CHEMISTRY AND TECHNOLOGY OF CHEMICAL FIBERS

MODIFICATION OF POLYCAPROAMIDE COMPOSITES BASED ON 1*H*,1*H*,13*H*-RIHYDROPERFLUOROTRIDECAN-1-OL AND MONTMORILLONITE

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Modification of polycaproamide by 1H,1H,13H-trihydroperfluorotridecan-1-ol immobilized on montmorillonite produced an F-containing polymer composite. The structure of the resulting composite was investigated using x-ray structure analysis and solid-state ^{19}F *NMR spectroscopy. The polymorphous composition of this heterochain polymer was shown to reorganize to enhance its thermal stability and diminish its flammability. Possible mechanisms for the stabilizing effect of the used modifier that were related to the involvement of organo-clay paramagnetic centers in the binding of macroradicals formed during thermal decomposition of macromolecular chains were discussed.*

The properties of fiber-forming polymers can be improved by using poly- and perfluorinated compounds as modifiers [1-3]. For example, modification of polycaproamide (PCA), on which cords and many textiles are based, by polyfluorinated alcohols $H(CF_2CF_2)_nCH_2OH$, which are produced in industry by the reaction of tetrafluoroethylene with MeOH, helps to increase the thermal, light, and wear resistance of the resulting films and fibers [4, 5]. However, the use of microscopic amounts of these compounds (10^{-3}-10^{-4} mass%) makes it difficult to distribute them evenly throughout the polymer matrix bulk and impossible to add them directly to the polymer melt because of their low boiling points and irreversible binding to PCA macromolecules.

Highly disperse montmorillonite-type clays (nanoclays), which characteristically have anisotropically shaped particles and can stratify in a polymer matrix into unified monolayers ~1 nm thick, can be used as carriers of polyfluorinated alcohols to open fundamentally new possibilities for producing F-containing materials [3]. Addition of compositions based on polyfluorinated alcohols with degrees of telomerization n = 1-5 and montmorillonite to several heterochain polymers increased the property set of the obtained composites [6-8]. The influence of compositions of alcohols with higher molecular masses remains unstudied.

The aim of the present work was to study the influence on the structure and properties of a PCA composite based on a polyfluorinated alcohol (n = 6) immobilized on montmorillonite.

The polymer matrix was PCA (OAO Grodno Azot, Republic of Belarus; TU RB 500048054.009–2001) with relative viscosity 3.33 ± 0.03 in powder form with particle size ≤200 µm that was produced by cryogenic grinding of the granulated product. The powder was dried in a Snol 58/350 convection oven at 90ºC to a residual moisture content of 0.01 mass% as determined using an AGS50 moisture analyzer.

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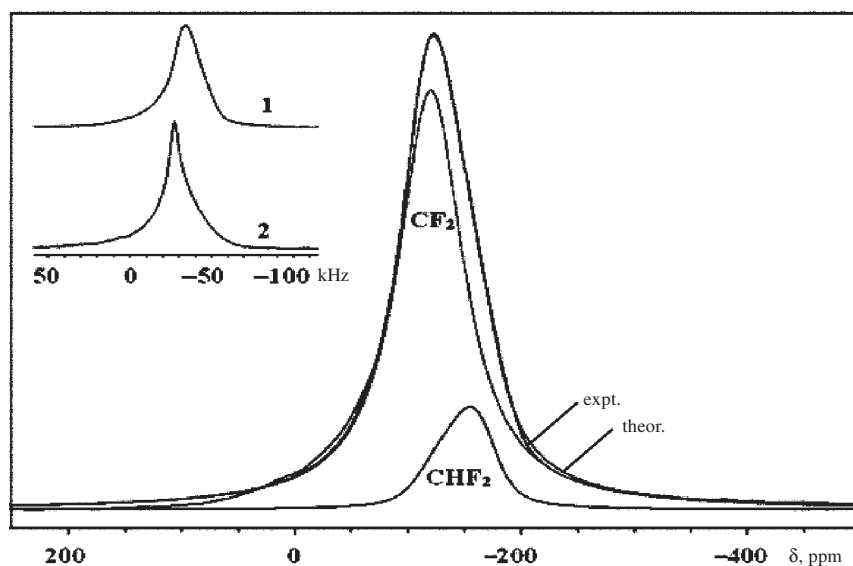
Fig. 1. ^{19}F NMR spectrum of modified PCA at 20°C. The theoretical (theor.) deconvolution of the experimental (expt.) spectrum into components is shown. The inset on the left shows for comparison spectra of modified PCA (1) and PTFE (2).

Table 1. X-ray Phase Analysis of PCA Samples

PCA sample	Content, mass%	
	α-form*	γ-form**
Starting	22	–
Modified	35	10

—————
*Reflections $2\theta = 20°$ (index 200) and $2\theta = 24°$ (002/202).
**Reflection $2\theta = 22°$ (100).

1*H*,1*H*,13*H*-Trihydroperfluorotridecan-1-ol (AO GaloPolimer, Perm; TU 2421-151-05807960–2005) was a white powder of purity 99.0 mass%, molecular mass 632.12, melting point 130°C, and boiling point at 760 mm Hg (normal conditions) 248°C.

Commercial Na$^+$-montmorillonite (TOO B-Clay, Kazakhstan) was a grayish-brown powder with a specific surface area of 595 m^2/g for H$_2$O and 64 m^2/g for N$_2$ and a cation-exchange capacity of 100 mg-eq/100 g. The purity of the base mineral in the clay was ≥98%.

The polyfluorinated alcohol ($n = 6$) was immobilized on the montmorillonite using ultrasonic dispersion (40 kHz) of weighed portions of the compounds in *i*-PrOH at 70°C as before [9]. The content of the fluorinated organic component in the resulting organoclay was 61.5 mass%. The particle size distribution in the organoclay was <50 nm, 2%; 50-100 nm, 8%, <1 μm, 80%, and <10 μm, 10%.

Polymer composites were prepared by preliminary dry mixing for 0.5 h of weighed portions of PCA and modifier in a BLM-2 ball mill followed by extrusion using a Haake Rheocord 9000 single-screw computerized extruder (Germany) at V. A. Belyi Institute of Metallopolymer System Mechanics, NAS of Belarus (Gomel). The temperatures in the material cylinder zones were zone 1, 220°C; zone 2, 230°C; zone 3, 240°C; and zone 4 (head), 250°C. The mixing screw had a constant rotation rate of 80 rpm for 7 min. Then, the resulting composite was granulated. The PCA samples contained 6 mass% of the F-containing modifier.

X-ray structural analysis used a Bruker D8 Advance automated diffractometer in Bragg–Brentano geometry (reflection). The exposure parameters were Cu Kα-radiation ($\lambda = 1.5418$ Å) and Ni filter. Experimental diffraction patterns were processed using DIFFRAC.EVA and DIFFRAC.TOPAS programs.

Solid-state ^{19}F NMR spectra of PCA samples were recorded at room temperature on a Bruker DRX 300 spectrometer (300 MHz). Chemical shifts were calibrated relative to the resonance of 1,1,1,3,3,3-hexafluoroisopropanol

Table 2. Thermal and Flame Resistance of PCA Samples

PCA sample	Starting temp. of extensive decomposition, °C	Acid index, vol%
Starting	353	19.0 ± 0.5
Modified	362	27.0 ± 0.5

as a secondary standard and adjusted to a scale relative to trichlorofluoromethane ($CFCl_3$). A single-pulse experiment with accumulation of eight successive scans and relaxation time 15 s was used. Ground PCA powders were studied in the NMR experiments.

Thermal analysis of modified PCA samples was performed in air on a Netzsch TG 209 F1 Libra synchronous thermal analyzer. The masses of the studied samples were 34-36 mg. The linear heating rate was 10 °C/min. Test results given herein are averages of three parallel measurements. The flammability of polymer composites was evaluated according to GOST 21793–76.

Polymorphism of the PCA manifested as the ability to crystallize in various forms (α, β, γ, δ), the fractions of which depended on the sample prehistory (formation method and conditions) and were identified using various instrumental methods [10]. Polyfluorinated alcohols are known to promote crystallization of this heterochain polymer primarily in the α-form [4] while montmorillonite nanoclay particles enhance crystallization of the γ-form or a metastable pseudohexagonal γ^*-form [5-7, 11, 12].

Table 1 shows that modification of the PCA composite based on 1H,1H,13H-trihydroperfluorotridecan-1-ol and montmorillonite led to noticeable reorganization of its polymorphous composition. Both an increase in the fraction of the α-form (crystalline monoclinic modification with a planar extended conformation of zigzag chains) and induced formation of the hexagonal γ-form were observed. The latter may have been due to strong interphase interaction at the modifier–macromolecule interface, which was observed by others [11-15] during the preparation of polyamide nanocomposites containing layered silicates and allotropic forms of carbon.

Figure 1 shows the ^{19}F NMR spectrum of modified PCA. It consisted of a broad asymmetric line, the half-width of which (~20 kHz) was comparable to that in the spectrum of polytetrafluoroethylene (PTFE). The line of PCA was asymmetric because it consisted of components with different chemical shifts δ (CSs) that corresponded to F atoms belonging to different atomic groups in polyfluorinated $H(CF_2CF_2)_6CH_2OH$.

The model (theoretical) deconvolution of the spectra assumed that the CSs of CHF_2 and CF_2 were approximately equal ($\delta = -135$ and -120 ppm, respectively [16-18]) while the ratio of their intensities was about 1:11, i.e., corresponded to the chemical formula of the polyfluorinated alcohol. The presence of a significant number of atoms with CSs more negative than those in PTFE caused the PCA spectral line to shift to the right relative to that of PTFE.

The combination of structural changes in the obtained PCA composite was responsible for increasing its thermal and flame resistance (Table 2). A dense coke covered a significant part of the surface after combustion of the fluoropolymer composite. It and elements (including Si, P, Al, Mg, Ti, Mn, Fe, S) in the highly disperse organoclay particles in the polymer matrix acted as a heat and diffusion barrier (labyrinthine path) to the material burning front, allowing the process to shift to reduced thermal effects because of more efficient heat dissipation and thereby a decreased heat release rate and the ability to ignite released combustible products.

Another possible reason for the increased thermal stability and flame resistance of the PCA is the inhibition of radical reactions by paramagnetic iron [19] present in significant amounts in the montmorillonite (3.03 mass% according to quantitative EPR spectral analysis) and the Lewis acidity of the montmorillonite (primarily at edges of aluminosilicate layers) [11, 12] associated with isomorphous substitution in its crystal structure and allowing single electrons to be accepted from donor molecules, thereby binding organic free radicals [19, 20]:

$$R\bullet \xrightarrow{\quad MMT \quad} R^+ + e^-$$
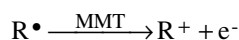
The presence of proton-donating HCF_2 and OH groups in the examined polyfluorinated alcohols $H(CF_2CF_2)_nCH_2OH$ was a unique chemical structural feature that was responsible for multicenter interactions with PCA

Table 3. Total Energy (E_0), Charge on H (qH) and O Atoms (qO) of $^\bullet(CF_2CF_2)_6CH_2OH$ Free-radical OH Group, and Charge on H Atoms (qH) of HCF_2 and O Atoms (qO) of $H(CF_2CF_2)_6CH_2O^\bullet$ Groups

Free radical	DFT-PBE0/6-311g** calculation method		
	E_0, kJ/mol	qH	qO
$^\bullet(CF_2CF_2)_6CH_2OH$	−7786962	0.246	−0.366
$H(CF_2CF_2)_6CH_2O^\bullet$	−7786940	0.185	−0.191

macromolecules that led to the formation of more densely packed structures [5-7, 21]. Furthermore, electrophilic radicals could be generated from 1H,1H,13H-trihydroperfluorotridecan-1-ol:

$$H(CF_2CF_2)_6CH_2OH \xrightarrow[-RH]{R^\bullet} {}^\bullet(CF_2CF_2)_6CH_2OH$$
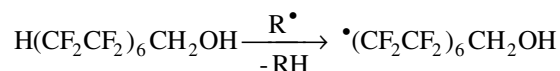
that differed from nonfluorinated analogs by retaining a tetrahedral configuration, as shown by previous research [22], which caused them to interact with the corresponding macroradicals formed during thermal decomposition of polymer chains. This terminated radical processes in both the gas and condensed phases.

Further transformations of $^\bullet(CF_2CF_2)_6CH_2OH^\bullet$ species could be related to the formation of fluoroalkoxy radicals:

$$^\bullet(CF_2CF_2)_6CH_2OH \rightleftarrows H(CF_2CF_2)_6CH_2O^\bullet,$$
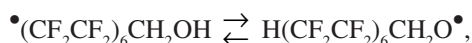
stabilized by intramolecular interactions $CF_2H\cdots^\bullet O-CH_2$ and $CH_2\cdots F_2C$. These last destructive processes would result in the formation of middle radicals $CF_2-C^\bullet F-CF_2-$.

The electronic and geometric structures (charge 0, multiplicity 2) of the terminal free radicals were investigated by classical quantum-chemical density functional theory (DFT) (with optimization of the geometry over all parameters by the standard gradient method embedded in the Firefly program [23] that is partially based on the initial code GAMESS (US) [24] in the isolated gas-phase particle approximation) (Table 3). The dipole moments of $^\bullet(CF_2CF_2)_6CH_2OH$ and $H(CF_2CF_2)_6CH_2O^\bullet$ species were 1.46 and 1.67 D, respectively.

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