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The distinctive features of carboxymethylcellulose sodium salt surface polyfluoroalkyl-modification

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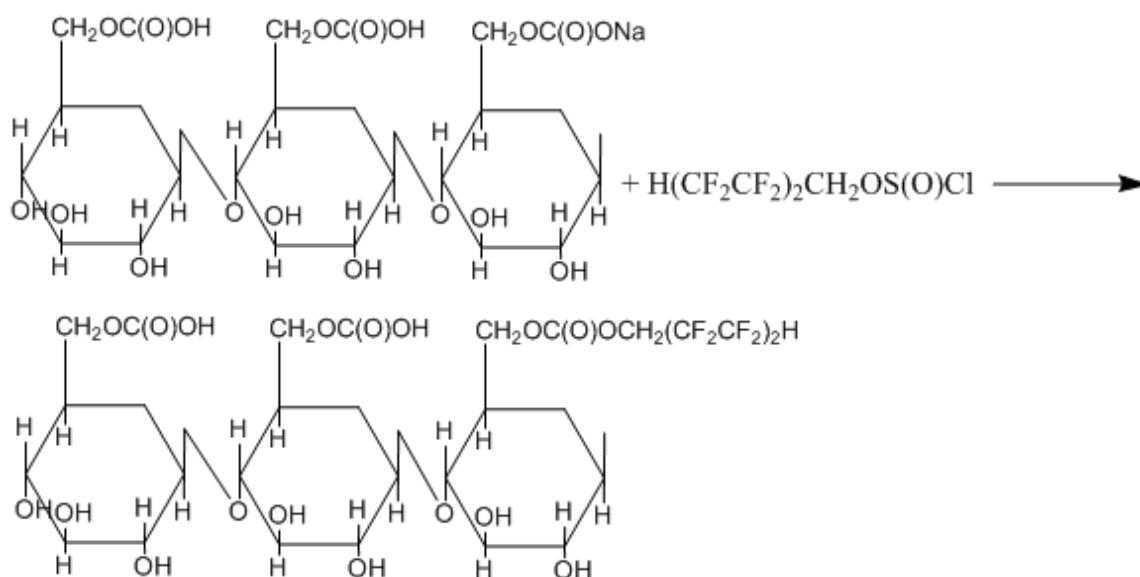
Abstract: It is shown that the surface polyfluoroalkyl modification of carboxymethylcellulose sodium salt with octafluoropentylchlorosulfite resulted in the formation of octafluoropentyl esters and ethers with total content of fluorine 6.67%, and allows considerable reduction of roughness on the surface of solids sized up to 1.4 μm .

Keywords: carboxymethylcellulose sodium salt, octafluoropentylchlorosulfite, esters and ethers, roughness of surface.

Research of heterophase polyfluoroalkylation of surfaces that involve hydroxyl and carboxy groups was exemplified by the modification of detonation nanodiamonds [1]. It was a multistep modification process that included the surface treatment with thionylchloride, after that the chloroanhydride groups and chlorine atoms thus formed reacted with sodium alcoholate of perfluorobutylmethanol.

We carried out the modification of carboxy- and hydroxyl- groups on the surface of 50-100 μm solid particles of carboxymethylcellulose sodium salt via their reaction with octafluoropentylchlorosulfite according to our earlier disclosed techniques [2-8].

The study on the modified carboxymethylcellulose structure by Fourier-transform spectrometry has shown that polyfluoroalkylchlorosulfite reacted with Na-carboxylate and HO-groups resulting in polyfluoroalkyl ethers and esters with total fluorine content of 6.67% according to the schedule as follows:



Octafluoropentyl ester groups were identified in IR spectra (Fig. 1, table 1) by the carboxy group absorption band (observed at 1720 cm^{-1}), assigned to the ester substituent valence vibrations, while a very intensive band at 1213 cm^{-1} evidenced the presence of a polyfluoroalkyl group. It is very probable

that the band at 1139 cm^{-1} belongs to $>\text{C}-\text{O}-\text{CH}_2(\text{CF}_2)_4$ -group. The said valence vibrations are not present in the IR spectra of original carboxymethylcellulose.

Table 1. IR absorption bands in the spectra of original carboxymethylcellulose sodium salt and in those of carboxymethylcellulose octafluoropentyl ethers and esters.

#	Groups	IR absorption bands, cm^{-1}	
		Na-CMC	F-CMC
1	HO, COOH	1284,1310,1381,1421, 3500-3600	1390, 1412, 3400-3600
2	-COONa	1594	1601
3	Cyclo- $\text{CH}_2-\text{O}-\text{CH}_2-$	1064	1064
4	$-\text{C}(\text{O})\text{O}-\text{CH}_2(\text{CF}_2)_4\text{H}$	-	1720
5	$-\text{C}-\text{O}-\text{CH}_2(\text{CF}_2)_4\text{H}$	-	1139
6	$-(\text{CF}_2)_4-$	-	1213

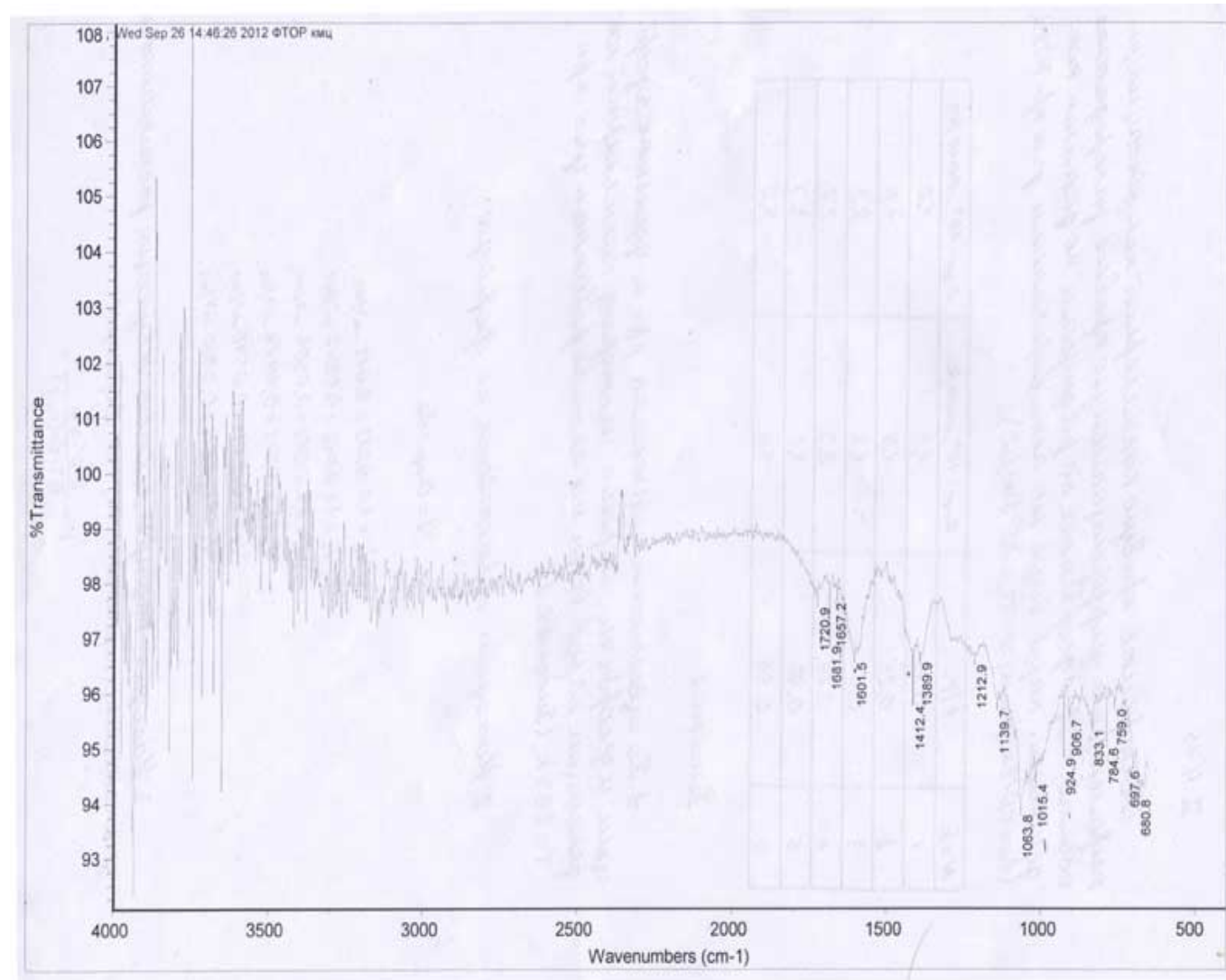


Figure 1. Fourier-transform spectrum of modified carboxymethylcellulose

The surface of modified carboxymethylcellulose sodium salt was studied by the method of atomic force microscopy with the help of "Solver Pro" probe atomic force scanning microscope, and compared with the surface of original carboxymethylcellulose sodium salt (Fig.2). The most important conclusion derived from the obtained results is that roughness of the modified carboxymethylcellulose surface reduced to $1.4 \mu\text{m}$ (while in original carboxymethylcellulose sample it exceeded $3 \mu\text{m}$), the fact is attributable to the introduction of polyfluoroalkyl chains $(\text{CF}_2)_4$ belonging to the ester and ether groups. The said groups are known to provide hydrophobicity, decreasing the probability of associative inter- and intra-molecular interactions, reducing therefore the surface "roughness".



Figure 2. Diagram of roughness on the surface of modified carboxymethylcellulose.

Figure 2 presents the variation in the surface roughness within 5cm sector. This variation reaches its maximal value at about $1.4 \mu\text{m}$. This observation is confirmed by three-dimension image (Fig. 3).

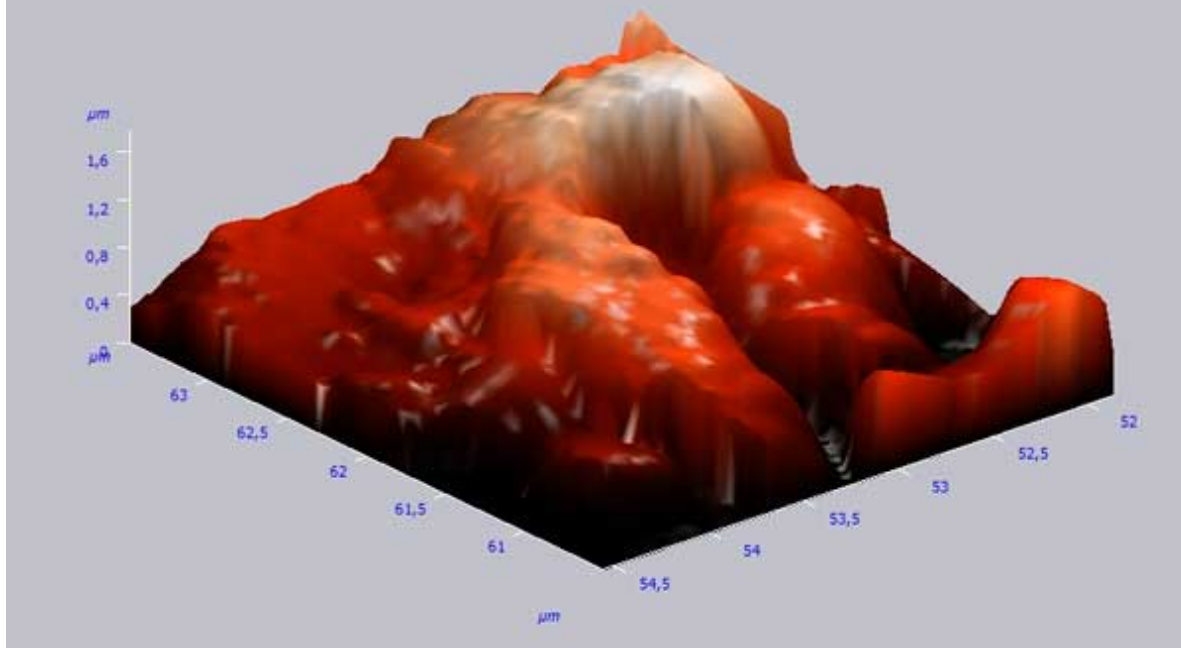


Figure 3. Three-dimensional image of the modified carboxymethylcellulose surface.

Therefore, polyfluoroalkylation of carboxymethylcellulose sodium salt by octafluoropentylchlorosulfite makes it possible to reduce its surface “roughness” and add hydrophobicity.

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