

Strain modulation of crystallinity, orientation and piezoelectric properties of poly-(vinylidene fluoride):poly(methyl methacrylate) blends

Wrocław University of Science and Technology

7-7.5 min



<u>Michał Wyskiel</u>¹, Kamal K. Meena², Krzysztof Janus¹, Konrad Schneider², Adam Kiersnowski¹

(1) Molecular & Macromolecular Electronic Materials Group at Department of Physical and Quantum Chemistry Wroclaw University of Science & Technology Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland

(2) The Leibniz Institute of Polymer Research, Hohe Str. 6, 01069 Dresden

Preparation of the blends and specimens



🖲 5 min 📕 50 MPa T

🕑 1 min 👢 10 MPa 🖣

Motivation

Technologically-relevant semicrystalline, electroactive polymers such as poly(vinylidene fluoride) (PVDF) have attracted a lot of attention because of their potential applications in sensors and energy harvesting units. PVDF can exhibit piezo-, pyro- and ferroelectricity due to the relatively high dipole moment of vinylidene fluoride monomer units incorporated in the PVDF main chain. The electric properties of PVDF depend on phase composition. There are several technologically-proven strategies to render PVDF piezoelectric. One of the strategies is based on blending of PVDF with poly(methyl methacrylate) (PMMA). Imparting piezoelectricity to PVDF uniaxially, homogeneously requires and permanently oriented dipole moments of CH₂-CF₂ monomer units in polar crystal polymorphs. Well

α-phase
β-phase
γ-phase
γ-phase
Figure 1. PVDF α, β and γ phases chains conformation

- fluorine 🔵 - hydrogen

- carbon 🌑

known method to enhance orientation and improve polar phases of PVDF is streaching. Mechanical treatment in the solid state causes PVDF to recrystallize and force crystals to orient along the deformation axis. However, the mechanism of formation of polar crystals and recrystallization of non-polar polymorphs raise controversies especially for blends.



Our study was aimed, therefore, at explaining the role of PMMA on formation of polar polymorphs of PVDF, i.e. the β and γ crystal phases. Our experiments were also supposed to shed light on mechanism of transforming of the isotropic non-

II. cooling rate 0.9-1.0 °C/min 220°C 25°C Figure 2. Skeletal formula of PVDF a) polar PVDF polymorph (the α -phase) into oriented polar crystals during deformation blends in a viscoelastic state.

Wide-Angle X-ray Diffraction (WAXD)

In situ WAXD measurements were performed at the MiNaXS Beamline (P03) at Deutsches Elektronen Synchrotron (DESY), in Hamburg, Germany WAXD 1D patterns made during the stretching were collected in false-colors maps WAXD intensity vs. sattering vector, figure (5 and 6). The black, vertical lines in these plots indicate the point where the 120/021/111 peak group visible at q~18.7 nm-1 of the α-phase merges into the background.



In the same scale of Hancky Strain is also shown Hermans orientation factor f_H (white line), scalar value giving a simple assessment of crystal orientation in a polimer. Briefly, the meaning of the f_H is following: when the chains reveal no preferential alignment the $f_H = 0$. The $f_H = 1$ is when the chains are perfectly aligned along the stretching angle. Based on the WAXD data, the contents of α , β and γ phases were determined figure (7 and 8).

For figure 5-11 the following label was adopted: a) PVDF b) PVDF/PMMA80/20,c) PVDF/PMMA70/30 and d) PVDF/PMMA60/40.



FTIR spectroscopy

Ex-situ Fourier transform infrared spectroscopy (FTIR) was used to refine the conclusions from WAXD. The FT-IR spectra are shown in the figure (10 and 11) and corresponding vibration bands are labelled as per the presence of crystalline phases. FTIR spectra sign by: **light blue - 1, green - 2, orange – 3**, correspond to the regions of symmetric increasing stress shown on the figure 7. Reference spectra was done for each sample before stretching (black plots).



Figure 9. Simulation illustrating stress distribution in specimen during deforma-tion. Marked by 1,2,3 regions correspond to increasing stress from edges to centre.





Figure 5. WAXD intensity (false-color maps, vs. scattering vector, q) and Herman's orientation factor (f_{H_1} , white lines) vs. Hencky strain (ϵ_{H}) for **quenched** samples.





Figure 8. Crystal phase (X) content vs. Hencky strain ($\epsilon_{\rm H}$) for slowly cooled samples.

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Results and observations

- The cooling history and blend ratio had strong influence at initial (mechanical tretment) crystal phase content
- Increasing PMMA causes decreasing crystallinity and decline pronounced yield point
- Uniaxial stretching couses the transformation from α non-polar phase to β + γ phase
- Amorphous phase content during stretching remained approximately unchanged
- Amount of B-phase is closely correlated with the orientation of the sample
- Results of infrared spectroscopy indicate that higher amount of PMMA (more than 20 wt.%) in blends favours more α to γ than α to β phase transition
- The collected data indicate that the crystallinity in the initial state is an important factor influencing the effective non-polar to polar phase transition during stretching