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Structure and properties of tetrafluoroethylene–ethylene modified with fibre crystals

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New types of engineering materials of tetrafluoroethylene–ethylene copolymers and fibre monocrystals (up to 20 mass %) of alkali titanates were obtained. The structure and physical properties of these materials have been investigated by applying a variety of complementary methods: X-ray analysis, differential thermal analysis, differential scanning calorimetry and rheometry. Fibre monocrystals act as nucleators on the polymer melt crystallization and change the rheological behaviour of the compositions. Modified tetrafluoroethylene–ethylene copolymers possess good mechanical and thermal properties, high chemical resistance and can be used as engineering materials operating at high temperatures and in aggressive media.

1. Introduction

The extreme operating conditions in many practical fields require application of polymers with unique properties. Such properties are possessed by the materials based on fluoropolymers. Of these the tetrafluoroethylene–ethylene (TFE–E) copolymers are among the most important ones, owing to their high thermochemical and radiation stability, good mechanical and dielectric properties [1].

The preparation of polymer engineering materials with enhanced physicochemical properties can be achieved by modification of the copolymer during synthesis or by development of polymer compositions. As fillers in the composite materials based on TFE–E copolymers, glass fibres [2–4], carbon fibres [5–7], polytetrafluoroethylene [6] and combinations of these [6, 8] are the most frequently used.

Among the new and prospective fillers for modification of the copolymer are the fibre monocrystals (FMC) based on alkali titanates. Their small diameter and defect-free structure determines their high strength (> 14 GPA) and hardness [9].

Rather few papers in the literature have been devoted to the modification of fluoroplastics with FMC (and particularly with FMC based on alkali titanates) [10–12]. The introduction of FMC usually enhances the stress–strength characteristics [10] and the anti-friction properties [11]. Compositions of TFE–E copolymer with FMC are characterized by decreased shrinkability [12]. No systematic study on the structure changes in the compositions, their rheological characteristics, thermophysical, mechanical and other properties, has been reported. The present work was an attempt to make a complex study of the influence of the FMC based on alkali titanates on the crystallization and properties of TFE–E copolymers.

2. Experimental procedure

2.1. Materials

Tetrafluoroethylene–ethylene copolymers were prepared by semi-flow suspension polymerization according to the technique described elsewhere [13].

The fibre monocrystals were prepared by pyrolysis of alkali titanates obtained from the Harkov Polytechnical Institute. Their composition was 14.51% K_2O and 85.49% TiO_2 and their characteristic proportional length/diameter $(L/d) = 100$.

2.2. Preparation of the compositions

The concentrations of FMC in the compositions were 0.3, 1, 3, 10 and 25 mass % with respect to the mass of the copolymer.

The components were mixed in a laboratory mixer (type "Henshel") at 8 s^{-1} stirring rate for 2 min and then were granulated on a Brabender plastograph at 553–593 K and a driving momentum of 0.10 N m.

2.3. Physicochemical analyses

The density of the compositions was determined picnometrically in distilled water at a temperature of 293 K. DTA was carried out on a derivatograph OD-1002 (MOM, Hungary) at a heating rate of 6 K min^{-1}. The DSC curves were taken on a calorimeter DSC-111 (Setaram, France) at a scanning rate of 10 K min^{-1} in an argon medium. The thermostability was determined by the weight loss, in per cent, at 548 ± 5 K for 5 h in air. The Vicat softening temperature was determined at 10 N load. The temperature of loss of strength was determined by the temperature at which the operational part of the samples was destroyed at a load of 0.4 MPa. The X-ray analysis was

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carried out on a TUR-M-61 (Carl Zeiss, Germany) instrument with H2K-3 diffractometer and by using $\mathrm{Cu}K_{\alpha}$ emission under conditions of refraction. The tensile strength and elongation to break were measured on a Tiratest 2220(Germany) apparatus at 100 mm min^{-1} and room temperature, and the dynamic elasticity modulus by the acoustic method [14]. The antifriction properties were determined on a tribological testing apparatus with steel disc counterbody at 1 m s^{-1} gliding speed and 0.5 MPa load. The rheological characteristics of the compositions were determined on a high-temperature rotation viscosimeter RV-2 (Haake, Germany) in the temperature range 543–583 K.

3. Results and discussion

The synthesized TFE–E copolymer possessed alternating composition and orthorhombic crystal structure [15]. It could be supposed that the FMC introduced into the copolymer would act as artificial nucleators and would influence the crystal structure and, hence, would affect the whole complex of properties of the fluoro-containing polymeric compositions.

3.1. Influence of FMC on the structure of TFE–E compositions

The basic X-ray data are shown in Fig. 1. The diffraction maxima of the copolymer lay in a narrow interval of angles ($2\theta = 19.30°$ and $21.30°$) and as a result they were partly overlapped. The appearance of new diffraction maxima was connected with the crystal structure of the metal oxides building the FMC. The intensities of the diffraction maxima of the polymer decreased with the introduction of the FMC while the intensities of the maxima assigned to the FMC increased. The dimensions of the crystallites (L_{θ}, nm) were calculated by the Debye–Scherrer equation using the integral halfwidth of the crystal. With the introduction of the FMC, L_{θ} decreases compared with the pure copolymer (18 nm) to 16 nm for 0.3 mass % and 14.5 nm for 25 mass % FMC, which confirms the formation of finer-grained structure compared with the pure copolymer.

By the DSC method the crystallization ability of the TFE–E compositions with FMC was studied. The thermodynamic values of melting and crystallization of the initial and the modified copolymer are shown in Table I. Obviously, the FMC in concentrations up to 1 mass % increase both the enthalpies of melting, ΔH_{m} and crystallization, ΔH_{c}, which is connected with the increase of the degree of crystallinity and the formation of more perfect crystal structure of the compositions. The increase of ΔH_{c} from 77 kJ g^{-1} to 82 kJ g^{-1} for compositions containing up to 1 mass % FMC is connected with the filler playing the role of nucleator. These results correlate well with our earlier studies [16].

With increase of the FMC concentration over 1 mass %, ΔH_{c} decreases compared with the pure copolymer due to the restriction of the crystallization process with increasing filler concentration in the compositions. FMC concentrations up to 3 mass % lead to an increase of ΔH_{m} (and, therefore, the degree of crystallinity) of the compositions compared with the pure copolymer.

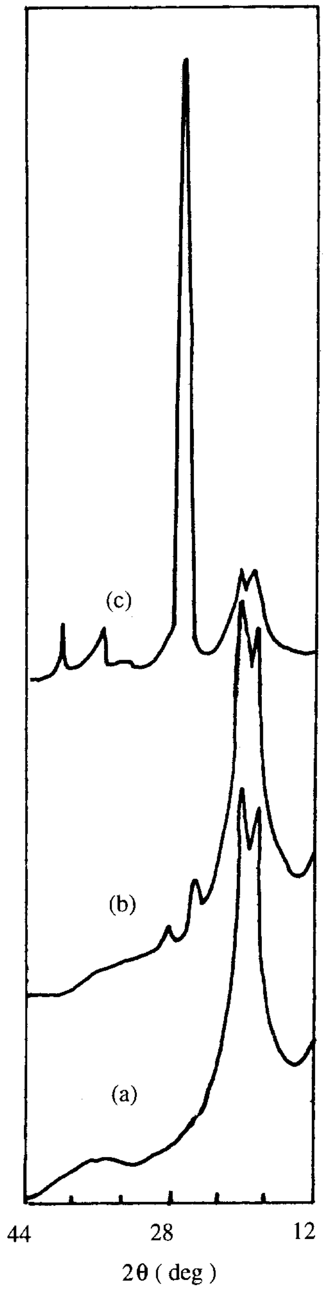

Figure 1 X-ray diffractograms of (a) pure and modified with (b) 0.3 mass % and (c) 25 mass % FMC TFE–E copolymer.

The process of crystallization of TFE–E copolymers modified with small quantities of additives (up to 1 mass %) and filler (up to 25 mass %) gives compositions significantly different by temperature–time characteristics, which should be taken into account during both their preparation and processing.

3.2. Rheological properties of TFE–E copolymers modified with FMC

FMC, at low temperatures, affect the rheological properties of the polymer melt which was assigned to their structure-forming effect even in the melt.

The flow curves of pure and 0.3 mass % modified FMC copolymer are shown in Fig. 2. The dependence

TABLE I Melting and crystallization of pure and modified TFE–E copolymer

Properties	FMC content in the compositions (mass %)					
	0	0.3	1.0	3.0	10.0	25.0
Melting temperature (K)	546	550	549	548	548	547
Enthalpy of melting, (kJ kg^{-1})	65	70	85	84	71	49
Crystallization temperature (K)	533	536	534	533	533	532
Enthalpy of crystallization (kJ kg^{-1})	77	79	82	76	70	60
Degree of crystallinity (%)	52	55	60	59	50	34

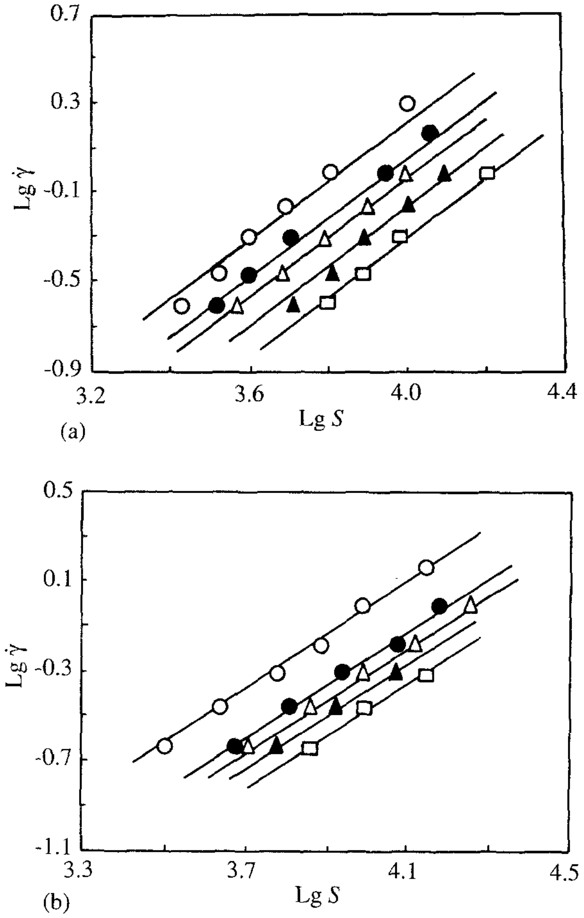

Figure 2 Flow curves of (a) pure, and (b) modified with 0.3 mass % FMC TFE–E copolymer at different temperatures (K): (□) 543; (▲) 553; (△) 563; (●) 573; (○) 583.

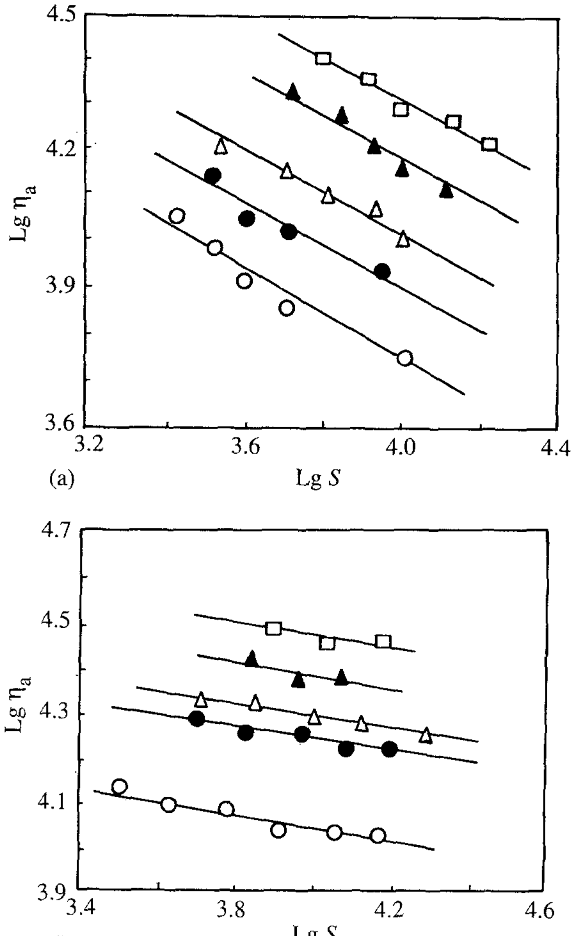

Figure 3 Dependence of lgη_a on lg$S$ for (a) pure and (b) modified with 0.3 mass % FMC TFE–E copolymer at different temperatures (K): (□) 543; (▲) 553; (△) 563; (●) 573; (○) 583.

of shear rate, $\dot{\gamma}$, on shear stress, S, in logarithmic coordinates is linear, confirming the applicability of the well-known Ostwald power law. The power factor, n, was determined from the slope of the curves and was found to be within the interval 1.1–1.3, proving that both melts behave as pseudoplastic fluids, like most polymer melts. It is of substantial practical interest to study the influence of 0.3 mass % FMC on the effective viscosity, η_a, of the melts (Fig. 3). The introduction of FMC into the copolymer leads to an increase of η_a and changes the temperature coefficient of viscosity. The change of η_a during its temperature processing is more pronounced for the pure copolymer compared with the composition containing 0.3 mass % FMC.

The activation energy, E_a of the viscous flow was calculated from the values of lgη_a as a function of temperature in Arrhenius' coordinates, at a constant shear stress (Fig. 4). With the introduction of FMC into the copolymer, E_a decreases to 64 kJ mol^{-1} (compared with 83 kJ mol^{-1} for the pure polymer) which is supposed to be connected with preservation of the ordered structure at temperatures above T_m within the interphase boundary polymer–filler, as proved for other thermoplastics modified with small amounts of fillers [18].

3.3. Thermal properties of TFE–E copolymers modified with FMC

During the thermal oxidation processes at temperatures above 518 K, hydrogen fluoride is liberated, degrading the properties of the copolymers [18]. Therefore, the influence of the FMC on the thermal properties of the copolymers is of practical interest.

The alkali titanates, as thermally stable chemical compounds, do not undergo changes in the temper-

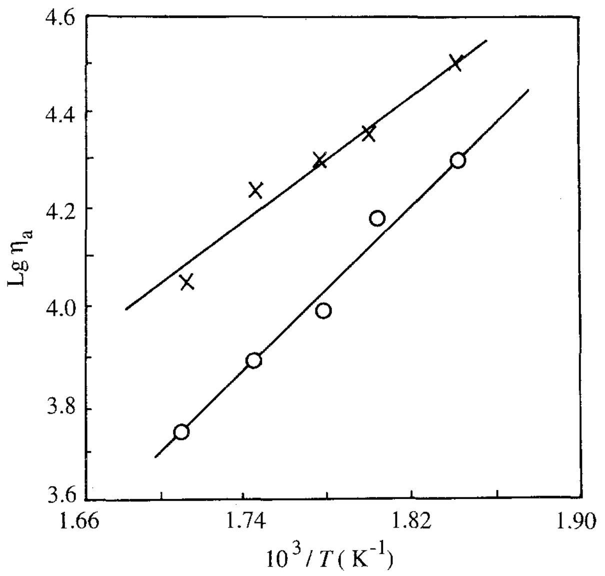

Figure 4 Dependence of $\lg\eta_a$ on temperature in Arrhenius' coordinates for (○) pure and (×) modified with 0.3 mass % FMC TFE–E copolymer at S = const.

ature interval discussed up to the polymer decomposition temperature, which was confirmed by the DTA analysis.

The influence of the FMC on the thermo-oxidation destruction of the compositions is illustrated in Table II. It can be seen that the introduction of additives into the compositions increased the initial destruction temperature, T_d by approximately 20 K compared with the pure copolymer. The presence of FMC also increased the activation energies of both thermal and thermo-oxidation destruction, E_d, proving their thermostabilizing effect as effective acceptors of hydrogen fluoride, beginning at 0.3 mass %. The deceleration of the destructive processes was also confirmed by the highest temperature of the highest destruction rate (748 K). The temperature difference, ΔT, between the initial destruction temperature and the melting temperature is one of the conditions necessary for stable processing of the materials. For all the compositions studied the values of ΔT were from 100–108 K and they were higher than the ΔT of the pure copolymer.

The data obtained from the DTA analyses were confirmed by the results of the thermostability tests (Table II). It can be concluded from these results that the FMC act as stabilizers of the thermo-oxidation processes. The weight loss decreased starting from 0.3 mass % FMC content in the compositions, and further increase of the concentration did not affect the destruction.

The compositions containing alkali titanates did not undergo thermo-oxidation colouring and did not foam (Table II). The analysis of the results obtained showed that the FMC, having a basic nature, accept hydrogen fluoride, thus preventing it acting as a catalyst of thermal destruction.

Compositions containing FMC possess higher thermoresistance compared with the pure polymer (432 K) due mainly to their increased degree of crystallinity (Table II). Their operation temperature usually exceeded, by 30–40 K, the thermoresistance determined by Vicat of the pure polymer (450 K) and was from 480–500 K.

The modification of the copolymers with FMC increased the temperature at which loss of strength occurred (Table II). The compositions obtained can be characterized by a higher strength-loss temperature at 0.4 MPa loading compared with the pure copolymer, which is another improved operation feature.

3.4. Physical properties of TFE–E compositions modified with FMC

The basic physical properties are shown in Table III. With increase of filler content up to 25 mass %, a tendency for increase of strength at break was observed. This can be explained satisfactorily by the common theory of the synergetic effect of the filler. The high brittleness of the FMC prevented an enhanced realization of their specific properties in the thermoplastic matrix and the strength at break increased up to 44%. The elasticity of the compositions decreased with increasing FMC content. The dynamic elasticity modulus, E', determined by acoustic method at 25 mass %, increased three times compared with the pure copolymer (Table III). These results show that by

TABLE II Thermal properties of pure and FMC-modified TFE–E copolymers

Properties	FMC content in the compositions (mass %)					
	0	0.3	1.0	3.0	10.0	25.0
Initial decomposition temperature (K)	638	658	663	653	663	653
Temperature of 10% weight loss (K)	698	708	723	703	713	703
Temperature of 50% weight loss (K)	733	738	738	733	733	743
Temperature of max. destruction (K)	733	748	738	738	738	738
$\Delta T = T_d - T_m$ (K)	92	108	114	105	115	106
Thermostability (%)	0.7	0.1	0.3	0.3	0.3	0.3
Colour change of samples[a]	+	0	0	0	0	0
Vicat softening temperature (K)	423	463	468	466	458	434
Operating temperature (K)	455	500	500	500	490	470
Temperature of strength loss (K)	528	534	540	534	543	538
Coefficient of linear expansion (10^{-5} K^{-1})						
323–373 K	10	9	7	6	6	5
403–453 K	16	13	11	7	5	4
E_d of destruction (kJ mol^{-1})	187.3	203.6	231.3	206.3	212.8	216.6

[a] 0, no change in colour and foaming; +, insignificant change in colour and foaming.

TABLE III Physicomechanical properties of pure and FMC-modified with FMC TFE–E copolymers

Properties	FMC content in the compositions (mass %)					
	0	0.3	1.0	3.0	10.0	25.0
Density ($kg\,m^{-3}$)	1710	1830	1850	1860	1880	2020
Tensile strength at break (MPa)	25	27	27	28	30	37
Coefficient of reinforcement (%)	–	3.5	5.8	8.2	16.7	44.0
Elongation at break (%)	220	140	115	100	21	4–6
Dynamic elastic modulus (GPa)	2.0	2.1	2.2	2.4	2.7	6.6
Shrinkability (%)	5.0	0.0	0.0	0.5	1.0	0.4
Coefficient of friction on steel	0.50	0.53	0.53	0.53	0.27	0.36

TABLE IV Chemical stability of pure and FMC-modified TFE–E copolymers at room temperature for 7 days

Conditions	Weight increase (%) at FMC content (mass %)		
	0	0.3	25
Base-acid resistance			
60% NaOH	0.0	0.0	0.0
CH_3COOH	0.0	0.0	0.0
Conc. HCl	0.0	0.0	0.0
10% HCl	– 0.3	– 0.8	– 0.6
Conc. HNO_3	0.0	0.0	0.0
10% HNO_3	– 0.7	0.0	0.0
Conc. H_2SO_4	– 0.7	– 1.0	– 1.3
30% H_2SO_4	– 1.2	0.0	0.0
Solvent resistance			
Acetone	– 0.7	0.0	0.0
Xylene	0.0	0.0	0.0
Water	0.0	0.0	0.0

the introduction of FMC the hardness of the compositions increased, thus stipulating a small reversible deformation. The compositions showed lowered shrinkability (Table III) which makes them applicable as engineering materials where exact dimensions are required.

The average coefficient of linear expansion justifies the preciseness and stability of the compositions at high temperature. The coefficient of dry friction on steel varied from 0.27–0.53 (Table III).

3.5. Chemical stability of TFE–E copolymers modified with FMC

The chemical stability of the TFE–E copolymers filled with FMC in various aggressive media is shown in Table IV.

The introduction of FMC into the polymer matrix decreases the mass of the samples in 10% HCl and concentrated H_2SO_4 due to partial dissolution of the filler. In other mineral and organic acids, bases and organic solvents, the compositions were chemically resistant.

4. Conclusions

Structure modification of tetrafluoroethylene–ethylene copolymers with fibre monocrystals of alkali titanates was carried out. The latter were found to be artificial crystallization nucleators in small concentrations (up to 1 mass %).

The addition of fibre monocrystals of alkali titanates did not change the character of the pseudoplastic flow of the polymeric melt but increased the viscosity and decreased the activation energy of the viscous flow.

The fibre crystals in the tetrafluoroethylene–ethylene copolymers exerted a thermostabilizing effect and improved the thermal and heat resistances of the compositions.

The introduction of fibre monocrystals improved the mechanical properties of the copolymers. The compositions obtained possessed good chemical stability in bases, acids and solvents but dissolved in hydrochloric and sulphuric acids to some extent.

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