Composite proton-conducting membranes with nanodiamonds

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Abstract

A new approach was applied to improve the proton conductivity mechanism in perfluorinated membranes for hydrogen fuel cells. The composite short-side chain membranes were modified with functionalized diamond nanoparticles. Carboxylated nanodiamonds embedded in the polymer matrix provide an increase in conductivity at a moderate nanodiamond content, while the mechanical strength of the membranes remains high. The casting method of membranes preparation from solutions in N,N-dimethylformamide allowed saving the general channel structure in membranes at the presence of nanodiamonds, in agreement with neutron scattering data. We propose the formation of additional areas of conductivity, formed controllably, due to nanodiamond particles associated with polymer chains, on the surface of which accelerated diffusion of protons through the hopping Grotthus mechanism from the centers of proton adsorption proceeds with the transition to proton-conducting channels of the matrix covered with sulfonic groups.

Keywords: nanodiamonds, polymers, proton conductivity

Introduction

Perfluorinated proton-conducting membranes have great opportunities for the use in hydrogen fuel cells (FC). The main property of membranes – ionic (proton) conductivity, realized by the presence in membranes ionic negatively charged functional groups. Based on the ability to dissociate, hydration (retention of bound water) and chemical resistance, it is preferably to use sulfonic acid groups, which is realized in Nafion® and Aquivion® membranes and their analogues.

The development of the membranes for FC includes the progress in methods of synthesis of perfluorinated monomers [1-7]. The authors have provided a novel method of producing the membrane materials in aqueous emulsions of fluorinated monomers [8-11], where the heterogeneous copolymerization of sulfonated monomer FS-141 with tetrafluoroethylene is realized till the high degree of sulfonated monomer conversion (~90%) along with preserving the composition of the obtained copolymer.

These membranes have porous structure. The conducting channels in the polymer are formed by the local segregation of polymer matrix to hydrophobic and hydrophilic phases. Several structural models were suggested to describe Nafion® membranes [12-15]. The most appropriate is fibrillar model describing the conductivity routes as hydrophilic channels in a polymer matrix, which surface is covered by sulfonic acid groups on the end of copolymer side chains.

The authors have prepared and tested Russian analogues of Nafion® и Aquivion® membranes. We have found structural differences and the correlation of the structure of short side chain membranes with their equivalent weight and molecular weight [16,17].

Short side chain Aquivion®-type membranes are of special interest due to their high performance in a wide temperature range. Various types of modifications are also being applied to improve the membranes properties [18].

To improve the functional properties of membranes it seems reasonable to use nanodiamonds to fill the polymers as additional linkages between the polymer chains. It is known that diamond nanoparticles can raise the mechanical strength of the composites, as well as their thermal conductivity and chemical stability [19-22]. So the elastic strength properties of polyvinyl alcohol-based composites are significantly improved at addition only 0.6 % DND. Diamonds in fluoroelastomers reduce their permeability for polar solvents [23].

The development of the new type of composite membranes based on a polymer matrix modified by particles of functionalized detonation nanodiamond (DND) allows solving the fundamental task to improve the proton conductivity mechanism of the composite, at the same time saving the strength and thermal stability of polymer matrix. Nanodiamond surface may serve as storage for additional protons, which could migrate along the polymer-diamond border using the chain-like nanodiamond aggregates. This mechanism has advances over the traditional narrow channel pores being formed in Nafion® or Aquivion®. The authors have developed methods for preparing nanodiamonds as perfect crystals (sp3-hybridization) with negative ζ-potential in hydrosols, without surface regions with sp^2-hybridized carbon atoms. Recently the method of obtaining perfect nanodiamonds (sp^3) was developed with a formation of stable hydrosols and gels due to surface functional groups [23-25]. This makes possible to regulate the ordering of nanodiamond ensembles in the resulting polymer matrix during the sublimation of the solvent from the layers of the solution with the polymer and diamond components during the preparation of membrane films by casting from solution.

Until now very few examples of proton-conducting membranes modified with diamonds are known. Postnov et al. [26] have produced Nafion and Aquivion composites, when the membrane films were obtained by evaporating the solution on the surface. The significant rise of conductivity was found only at low RH. But at high degrees of swelling the difference in conductivity disappears. Hou et al. [27] have discussed introducing the nanodiamonds into SPEEK material (Nafion alternative) to rise the mechanical strength. Thus, the development of FC membranes modified with nanodiamonds is just starting, and first results are encouraging.

Experimental

Samples preparation

Short-side chain copolymer with EW 890 g/mol was synthesized by the developed aqueous-emulsion technique [28,29]. The monomer FS-81 (perfluoro-3-octapentensulfonilfluoride) was used in copolymerization [30]. The membranes were prepared by casting method from 2 wt.% dimethylformamide (DMF) solution of $–SO_3Li$ form of copolymer, evaporated at 70-80°C followed by annealing at 170-200°C during 1-2 hours and reduced to $–SO_3H$ form, according to the described technique [17]. To prepare compositional membranes the suspension of DND in DMF was used, prepared from carboxylated DND hydrosol, obtained from industrial nanodiamonds produced by Special Design and Technology Bureau "Technolog" (St. Petersburg, Russia) according to [31]), evaporated and dispersed in DMF using ultrasonic generator. The size of primary DND particles in aqueous and DMF suspensions was 4-5 nm which is in good correspondence with the results described earlier for aqueous suspensions [25]. 2 wt.% of sulfonated copolymer solution was mixed with 1 wt.% DND suspension in DMF with the variable ratio, allowing to obtain DND content in membranes from 0.25 to 5 wt.% after removing the solvent. Formation of membranes from DND-copolymer mixtures was produced using the technique for pure polymer [17]. Finally, we have prepared six membrane samples with 0, 0.25, 0.5, 1, 2 and 5 wt.% of DND. The thickness of membranes in dry condition was 50 ± 8 μm.

Methods of investigation

The obtained membranes were examined on their hydrogen-conducting properties at 20 and 50°C, mechanical properties at constant RH 50 ± 3 %, fine structure was studied by small and very small angle neutron scattering and atomic-force microscopy, and finally the hydrodynamic properties of copolymer at the absence and presence of DND were studied by capillary viscometry in DMF medium.

Results and discussions

Proton conductivity

Proton conductivity was measured by impedance spectroscopy at 20 and 50°C in the equilibrium state of saturation with water after boiling at 100°C during 1 h. A Z-3000X impedance meter (Elins, Russia) using a cell with stainless steel electrodes in the four-electrode scheme in the frequency range 10–150 000 Hz was used.

Fig. 1 shows conductivity as a function of the DND content in membranes. At 20°C the conductivity of the compositional samples decreases, only membrane with 0.25 wt.% DND demonstrates a small increase in conductivity. At 50°C the doping of nanodiamonds from 0.25 to 1 wt.% leads to 10 % increase in conductivity, but the following addition of DND to 2 and 5 wt.% leads to significant fall of conductivity.

Several reasons may cause this complicated behavior of conductivity. DND particles with 4-5 nm size may close thin conducting channels, especially at high DND content, resulting in formation more complicated pathways for protons that decrease the conductivity. The carboxylic groups on the surface of DND particles, being low acidic, may serve as proton collectors that give away their protons into conducting channels with low efficiency. The temperature could be an accelerating factor, and the found temperature-dependent effect for the compositional membranes with low amount of DND demonstrated that the proposed improving the conductivity mechanism works. The measured rise of conductivity at 50°C is very encouraging and gives the basis to expect the larger effect at typical working temperatures of the membranes ~130°C.

Mechanical strength

The mechanical properties of the membranes were tested in uniaxial stretching mode on the AG-100X Plus instrument (Shimadzu Corp.) using the described technique [17]. The measurements were performed at a fixed stretching velocity 100 mm/min. and RH = 50 ± 3%. We have measured the Young's modulus (E), yield strength (σ_Y), ultimate tensile strength (σ_T), and ultimate deformation before destruction (ε_D).

Fig. 2 demonstrates, that moderate amount of DND in membranes (≤ 1 wt. %) does not change significantly their mechanical properties. At higher DND content (2-5 wt.%) the Young's modulus increases from ~210 to 250 MPa meaning that the compositional membranes became stronger.

Safronova et al. showed that decreasing the number of ion-exchange groups in Aquivion® membranes (i.e. the rise of EW) makes the interactions between ionic groups weaker and the crystallinity of material becomes higher [32]. We should note the fact that the degree of crystallinity for SSC membranes, analyzed from neutron scattering data, in fact generally rises with EW, but in details they are related in more complicated way [33]. It was found that the rise of crystallinity for Aquivion membranes correlated with their EW leads to increasing the Young's modulus and therefore makes the mechanical properties fairly high and more preferable for the use in electrochemical devices and as electrolyte in fuel cells [32].

The higher content of nanodiamonds, 2-5 wt. %, used in our composite membranes, also solves the task to arise Young's modulus (Fig. 2a), which is equal to the effect of rising the EW of copolymer.

At the same time the ultimate deformation before destruction decreases greatly from ~340% to 240% showing that these composite membranes with high DND content are more fragile. This leads to ultimate tensile strength decrease at 5wt.% of DND from 24-25 to 20 MPa, while membrane with 2wt.% DND still has σ_T similar to a sample without DND (Fig. 2b). Finally, we found that yield strength does not change in the whole range of compositions.

As a result, we have found the preferred limit of DND content in membranes to be 1-2wt.% to save the mechanical properties and improve the conductivity.

Neutron scattering

Small-angle neutron scattering (SANS) experiments were carried out at the YuMO spectrometer [34,35] (Joint Institute for Nuclear Research, Dubna, Russia) in the range of momentum transfer $q = (4\pi/\lambda)\sin(\theta/2) = 0.006–0.8$ Å^{-1}, where θ is the scattering angle, and the neutron wavelength $\lambda = 0.05–0.8$ nm. This q-range allows finding structure peculiarities at the scale of $\sim 2\pi/q \sim 1–100$ nm. The measured scattering curves (scattering intensities, I vs. momentum transfer, q) were normalized to absolute values of the scattering cross-section dΣ/dΩ(q) with the use of vanadium measurements as a standard for absolute intensity calibration in the program SAS package [36].

SANS data were complemented with very small-angle neutron scattering (VSANS) measurements performed at KWS-3 spectrometer (Heinz Maier-Leibniz Zentrum, Garching, Germany) at $q = 2 \cdot 10^{-4}$ - $2 \cdot 10^{-2}$ Å^{-1}, $\lambda = 12.78$ Å, covering the range of submicron scale [37]. Two standard sample-detector distances 1.3 m and 9.5 m were used.

Samples were packed in several layer stacks for measurements to obtain optimal scattering intensity. All samples were studied in air-dry condition (**dry** series) and saturated in H_2O (**H** series) or D_2O (**D** series). The use of H_2O/D_2O allows varying the nuclear contrast sample environment (polymer–water) that helps to highlight additional structural features. Samples were wrapped in aluminum foil, which is transparent for neutrons and prevents saturated samples from drying during measurements, and measured at ambient temperature, 20°C.

The combined SANS and VSANS data are presented in Fig. 3 for the membranes with 0 and 5 wt.% of DND (intermediate samples are not shown). The scattering curves allow discussing several structural levels of organization in membrane material. We should focus on three structural peculiarities.

The fact of the greatest interest is that the ionomer peak at $q = 0.15 - 0.20$ Å^{-1} remains unchanged at the presence of nanodiamonds. This peak corresponds to correlation of the fine structure elements – thin proton conducting channels, being organized in pairs (bundles) at fixed distances (3-5 nm) between elementary channels [33,38]. The unchanging of position and profile of ionomer peak both in dry and saturated state shows that nanodiamonds do not disturb the basic channel structure of the membrane. In other words, the presence of nanodiamonds in DMF solution does not affect the self-assembling process for polymer chains to form the conducting channels.

The q-range of 0.03-0.08 Å^{-1} provides matrix knee disappearing at the presence of DND. This wide peak is attributed as a degree of crystallinity – ordering of bundles of channels at distances of 10-20 nm without DND. At the presence of 5% DND ordering completely disappears, showing that the structure at these scales became more uniform. Probably, DND particles can be incorporated between bundles of conducting channels that breaks their ordering.

Another peak should be noted at $q \sim 0.004$ Å^{-1} for H_2O-saturated membranes. This peak corresponds to inhomogeneities at the scale ~ 150 nm. The applied contrast variation technique (this peak does not exist in D_2O-saturated membranes and poorly detected in dry state) allows to attribute it as hydrophobic areas 150 nm in size, surrounded by hydrophilic phase of polymer. This segregation to hydrophilic and hydrophobic parts becomes less pronounced at the presence of 5% DND – the peak blurs (Fig. 3b), corresponding to disordering of the structure.

Atomic force microscopy

AFM measurements have confirmed the structure changes observed by VSANS. Surface topographical were analyzed using a P47 AFM (NT-MDT, Russia) in a semicontact mode. The probes used were RTESPA MPP-11120-10 by Bruker. Scan frequency was 1 Hz.

Hydrophobic globules 100-150 nm in size are clearly seen in dry membranes (Fig. 4). At the presence of DND larger objects appear with size 300-500 nm and sharp borders. This allows considering, that DND particles are not spread uniformly in membrane, but mostly accumulated in hydrophobic areas. Moreover, the compatibility of DND to hydrophobic part of the polymer should not be high. The DND-DND interactions are more preferable, than DND-polymer, which results during the casting process in formation of larger areas, containing condensed DND particles, surrounded by hydrophobic phase of polymer chains.

Viscosity measurements

To find the type of interactions existing in the polymer-DND mixtures, resulting in non-uniformly spreading of DND in membranes, the hydrodynamic properties for polymer and polymer-DND mixture in DMF solutions were studied by viscosity measurements. The capillary Ubbelohde viscometer at 25 and 80 °C was used. The weight ratio of DND in the mixture was 5%, equal to the used for casting the membrane with maximal studied wt.% of DND.

Fig. 5 shows the reduced viscosity $\eta_{red} = (\eta_r - 1)/C$ plot as a function of the polymer concentration, where η_r is the relative viscosity calculated after measurements times of flow for the sample and the solvent (DMF). At high concentrations the viscosity curves have very low slope, corresponding to very high quality of the solvent (polymer-solvent interactions exist rather than polymer-polymer). At low concentrations the polyelectrolyte effect is detected – the rise of η_{red} upon diluting. Thus, the polymer in DMF is a polyelectrolyte; the sulfonic groups on side chains are dissociated and charged. The polymer coils are swelling in DMF very well; the chains become more rigid, occupying larger volume. This provides formation of large intermolecular associates ~1μm in size [17] that makes excellent mechanical strength after the solvent evaporation. The reduced viscosity rises with increase of the temperature. Thus the affinity of the polymer with the solvent becomes even larger at higher temperature.

The presence of DND changes the viscosity only for low concentrations, at 25°C. The polyelectrolyte effect becomes slightly weaker, making sure that the polymer chain did not became more charged. This corresponds to rather low compatibility of DND to the polymer.

Apparently, they do not form a complex in DMF solution, DND particles repulse from polymer chains since they both are charged negatively. This effect almost disappears at 80°C due to the acceleration of thermal motions in solution.

Thus, the DND particles repulse from hydrophilic charged polymer chains and are able to make a complex only with hydrophobic part of polymer matrix. Removing the solvent during the formation of the membrane makes a composite with DND particles agglomerated in hydrophobic polymer globules, as accompanied by results obtained from neutron scattering and AFM.

As a result, we propose a model of a composite membrane with modified conductivity properties. DND particles are embedded in clusters between bundles of channels and also forming larger scale agglomerates, but do not incorporate into the primary conducting channels (Fig. 6). As a result, the general mechanism of proton conductivity remains, but modified by the presence of nanodiamonds. At low temperatures DND may serve as accumulators of additional protons and can take some protons from the channels that decreases the conductivity. At larger temperatures the protons mobility becomes higher, they are able to migrate from DND surface to the channels and the conductivity rises.

Conclusion

The composite perfluorinated Aquivion-type membranes with nanodiamonds, prepared by casting method, provide temperature-dependent effect of modified proton conductivity mechanism. Nanodiamonds serve as proton reservoirs, accumulating protons at low temperatures. At higher temperatures the additional protons penetrate to the conducting channel system, thus, increasing the conductivity. The measured effect of raising the conductivity at 50°C and good mechanical properties makes us sure in improving the performance of this type of membranes at real working temperatures in fuel cells ~ 130°C.

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Fig. 1. Proton conductivity of compositional membranes at 20 and 50°C *vs*. DND content.

Fig. 2. Mechanical properties of compositional membranes: a - Young's modulus E and ultimate deformation before destruction ε_D, b - yield strength σ_Y and ultimate tensile strength σ_T.

Fig. 3. Neutron scattering on membranes in dry condition (a), saturated in H_2O (b) and D_2O (c). 1 – sample without DND, 2 – membrane with 5 wt.% DND.

Fig. 4. AFM height (a, b) and phase (c, d) images for dry membranes without DND (a, c) and with 5 wt.% DND (b, d).

Fig. 5. Reduced viscosity of the polymer and its mixture with DND in DMF at 25 and 80°C.

Fig. 6. The model structure of composite membrane with nanodiamonds.

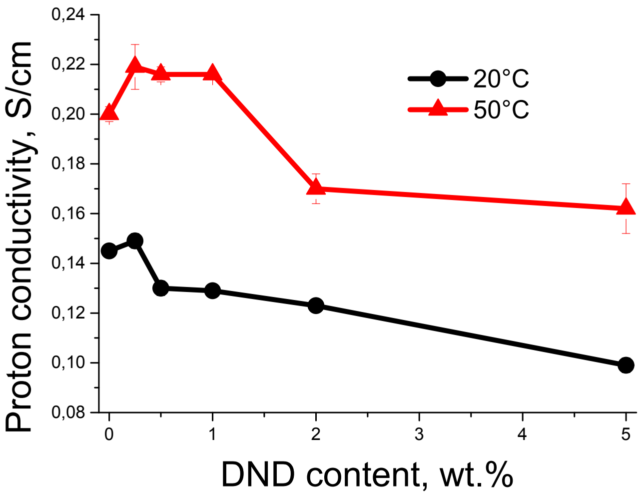
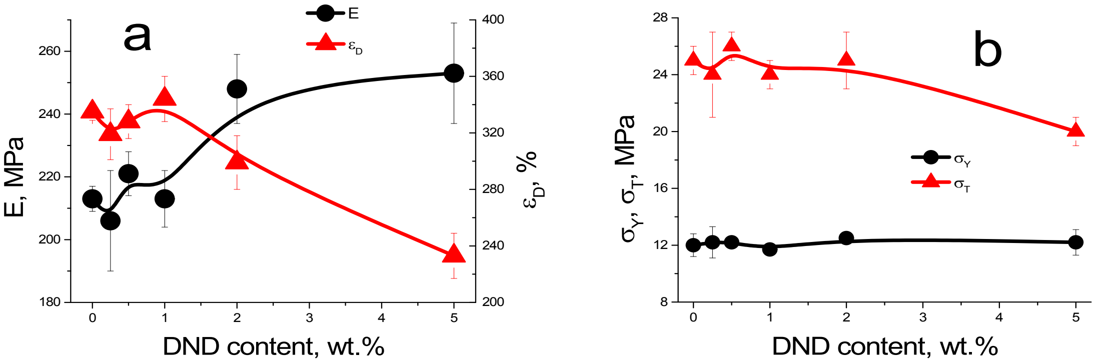

Proton conductivity, S/cm
0,24
0,22
0,20
0,18
0,16
0,14
0,12
0,10
0,08
0
1
2
3
4
5
DND content, wt.%
20°C
50°C

Fig. 1.


a
E
ε_D
E, MPa
ε_D, %
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200
220
240
260
200
240
280
320
360
400
0
1
2
3
4
5
DND content, wt.%
b
σ_Y
σ_T
σ_Y, σ_T, MPa
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16
20
24
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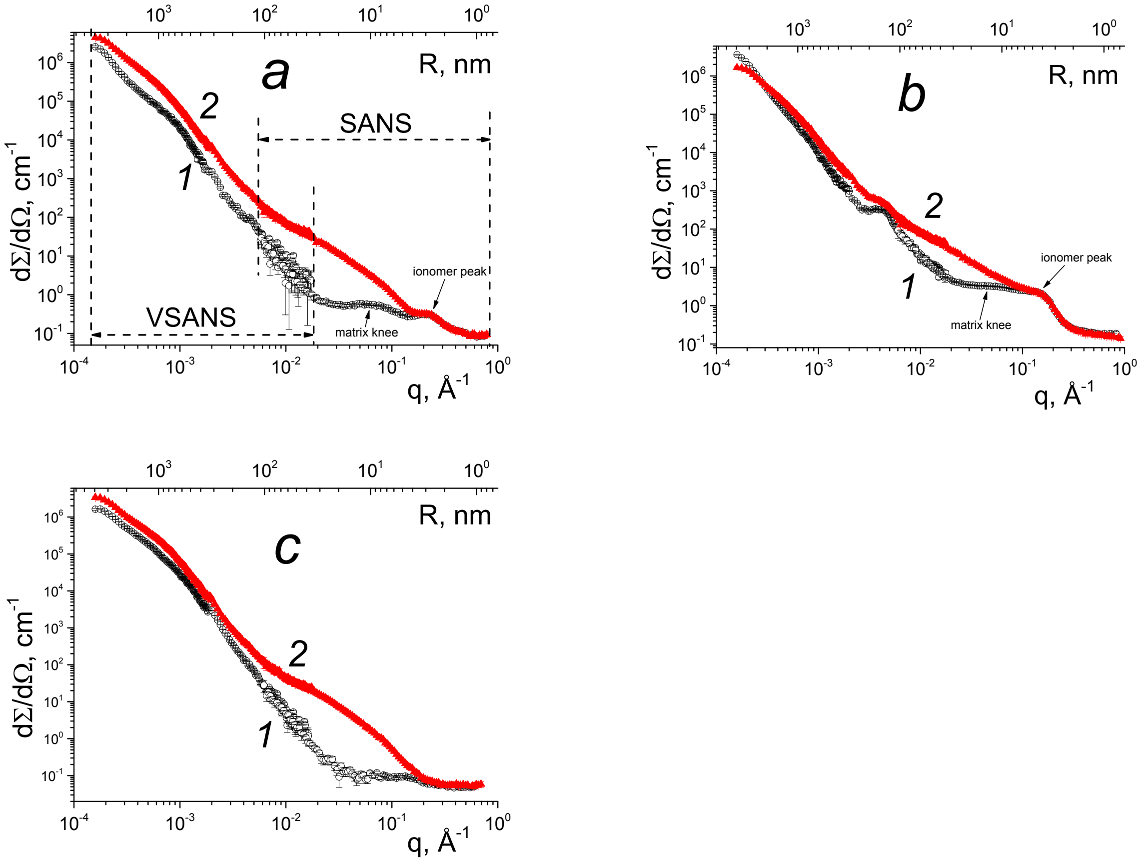
1
2
3
4
5
DND content, wt.%

Fig. 2.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b
c
R, nm
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10^2
10^1
10^0
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q, Å^{-1}
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10^{-2}
10^{-1}
SANS
VSANS
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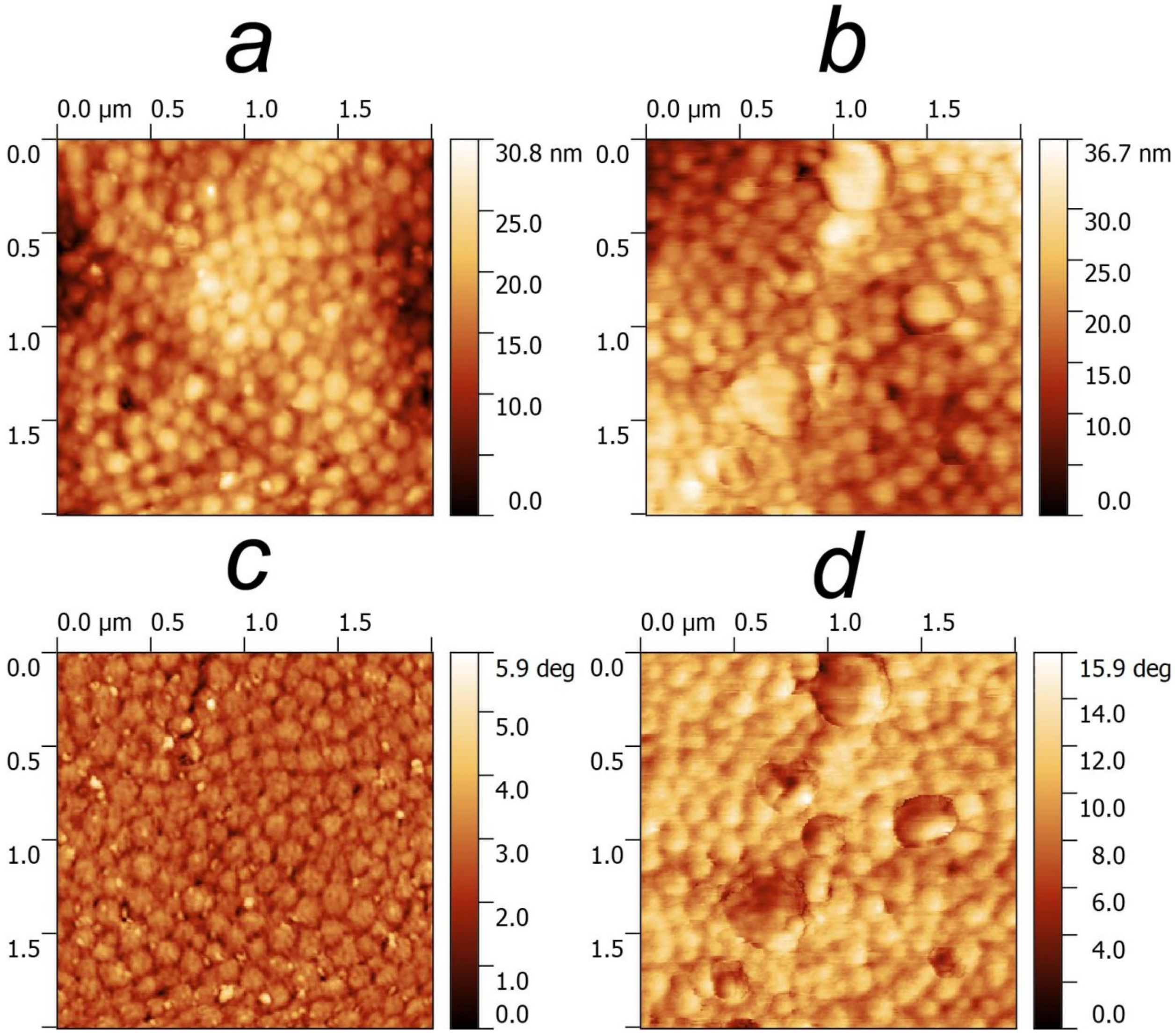
2
ionomer peak
matrix knee

Fig. 3.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0.0 0.5 1.0 1.5
30.8 nm 25.0 20.0 15.0 10.0 0.0
b
0.0 µm 0.5 1.0 1.5
0.0 0.5 1.0 1.5
36.7 nm 30.0 25.0 20.0 15.0 10.0 0.0
c
0.0 µm 0.5 1.0 1.5
0.0 0.5 1.0 1.5
5.9 deg 5.0 4.0 3.0 2.0 1.0 0.0
d
0.0 µm 0.5 1.0 1.5
0.0 0.5 1.0 1.5
15.9 deg 14.0 12.0 10.0 8.0 6.0 4.0 0.0

Fig. 4.

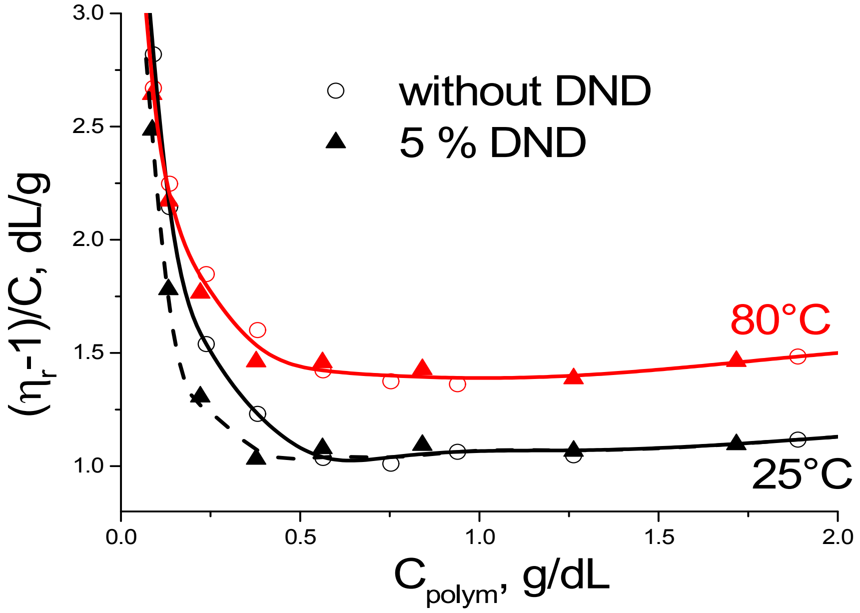
○ without DND
▲ 5 % DND
80°C
25°C
(η_r-1)/C, dL/g
C_polym, g/dL
3.0
2.5
2.0
1.5
1.0
0.0
0.5
1.0
1.5
2.0

Fig. 5.

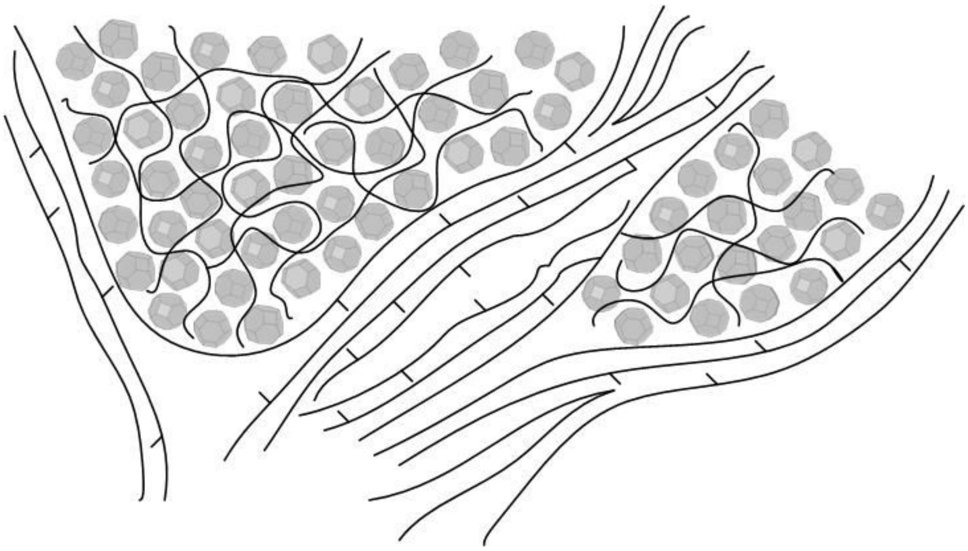

Fig. 6.