PVDF:PMMA Shape Memory Blends: Effect of Short Carbon Fiber Addition

Cheryl J. Campo and Patrick T. Mather

Case Western Reserve University, Macromolecular Science and Engineering Department, Cleveland, OH 44106

INTRODUCTION

Although shape memory (SM) in polymers has been observed in such diverse systems as chemically crosslinked thermosets and liquid crystalline elastomers, an industrially relevant approach to preparing materials that exhibit this behavior is to blend commercially available semicrystalline and amorphous polymers together in order to exploit both the physical crosslinking of the former and the temporary shape fixing capability due, in part, to the latter. As polymers are characterized by relatively slow heat transfer, meeting requirements for fast actuation necessitated by certain applications is a remaining challenge, particularly for shape memory blends. The inherently good thermal conductivity of carbon black, such as that of boron nitride, has previously been investigated for use in polymeric systems. Carbon black (CB) as well as short carbon fiber (SCF), both known to have good thermal conductivity, have also been used to fill polymer matrices, but mainly in order to investigate their effect on such properties as electrical conductivity. A goal of the work described herein is to enhance the demonstrated shape memory behavior of melt-miscible poly(vinylidene fluoride):poly(methyl methacrylate) (PVDF:PMMA) blends. This system is of particular interest because, depending on the processing protocol used, the blend transition temperature can be tailored in the vicinity of biologically relevant temperatures (i.e., 37°C < Tg < 60°C). This, in addition to the established biocompatibility of the two components, presents the possibility of the potential use of these blends for shape memory biomaterials. Notwithstanding the shape memory character exhibited by this blend, actuation has been determined to be somewhat sluggish. In order to optimize the shape memory properties, then, not only should the effect that addition of a thermally conducting filler has on heat transfer be studied, but even more fundamentally, so too should the filler’s effect on both the crystalline and amorphous phases since the nature of these two greatly influences SM behavior. In addition to its inherently good thermal conductivity, SCF is an ideal filler to consider for use in polymer blends since carbon, in general, has exhibited the added benefit of imparting enhanced biocompatibility to devices made of synthetic materials.

To test the hypothesis that SCF filler would act to improve the shape memory behavior of semicrystalline-amorphous PVDF:PMMA blends, different composites having a range of filler loadings were prepared and subsequent evaluation of the resulting materials was carried out via thermal characterization, thermomechanical testing, and SM cycling.

EXPERIMENTAL

Materials. PVDF, PMMA, and ThermalGraph® DKDx carbon fiber (Cytec) were obtained from commercial sources and used as received. The ThermalGraph fibers are characterized by an average filament width of 200 µm and a filament length of 10 mm.

Sample Preparation. A DACA microcompounder was used to melt blend and extrude strands of filled and unfilled PVDF:PMMA. For the unfilled 50:50 PVDF:PMMA, equal amounts of the two polymers were dry blended together then mixed in the DACA. Filled blends of 1, 3, 5, 15, 30, and 45 wt % short carbon fiber (SCF) loading levels were also prepared. Appropriate amounts of the three components were dry blended then melt mixed in the microcompounder for the 5, 15, 30, and 45 wt % SCF blends, while the 1 and 3 wt % SCF filled blends were prepared by melt blending cut up strand of a 50:50:5 PVDF:PMMA:SCF master batch with the same of 50:50 PVDF:PMMA. All blends were compounded at 200°C for 2.5 minutes and at 100 rpm. Following mixing in the DACA, extruded strand was cut up and made into films using a Carver press preheated to 200°C. A 0.5 mm spacer was used and 6 metric tons of pressure was applied. The films were kept at 200°C for 5 minutes, removed from the press and quenched to RT between water cooled plates. They were then put back into the press, the latter this time preheated to 70°C. The films were partially crystallized at 70°C for 30 min before being removed and quenched once again between water cooled plates.

Thermal Characterization. Differential Scanning Calorimetry (DSC) was used to determine the thermal transitions characteristic of the filled and unfilled 50:50 PVDF:PMMA blends. Experiments were performed with a TA Q100 DSC using a heating rate of 10°C/min and nitrogen as the purge gas.

Thermomechanical Testing. Thermomechanical properties of filled and unfilled 50:50 PVDF:PMMA annealed films were characterized using a Perkin Elmer Dynamic Mechanical Analyzer (DMA 7e) equipped with a tensile fixture. A frequency of 1 Hz and a heating rate of 2°C/min were used.

SM Cycling. The SM behavior of these filled and unfilled 50:50 PVDF:PMMA blends was investigated through the use of multiple cycles of shape fixing and recovery. Specimens approximately 2.5 x 0.5 mm² in cross-section were clamped to lengths of either 0.5 or 1 cm and stretched to approximately 75% strain in a 60°C water bath over a period of 30 sec after a 30 sec heating period. The samples, still subject to the applied force, were then transferred to an ice water bath and cooled for approximately 1.5 min. After, the test specimens were removed from the stretching device, recovered in a 60°C water bath, and the end length recorded. This cycle was repeated 4 more times for each sample.

RESULTS AND DISCUSSION

With increasing SCF content, the appearance of the extruded strand/annealed films became more black and opaque to the unaided eye. All blends up to and including the 45 wt % SCF 50:50 PVDF:PMMA could be visualized using optical microscopy (OM). Dispersion of the filler was observed to be homogenous with no apparent aggregation.

From the first heat curves post anneal shown in Figure 1, an increase in both Tg and crystallinity as indicated by the decrease in the recrystallization ΔH is observed. These results suggest that the filler either induces or nucleates crystallization with increasing loading levels and also improve heat treatment for 30 min at 70°C. Using polarized optical microscopy (POM), nucleation of crystallization at the surface of the filler was disproved given that the overall sample (excluding the space occupied by the SCF itself and as opposed to just the areas immediate to the filler) brightened over time when crystallized isothermally. The SCF, then, is believed to effectively draw PVDF out of the mixed amorphous phase (perhaps via the attractive adsorption), thereby enabling a higher degree of crystallinity to be obtained. This is in agreement with previous findings regarding carbon black-loaded PVDF:PMMA blends.
In general, the DMA curves corroborate the DSC results suggesting SCF’s ability to draw PVDF out of the mixed amorphous phase. From both the storage and loss modulus curves, a changing physical state is suggested by the decrease then increase in rubbery modulus once the glass transition temperature range is crossed. This is observed, in particular, for the lower content SCF filled blends, namely 0 – 15 wt % (although less of this phenomenon is observed for the 15 wt % blend, a rubbery modulus dip seen only in the storage modulus curve). This changing rubbery modulus is indicative of a non-equilibrated crystallization state, with recrystallization occurring once the chains are mobile above Tg thereby leading to a higher rubbery modulus after some time. For the 15, 30, and 45 wt % filled blends, not only is a general increase in rubbery modulus (with minimal if nonexistent decreasing/increasing behavior) observed, so, too, is an increase in Tg, the opposite being true for the lower carbon fiber content blends. Because of the increasing glass transition temperature at high SCF loading, it is believed that the short carbon fibers have an affinity for PVDF, pulling it out of the two-component amorphous phase, allowing the latter to be more PMMA-rich, hence the higher Tg. The increase in rubbery modulus, then, may also be attributable to an increase in effective (physical) crosslinking as one hypothesis might be that more crystallites are able to form as PVDF is drawn out of the amorphous phase. As for the trend in modulus/Tg of the lower carbon fiber content blends, interestingly, a decrease in both properties is observed upon initial loading at low levels (values for the 1, 3, and 5 wt % blends being lower/equal to that of the 0 wt % blend). Thus, at low CF loading, the contribution of the filler seems to be one of increased dissolutilon of amorphous PVDF in PMMA.

As for the SM cycling, the addition of SCF filler appears to enhance shape recovery up to 5 wt % loading after which recovery decreases as illustrated in Figure 3. (The 30 and 45 wt % CF containing blends were too brittle and broke on stretching.) These results suggest that the presence of the filler leads to the formation of “harder” crystals (physical crosslinks) enabling better memorization of the equilibrium shape. Cyclic deformation of the blends yields an increase then decrease in recovery with a maximum value consistently observed on the third stretching signifying either a need for material conditioning to achieve optimized shape memory or, more intriguing, strain induced crystallization yielding additional network points in the thermoplastic elastomer thereby improving shape recovery.

**References**

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