = 370,000$), and "Kynar[®] 761A" ($M_W = 625,000$) were used. Additional physical and chemical properties of each polymer are available from the manufacturer.¹⁶ The 1-methyl-2-pyrrolidone (NMP) solvent and dibutyltin dilaurate crosslinking catalyst are provided by Sigma Aldrich; the conductive filler is Vulcan[®] XC72 carbon black manufactured by Cabot, and the crosslinking agent is vinyl trimethoxysilane (VTMOS) provided by Acros Organics.

Formation of crosslinked PVDF/CB composite

Polymer dopes were made using 20 wt % polymer in NMP solution and placed in a Grant 200 orbital linear shaking bath providing 40 linear shakes per minute at 50°C. The sample was subjected to periodic stirring on a roller mixer until the mixture was fully homogeneous. CB was added slowly during agitation by a rotary impeller to ensure an even distribution throughout the polymer solution. The sam-

ple was stirred at 200 RPM for 2 h and placed on rollers for at least 12 h afterward. Protective masks, goggles, and gloves were worn as advised by the material manufacturers.

In a method adapted from Barzin et al.¹⁷ polymer crosslinking was achieved by first adding dibutyltin dilaurate crosslinking catalyst to the dope and rolling for 12 h. The dope was placed on a hot plate at 120°C. VTMOS was then added and was stirred for an hour. This procedure was conducted within a fume cupboard at all times. The general composition of each of the XL PVDF/CB dopes is shown in Table I.

To achieve phase inversion the sample was casted onto a flat glass sheet, quenched in water at a temperature of 20°C for 24 h, and then at 50°C for a further 24 h. The water was changed every 3 h to facilitate NMP removal from the composite by diffusion. An internal porous structure was created due to the intermixing between water and NMP.¹⁸

When dry, the sample was heated for 30 min at 190°C. This temperature and duration was chosen because it was the most effective at removing the NTC effect and promoting the PTC effect by heat treatment as seen in Figure 1.

Initiation of thermal cut off

A rectangular piece of the composite with dimensions $4.0 \times 1.5 \times 0.3 \text{ cm}^3$ was cut and each end was coated in silver conducting solution to aid connection. It was attached to a circuit comprising of a power supply unit (Manson EP-603), a programmable power meter (Hameg HM8115-2), a thermistor, and a computer to log data. The thermistor was attached to the surface of the sample in the center

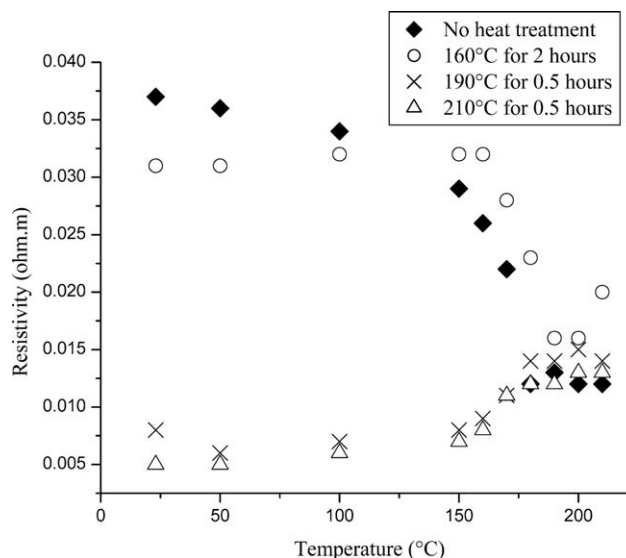


Figure 1 Effect of heat treatment on PTC properties of PVDF/CB composite.

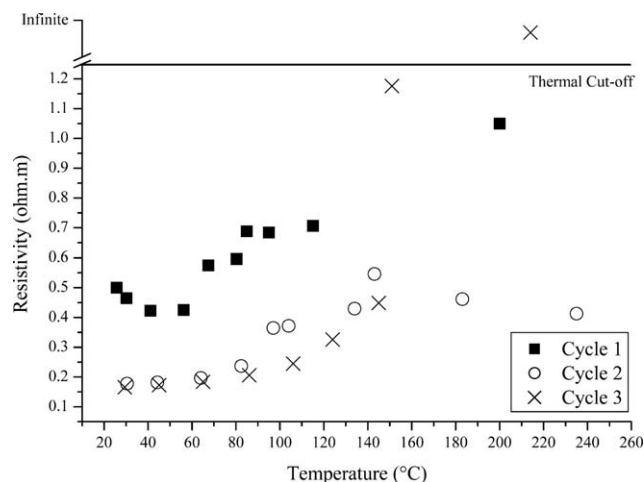


Figure 2 PTC curves of XL-PVDF 760/CB.

and the sample was housed in a small insulating enclosure to reduce the effect of heat loss. A voltage was applied to the sample to initiate a temperature increase from ambient conditions. After allowing time for resistance and temperature readings to reach steady state the voltage was increased within the range of 0–30 V until such temperature that a thermal cut off was observed. Resistance was measured as a function of temperature for each voltage applied.

SEM preparation

Samples of each composite were mounted on a sample tray using double sided adhesive carbon disks and were subjected to gold sputtering using an Edwards S150B Sputter Coater to aid in visualization. Samples were then placed in a Jeol 6310 SEM at a working distance of 12–14 mm and an accelerating voltage of 15–30 kV.

RESULTS AND DISCUSSION

XL-Kynar 760/CB composite (1)

Figure 2 shows how the resistivity of Composite 1 changes with temperature brought about by successive voltage increases over a number of heating and cooling cycles. The first cycle shows a steadily increasing PTC effect with fluctuations in resistance occurring at 200°C when 30 V was applied before settling. Further voltage increases were not investigated as these were deemed to be too high for low energy applications, and as such no thermal cut off was observed. The fluctuations arise from the redistribution of the PVDF in the composite structure at higher temperatures affecting the conducting CB pathways; the sample is close to achieving thermal cut off but the temperature is not enough to expand the polymer to the cut off point. Cycle 2 displays a

PTC effect followed by an NTC effect, reaching a maximum temperature of 235°C at 30 V and showing fluctuations of a higher magnitude than those shown in the first cycle before settling, however no temperature cut off occurred. Cycle 3 demonstrates a much smoother plot with fluctuations starting at 145°C. Fluctuations in resistance occurred at 21 and 24 V, over an increasing range as temperature increased before settling. At 27 V temperature cut off occurred at 210°C, dropping the temperature of the composite to 130°C due to the halting of conduction. After this the temperature increased to 210°C displaying a self regulation effect.

After the initial two cycles, the final cycle does not display any NTC effects before or after the PTC effect. This indicates that this composite is prone to the annealing effect where the structure of the sample alters such that it becomes predisposed to thermal expansion, allowing it to occur more readily with consecutive heating and cooling cycles. This is shown in Figure 2 as a reduction in resistivity. A temperature cut off is encouraged to occur sooner with each succeeding cycle and the PTC curve becomes smoother, perhaps due to the annealing effect. The increasing magnitude of the resistance fluctuations at 21 V up to the thermal cut off voltage of 27 V shows how the thermal expansion effect distorts the conducting CB pathways until the composite structure reaches stability, allowing a steady reading to be taken. Cycle 2 and 3 show a similar PTC curve before they deviate, indicating that the composite structure is beginning to reach a stable distribution.

XL-Kynar 761/CB composite (2)

The trends displayed in Figure 3 are very similar to those shown in Figure 2. Cycle 1 shows a small initial NTC effect, followed by a PTC effect of low

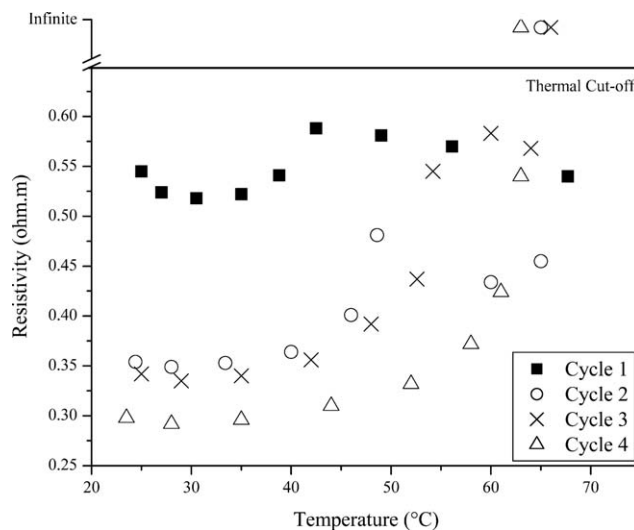


Figure 3 PTC curves of XL-PVDF 761/CB.

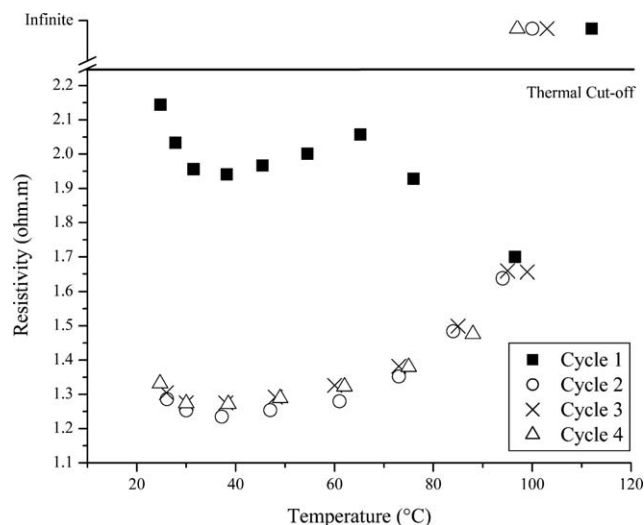


Figure 4 PTC curves of XL-PVDF 761A/CB.

intensity, ending with another NTC effect. Fluctuations in resistance occur at a temperature of 70°C when 30 V is applied, but no cut off is observed. Cycle 2 showed a relatively uniform PTC effect except for a single anomaly. Cut off was achieved at 65°C when 27 V is applied, a lower voltage but a similar temperature to that in the first cycle. The third cycle displays an initial resistivity similar to that of the second cycle, however in this case the PTC effect increases in magnitude cutting off at 66°C and 26 V. Cycle 4 shows a slowly increasing PTC effect with temperature cut off at 63°C when 24 V is applied.

Composite 2 shows an increase in susceptibility to thermal cut off at lower voltages after multiple heating and cooling cycles. The cut off temperature remains fairly constant at around 60–70°C implying that CB redistribution within the sample structure is occurring that allows for improved conduction with each subsequent cycle, but does not alter the thermal expansion effect of the polymer. Resistivity is decreasing with each cycle, indicating that cut off could be encouraged at lower voltages if more cycles were completed. All four cycles show dissimilar PTC curves, so direct comparison to determine trends is unfeasible until more cycles are done. Cycle 4 in Figure 3 clearly shows a smooth trend with a sharp cut off point as expected from a PTC effect. Thermal cut off occurred at a lower voltage than in previous cycles and the NTC effect is completely eliminated indicating that the composite structure has stabilized.

XL-Kynar 761A/CB composite (3)

Figure 4 shows that the first heating and cooling cycle follows the same trend as each of the first cycles of the PVDF 760/761 composites, but the PTC effect is of a lower magnitude. Despite this, the composite managed to reach a cut off temperature of

112°C on its first cycle, when 30 V was applied. The second, third, and fourth cycles follow the exact same trend, with resistivity lowered to a minimum value after only the first cycle and cut off voltages decreasing sequentially to 27, 26, and 24 V.

The cut off voltage decreases with each cycle, not showing signs of stabilization. Temperature cut off has already stabilized, cutting off at 100, 103, and 97°C for Cycles 2, 3, and 4, respectively. The similar trends of Cycles 2–4 in this composite and the minor differences in conducting ability indicate that the stabilization effect has occurred after only the first heating and cooling cycle. These results are similar to those achieved by Mironi-Harpaz and Narkis⁷ who utilized the dry melt mixing technique.

SEM analysis

Figure 5 shows a small area of the composite structure. It can be seen in Figure 5(a) that a concentrated layer of PVDF has formed on the outside of the sample after undergoing the phase inversion process. This is also evidenced by the smoothness of the PVDF/CB composite samples. Figure 5(b) shows an

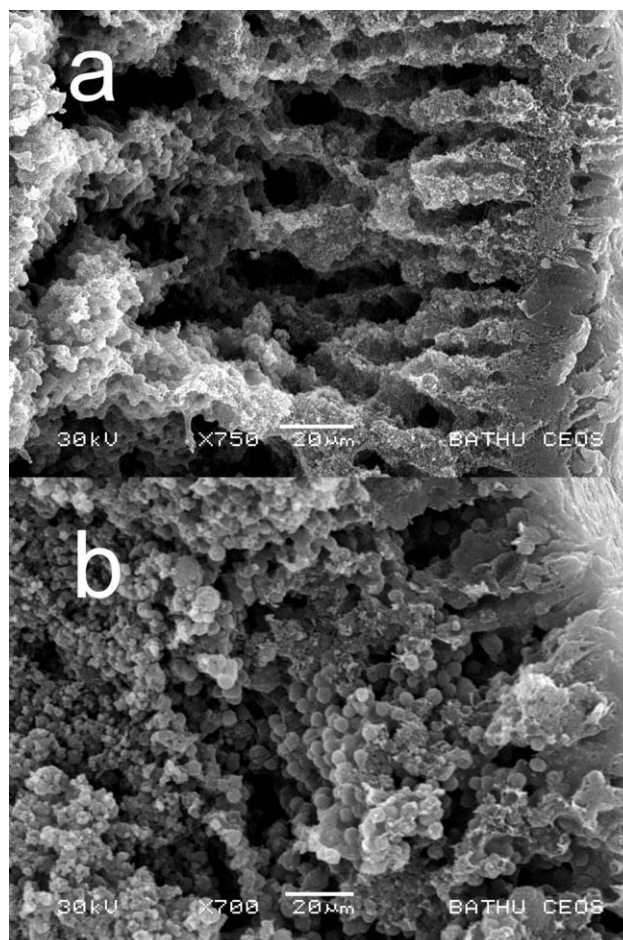


Figure 5 SEM photographs of XL PVDF/CB composite (a) before and (b) after thermal cycling tests.

image of the composite after undergoing several heating and cooling cycles with the agglomerated carbon particles clearly visible. It can be seen that the layer of PVDF has decreased in size due to its redistribution within the composite structure. This has aided the stabilization of the cut off temperature with successive cycles.

Figure 6(a) shows that the PVDF and CB in Composite 1 have mixed well. PVDF is distributed throughout the carbon black, creating denser and more porous areas. It is clear within Composite 2 [Fig. 6(b)] that the PVDF and CB are well mixed and macrovoids are present. These are formed because of the increased polymerization time due to NMP accumulation during the phase inversion process. As the SEM images for Composite 1 and 2 are so similar it can be concluded that the appearance of the composite structure is independent of the PTC effect and cut off temperature and could perhaps be attributed to the similar molecular weights of the PVDF molecules. The structure of Composite 3 [Fig. 6(c)] shows the carbon agglomerates fused together with PVDF, indicating that the polymer matrix throughout the sample is vast and well distributed, leading to the more stable PTC effect.

Figure 6(d) shows a highly macrovoidal structure formed during the novel casting, quenching, and coagulation process. This aids the thermal cut off because the NMP/water demixing during polymer coagulation leads to fewer CB linkages per any given cross-sectional area. As a result the magnitude of the thermal expansion effect can remain low to initiate a cut off, requiring lower applied voltages. The voids and the PVDF/CB are well distributed, helping to achieve polymer expansion and hence cut off throughout the composite. The CB agglomerates aid in conduction which facilitates the sharp PTC effect.

Comparison between composites

For each composite there is a large difference in the resistivity between the first and second cycles. The general trend of all three samples on their initial heating cycle is that the thermal cut off would occur after the peak of a PTC effect during an NTC effect. This was described as a "double" PTC effect by Feng and Chan¹⁹ because the resistance peaks twice. The double PTC effect usually arises in binary mixtures of polymers with different melting points; however as there is only one polymer in each sample it could be theorized that not all of the PVDF in the sample has become cross-linked, meaning that some parts of the sample would be stronger than others and would be more resistant to thermal expansion. With further heating cycles yielding thermal cut off during the first PTC effect, it would seem that either the crosslinked polymer decreases in strength, or the noncrosslinked polymer increases in strength over several cycles. This would allow thermal

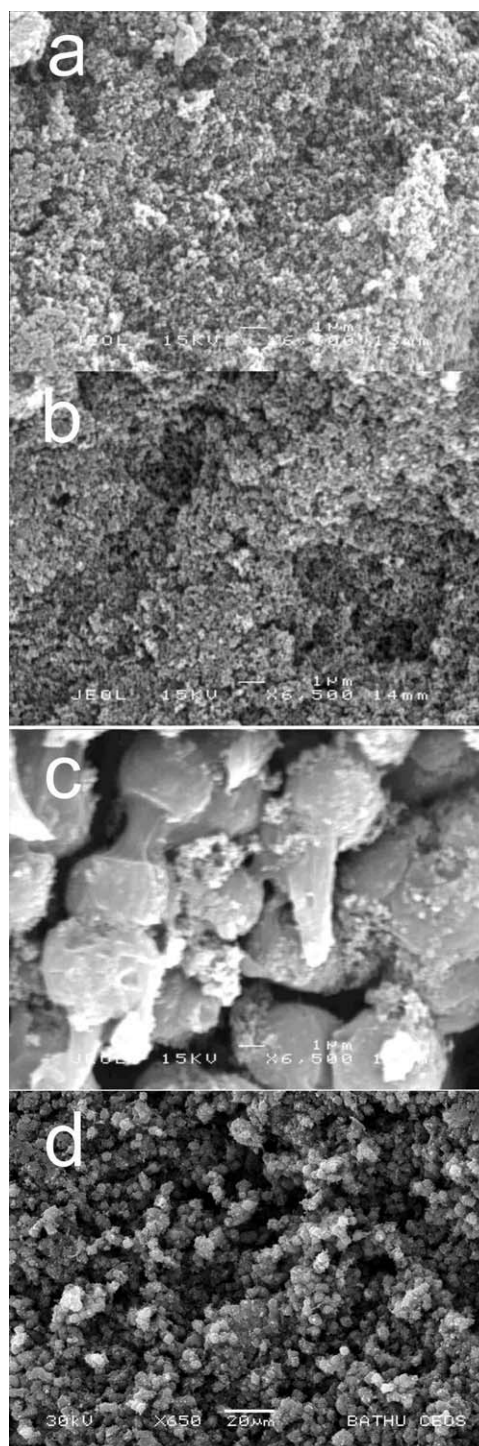


Figure 6 SEM photographs after final cycle. (a) XL-PVDF 760/CB, (b) XL-PVDF 761/CB, (c) XL-PVDF 761A/CB, (d) XL-PVDF/CB agglomeration within polymer structure.

expansion of the all the PVDF distributed in the sample to occur at the same temperature.

CONCLUSIONS

This study has shown that it is possible to utilize a solvent casting technique to create a composite that

can display a PTC effect with thermal cut off and self regulation at a low voltage. This effect was achieved in all three composites studied.

Kynar[®] 760 composite cut off at temperatures over 200°C and showed a decrease in the voltage required to induce cut off with subsequent cycles. Kynar[®] 761 composite cut off at around 65°C after the initial cycle, offering increased consistency over the Kynar[®] 760. The PTC curves do not provide conclusive evidence of a stabilization effect, however cut off voltage does decrease with ongoing cycling. Kynar[®] 761A composite showed a thermal cut off at around 100°C after the initial cycle, again showing consistency. The PTC curve had stabilized after only one cycle and cut off voltage continued to decrease from 30 to 24 V over four cycles.

This novel technique allows the formation of polymer/CB composites without the need for expensive equipment running at higher operating costs, and could be applied for a wide range of semi crystalline polymers. The evidence of fast stability, repeatability, and lowering voltage with Kynar[®] 761A indicate that this composite has the most potential for future research. Its composition could be altered to customize the cut off temperature, allowing its use in a wide range of process applications.

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