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Evolution of crystalline phases of P(VDF-TeFE) films filled with nanographite in various aprotic solvents

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Abstract. The work under discussion describes the preparation and study copoly(vinylidene fluoride–tetrafluoroethylene) (P(VDF–TFE)) films filled with chemically exfoliated nanographite and crystallized by drying from various solvents. The content of α, β and γ phases of PVDF was estimated via Fourier transform infrared spectroscopy (FTIR) and supported by Raman spectroscopy and X-ray diffractometry. Experimental study revealed that films made from a solution of dimethyl sulfoxide (DMSO) have a higher content of the polar β-phase and films filled with nanographite showed increased degree of of β-phase content.

Keywords: poly(vinylidenefluoride–tetrafluoroethylene P(VDF-TeFE), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), beta phase, FTIR, XRD, nanographite

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Материалы конференции
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Эволюция кристаллических фаз в пленках сополимера поливинилиденфторида и тетрафторэтилена П(ВДФ-ТФЭ), наполненных нанографитом, в различных апротонных растворителях

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Аннотация. Представленная работа описывает получение и исследование пленок сополимера поли (винилиденфторида–тетрафторэтилена) (П(ВДФ–ТФЭ)), заполненных электро-химически эксфолированным нанографитом и кристаллизованных из различных растворителей. Содержание α, β и γ-фаз в ПВДФ было оценено с помощью инфракрасной спектроскопии с преобразованием Фурье (ИКФС) и подтверждено методами рамановской спектроскопии и рентгеновской дифрактометрии. Было обнаружено, что пленки, изготовленные из раствора диметилсульфоксида (ДМСО), имеют более высокое содержание полярной β-фазы. Пленки, заполненные нанографитом, показали повышенную степень содержания β-фазы.

Ключевые слова: поли(винилиден-тетрафторэтилен) П(ВДФ-ТФЭ), диметилсульфоксид (ДМСО), диметилформамид (ДМФ), бета-фаза, ИК-спектроскопия, рентгенография, нанографит

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Introduction

The most prospective in terms of energy conversion are electroactive actuators, devices that transform electrical energy into mechanical one. They are increasingly being used in biological systems due to their promising properties. PVDF is extensively used in sensors and actuators, implantable devices and prostheses, energy harvesting power plants [1].

Currently, considerable attention in materials for actuators is focused on polyvinylidene fluoride (PVDF) and various composites based on it. PVDF can mainly be found in three crystalline phases: α, β and γ. Among the polar phases, the β phase is the most polar and, hence, have the strongest effect on the piezoelectric properties of PVDF. Fig. 1 shows crystalline phases of PVDF (Fig. 1, *a*) and dependency of the piezoelectric coefficient d_{33} on the β-phase content (Fig. 1, *b*) [2].

The purpose of this work is to assess the alteration in the content of the β phase of fluoroplast-42 filled with nanographite applying different solvents at different drying temperatures.

Materials and Methods

The copolymer of vinylidene fluoride and tetrafluoroethylene (fluoroplast grade F-42 mark B) is a crystalline polymer with a melting point of crystallites at 155–160 °C, having the chemical formula $[(-CF_2-CH_2-)n-(CF_2-CF_2-)m]k$ and containing 71% molar vinylidene fluoride (n) and 29% tetrafluoroethylene TFE(m). Electrochemically exfoliated nanographite was obtained in a two-electrode cell at a potential of 7 V in 0.6 M aqueous solution of ammonium peroxide sulfate obtained from graphite foil "Grapflex" RF 0.5 mm thick (with a carbon content of 99.5%, sulfur ≤ 0.12, chlorine ≤ 50 ppm). More details can found in our previous proceedings [3]. The crystallite size of the exfoliated nanographite (NG) was: thickness 14.86 nm; number of layers 44; basal size 17.08 nm. The next step, 0.25 g of the resulting powder was added into 95 g of aprotic solvent, DMSO or DMF. The solutions were mechanically dispersed using the FSH-2A unit at 2000 rpm for 1 hour and ultrasonically treated on the PS-30A unit at 180 Watts for 8 hours.

Fluoroplast-42, herein after referred to as F-42, was added to nanographite solutions in an amount of 5% by weight of the solution, and the nanographite content was 5% by weight relative to F-42. The solutions were alternately mixed at a temperature of 70 °C until F-42 was completely dissolved and treated with a mechanical dispersant FSH - 2A for 1.5 hours. Thus, 5% solutions of polymer F-42 filled with 5% of the mass of nanographite relative to the mass of F-42 were obtained. Further, solutions of F-42 were crystallized from DMSO and DMF at temperatures of 60 °C for 72 hours, 90 °C for 24 hours and 150 °C for 24 hours, respectively.

The study of F-42 films (50–450 μm) was perfomed by SEM Supra 40, Raman spectroscopy (Enspectr R532 spectrometer), infrared Fourier spectroscopy (Perkin-Elmer-TWO spectrometer), X-ray diffractometry (DRON 3M).

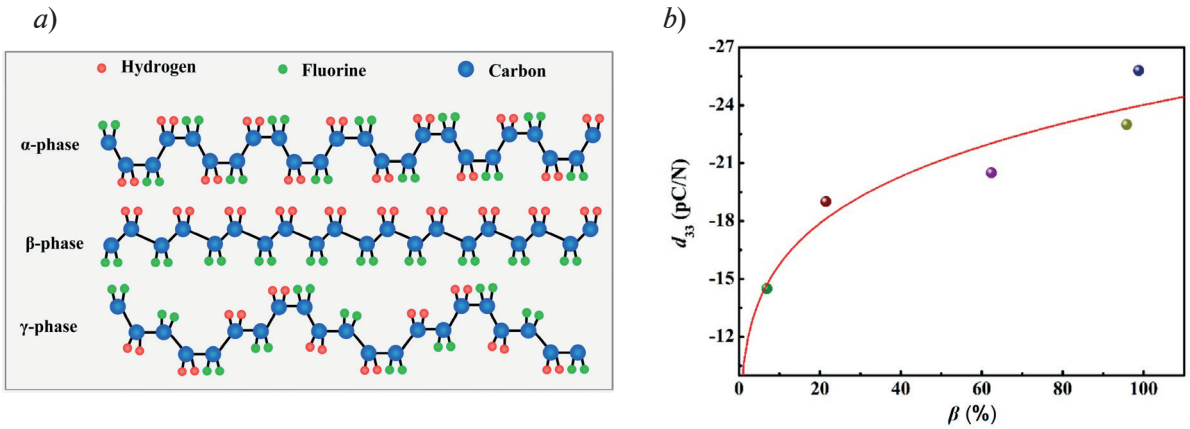

Fig.1. Crystalline phases of PVDF (*a*); dependence of the piezoelectric coefficient d_{33} on the β-phase content (*b*)

Results and Discussion

Figures 2, *a, b* show the typical FTIR spectra of F-42 samples and the fitting area for calculating the β-phase content. Peaks at 771 cm^{-1}, 840 cm^{-1}, 1234 cm^{-1} and 1275 cm^{-1} attribute to α-phase CF_2 bending, β or γ-phase CH_2 rocking, γ and β both to CF out-of-plane deformation vibrations respectively. The peak at 1251 cm^{-1}, as evidenced by [4] does not relate to either nanographite, PVDF or PTFE, but to the amorphous region of the copolymer as whole. The calculation of the β-phase is based on the ratio of the integral intensities of the decomposed peaks between the β- and γ- phases. The calculation based on the following equations for evaluation the content of the electroactive phase F_{EA}, polar β−phase $F(\beta)$ and γ−phase $F(\gamma)$ [5]:

$$F_{EA} = \frac{I_{EA}}{\frac{K_{840}}{K_{763}} I_{763} + I_{EA}} \times 100\% \quad (1)$$

$$F(\beta) = F_{EA} \times \left(\frac{I_{\beta}^{int}}{I_{\beta}^{int} + I_{\gamma}^{int}} \right) \quad (2)$$

where I_{EA} is the absolute peak intensity at 840 cm^{-1}, I_{763} is the absolute peak intensity at 763 cm^{-1}, K_{840} and K_{763} are extinction coefficients at the corresponding absorption frequencies equal to 7.7×104 and 6.1×104 cm^2/mol, respectively. I_{β}^{int} and I_{γ}^{int} are the integral areas of the peaks at 1275 cm^{-1} corresponding to the β−phase and at 1234 cm^{-1} corresponding to the γ−phase of F−42 in the spectral range of 1200−1300 cm^{-1}, after the peak separation procedure using the ACDLABS program.

Calculation given in [5] has no application for the current polymer, since there is a peak of the amorphous phase of the copolymer at 1250 cm^{-1}. To solve this problem, it is proposed to introduce spectrum processing in the 1200 cm^{-1}−1300 cm^{-1} region and subsequent peak deconvolution with calculation of integral peak intensities as replacement values in formula (2).

Figure 3 shows a diagram of the β-phase content of F-42 films under different manufacturing conditions. By making pairwise comparisons, it can be concluded that, compared with DMF, films crystallized from DMSO solution always have a higher β-phase content. Films filled with nanographite almost always have higher content of the β-phase. The alpha phase content fluctuates slightly from sample to sample and does not exceed 6%. Phase calculations were also performed based on XRD and Raman spectroscopy of the samples and the results in most cases correlate well with FTIR.

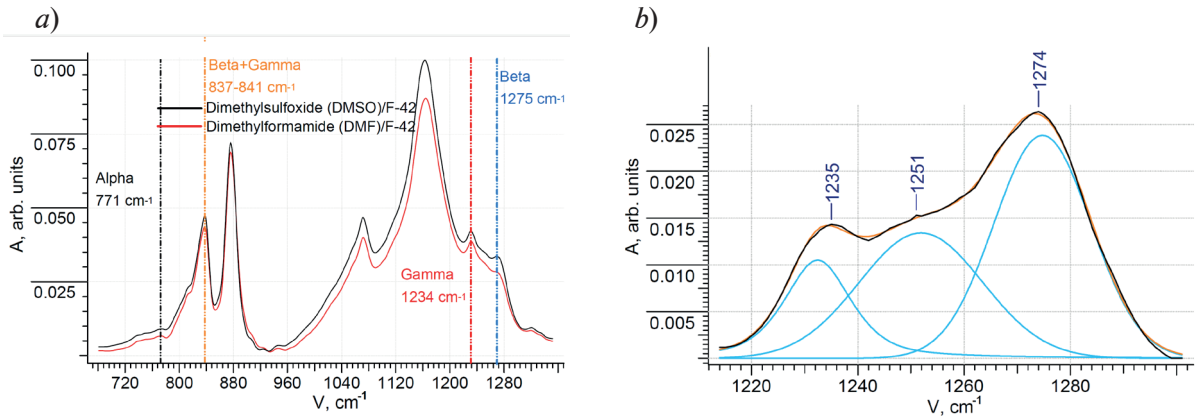

Fig.2. FTIR spectra of DMSO(DMF)/F-42 samples with nanographite at drying temperature 90 °C (*a*); FTIR fitting area for calculating the ratio of γ- and β-phases (*b*)

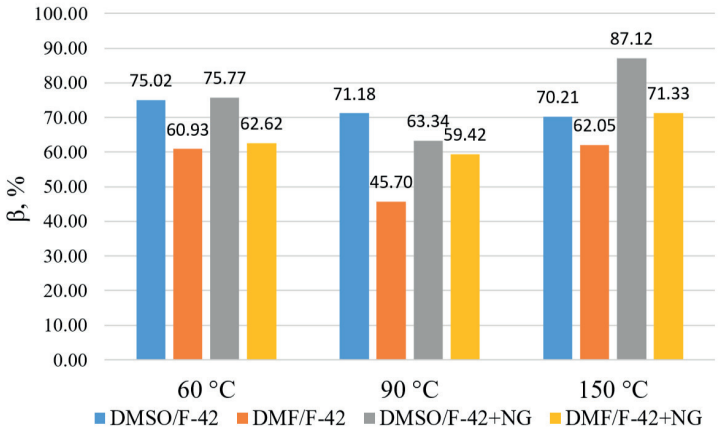

Fig. 3. Diagram of the beta phase content in F-42 films in different solvents, filling and drying conditions

Conclusion

Thus, DMSO is the best aprotic solvent for copolymer of vinylidene fluoride and tetrafluoroethylene F-42. Filling F-42 films with nanographite increases the beta phase content in the polymer. The alpha phase content does not exceed 6%, which indicates a large content of the electroactive phase as a whole. FTIR is sufficiently accurate to estimate the phase content in the polymer due to the simplicity of deconvolution of peaks in the region of 1200–1300 cm^{-1}.

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