Russian Supercomputing Days

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Predicting the Barrier Properties of Polymeric Materials with the MULTICOMP Package

Andrey Knizhnk,[1] Pavel Komarov,[2,3] Denis Shirabaikin,[1] Sergey Trepalin [1] and Boris Potapkin [1]

[1]Kintech Lab Ltd, Moscow, [2]Institute of Organoelement Compounds RAS, Moscow,
[3]Tver State University, Tver,

The work is performed on the basis of Kintech Lab Ltd.

the main problems associated with the preservation of foods and drugs

- Foods can degrade relatively quickly when they come into contact with oxygen-containing molecules in the environment because all organic materials (oils, lipids, sugars, and proteins) are not resistant to oxidation and many of them can bind to water.
- Medicines contain biologically active molecules (enzymes, hormones, vitamins, antibiotics, etc.) that have many chemically active functional groups (-S-, -OH, -C(O)OH, -C(O)O-, -NH-, -NH2, -NO2, etc.).
- Therefore, the penetration of even a small amount of oxygen or water molecules into the packaging can significantly reduce the consumer properties of the products and gradually lead to their complete deterioration.

the main goal

- The goal of the present study is to develop a computational technique for the rapid quantitative evaluation of oxygen and water vapor permeation through multilayer organic–inorganic barrier films for food packing applications.
- It is based on a multiscale modeling approach that combines several computational methods: MD, MC and Continual.

examples of the structures of multilayered packaging film

cook-in poultry or ham
- PA
- Nucrel® ethylene-acrylic acid copolymer

frozen seafood
- Surlyn® (ionomer)
- Nucrel® ethylene-acryli acid copolymer

granola bars
- Paper
- LDPE
- Foil
- Surlyn® (ionomer)

hot dog package
- Top seal
- PET
- Surlyn® (ionomer)
- Bottom

applesauce cups
- PP
- Bynel® adhesive
- EVOH
- Bynel® adhesive
- PP

toothpaste tubes
- LDPE
- Bynel® adhesive
- EVOH
- Bynel® adhesive
- LDPE

cereal box liners
- HDPE
- Bynel® adhesive
- EVOH
- Bynel® adhesive
- Pealable seal blend with Surlyn® (ionomer) or Elvax® EVA

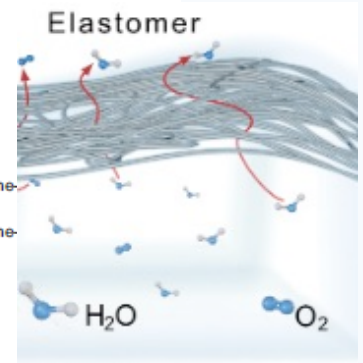
condiment packets
- PET
- LDPE
- Foil
- Nucrel® ethylene-acrylic acid copolymer

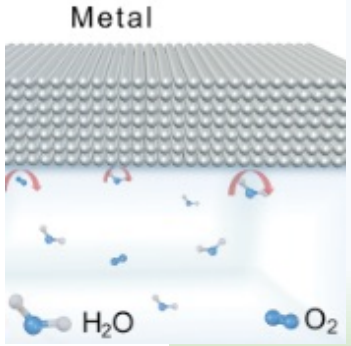
restaurant jelly cups
- Top seal
- PET
- Primer
- LDPE
- Appeel® lidding sealant resins

juice boxes
- Paper
- LDPE
- Nucrel® ethylene-
- Foil
- Nucrel® ethylene-
- LDPE

juice cartons
- Paper board
- LDPE
- Bynel® adhesive
- PA
- Bynel® adhesive
- LDPE

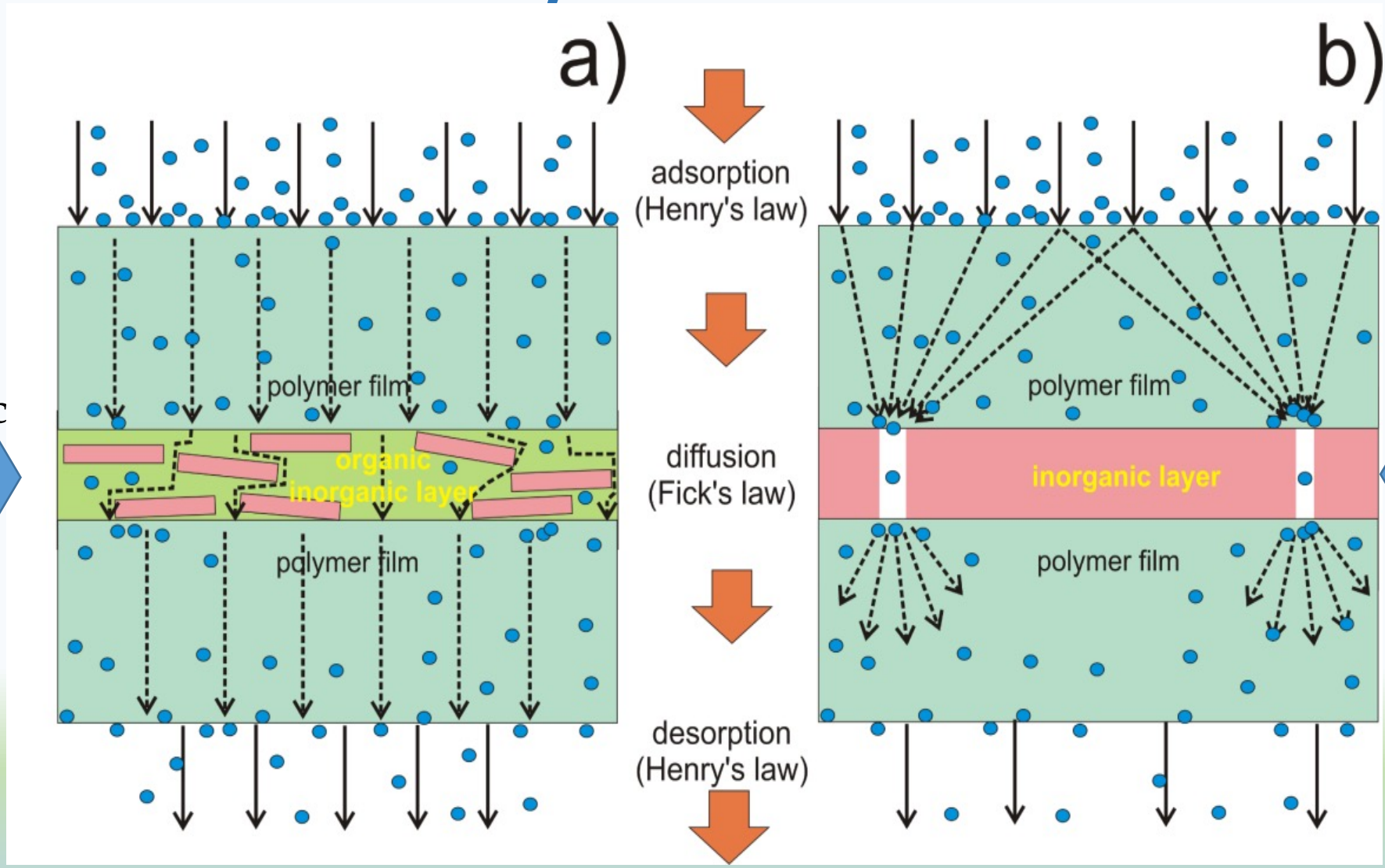
ketchup squuze tubes
- PP
- Bynel® adhesive
- EVOH
- Bynel® adhesive
- PP





Plastic Films in Food Packaging. DOI: http://dx.doi.org/10.1016/B978-1-4557-3112-1.00005-3

the mechanism of gas permeation in hybrid multilayer thin films

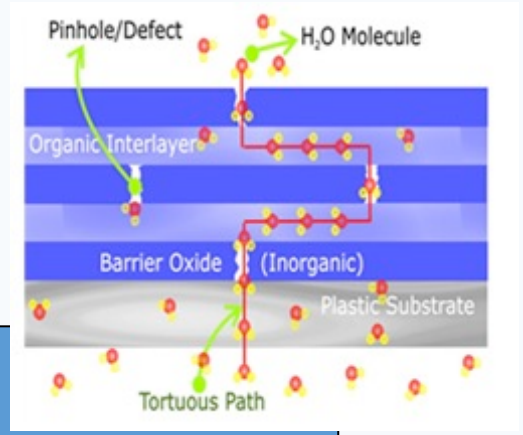


organic-inorganic layer

inorganic layer with defects

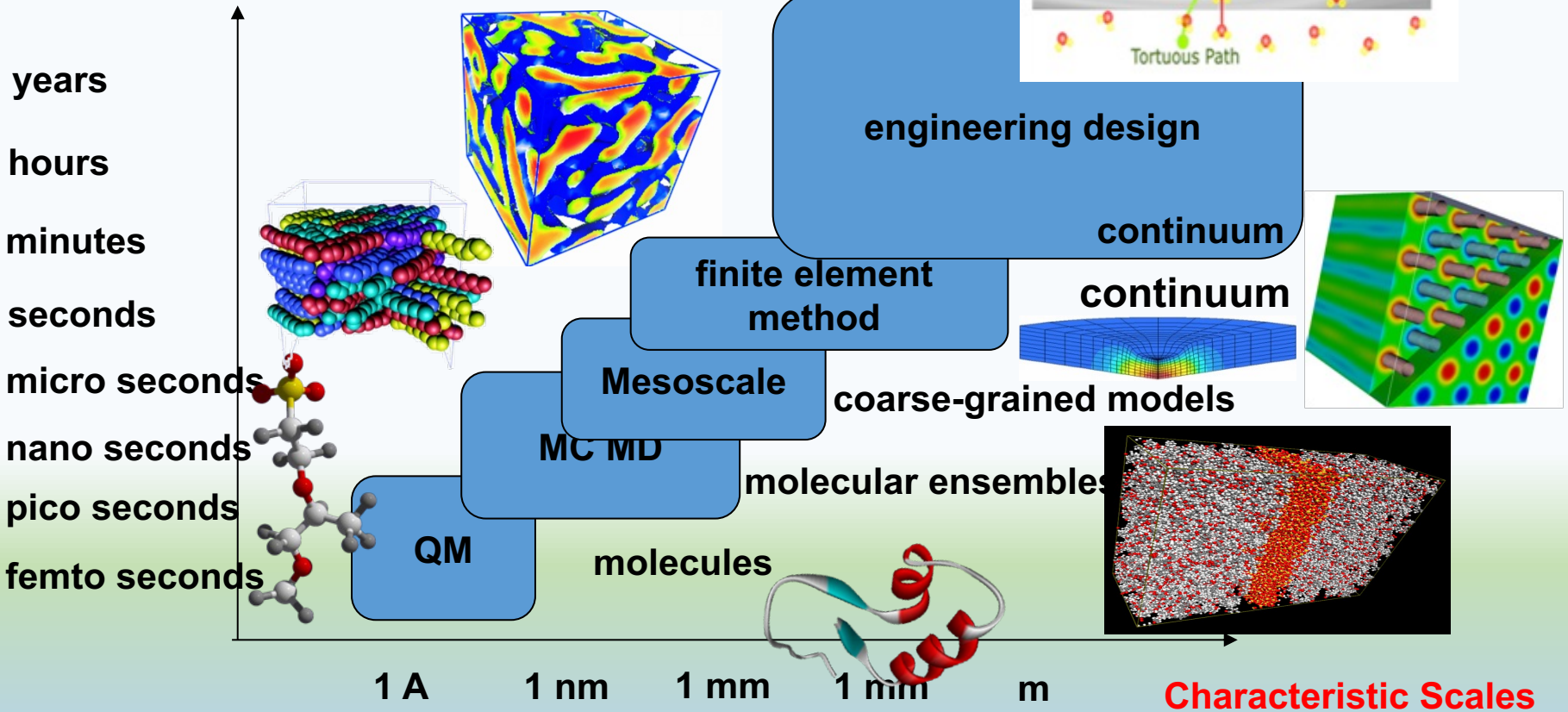
multiscale nature of polymer nanocomposites

technological level



In the case of nanocomposites, it is impossible within the framework of a one-level approach to combine high accuracy and large scale of consideration.

- **Atomistic level** - properties of nanosized filler and phase interaction
- **Mesoscal**e - the distribution of the filler in the matrix
- **Macro level** - effective material properties



used calculation technique MULTICOMP software package for multiscale modeling of the properties of polymer nanocomposites

Purpose

- Used for multilevel predictive modeling of morphology, thermal and mechanical properties of nanocomposites with a polymer matrix
- The package is specially designed for high-throughput screening of materials based on supercomputers
- Allows you to predict various material properties:
  - structural
  - mechanical
  - thermophysical
  - transport

Advantages

1. Effective scientific workflow for computing automation
2. Integration of models for calculating the properties of nanocomposites with micro-, meso- and macrolevels
3. Client-server architecture for leveraging remote high performance computing (HPC) resources
4. Open architecture: compute modules can be added, modified and replaced without developer assistance
5. Flexibility in adaptation and configuration
6. Convenient graphical user interface
7. Visual 1D-2D-3D-visualization of calculations

РОССИЙСКАЯ ФЕДЕРАЦИЯ

СВИДЕТЕЛЬСТВО

о государственной регистрации программы для ЭВМ

№ 2018615740

Multicomp

Правообладатель: *Общество с ограниченной ответственностью «Лаборатория Кинтех» (RU)*

Авторы: *см. на обороте*

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Руководитель Федеральной службы по интеллектуальной собственности Г.П. Ивлиев

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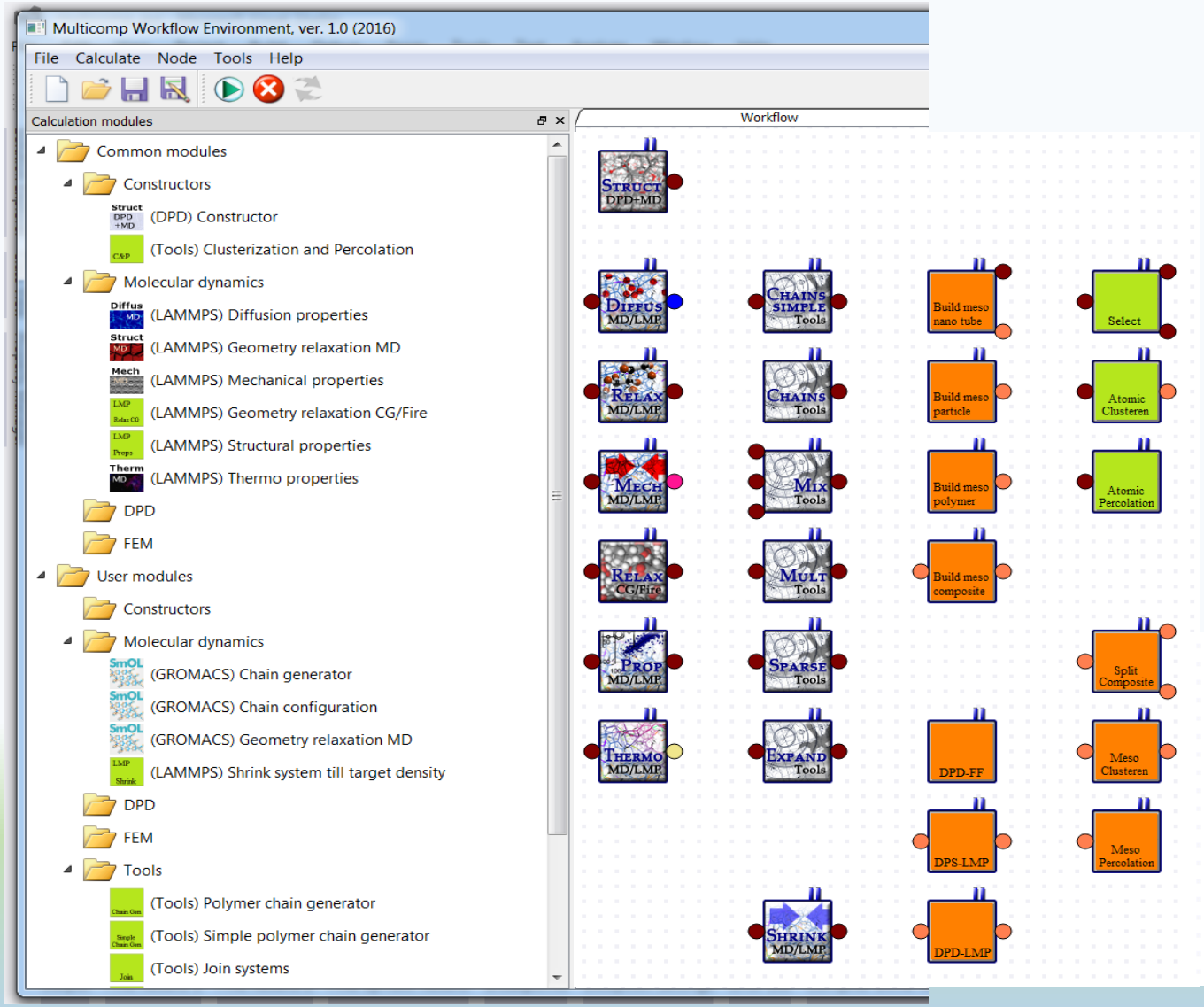
modules kit



constructors

Nano/Meso tube Generator

Atomistic Constructor (K23)

Linear Meso-polymer Generator and Mixer

service tools

Simple Polymer Chain Generator

Polymer Chain Generator

Multiply System by copying

Expand System by translation

Join Systems.

Sparse System into Separate Molecules

Mix Systems

Select and Split

simulations tools

Geometry relaxation CG/Fire

Geometry relaxation MD

Shrink system till target density

Meso Structure Relaxation MD

Meso Structure Relaxation CG

calculation and analysis of properties

Mechanical properties

Thermo properties

Diffusion properties

Structural properties

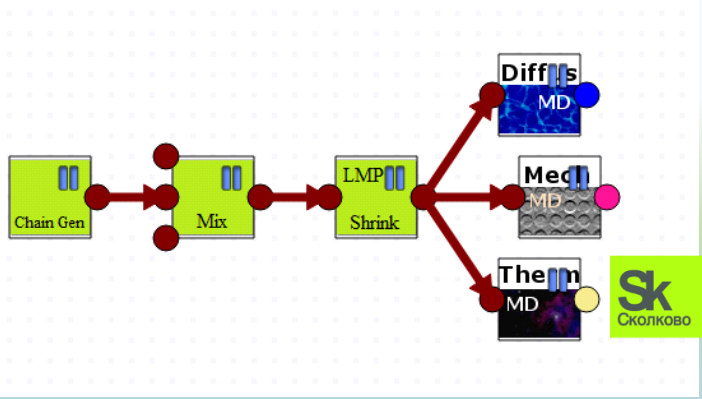
(density, RDF, XRD, SAED, porosity)

Clusterization

Percolation

Atomic Percolation

Mesoscopic Percolation



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multilevel modeling in the scientific workflow concept

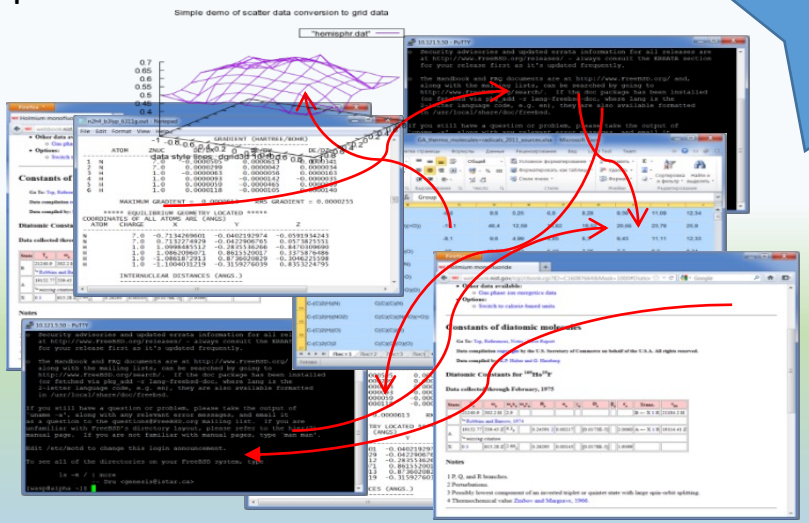
Problems with old approaches

A large number of programs
- Atomistics (Lammps, Gromacs, DLPoly) Mesoscale (DPD)
- Macro Level (FEM)

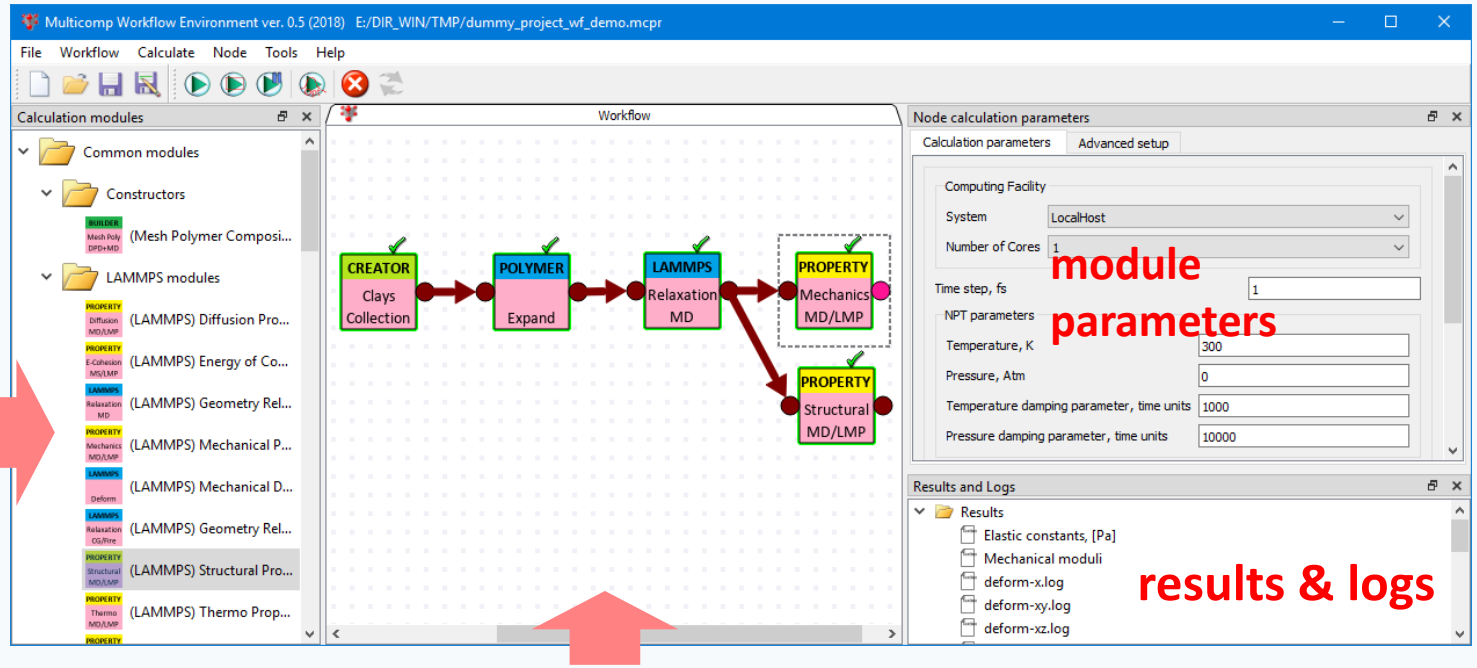
Various means of processing results
- Excel
- Gnuplot, Matplotlib
- Jmol, Ovito

Incompatible formats

Script Sets



modules kit



Calculation scenario constructor

Benefits of the Scientific Workflow Concept

- Open architecture: the user can add, modify and replace computational modules without developer assistance
- Multi-user collaboration and data exchange
- Data exchange between modules based on templates
- Highly scalable performance
- Flexibility in adaptation and configuration
- Isolating Modules: reduces risk and reduces impact on the whole system

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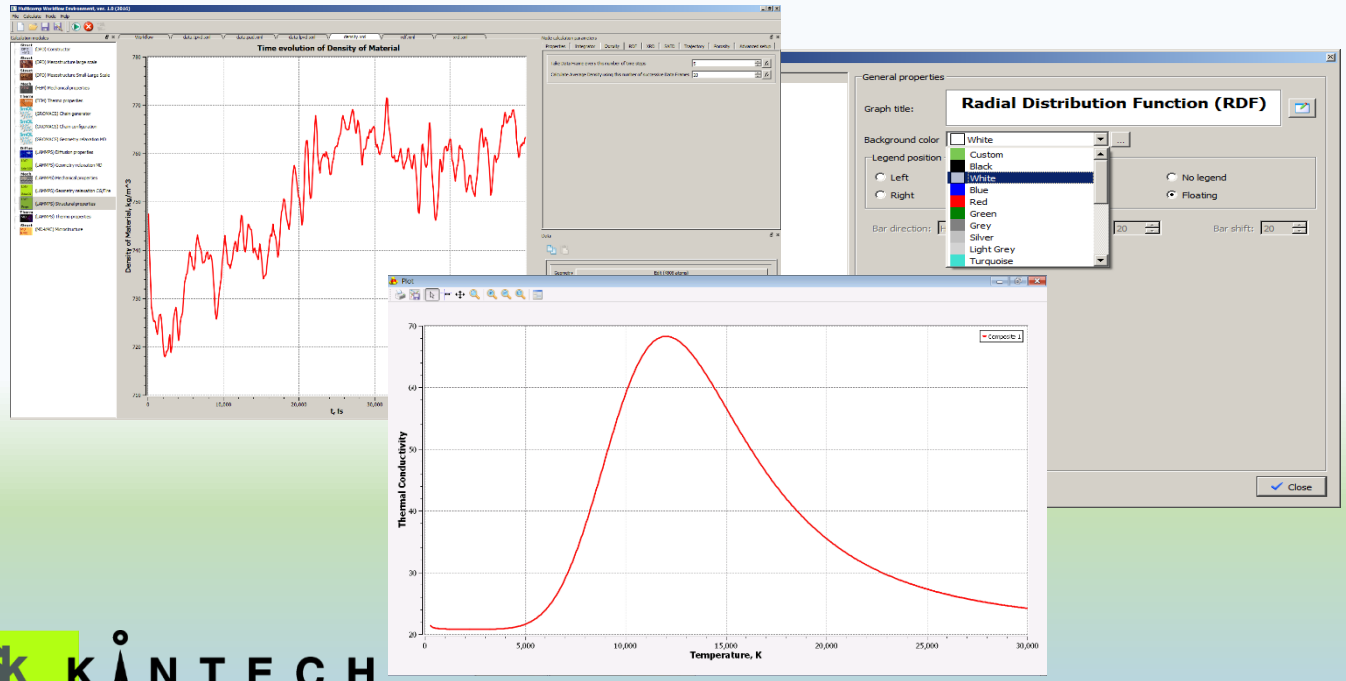
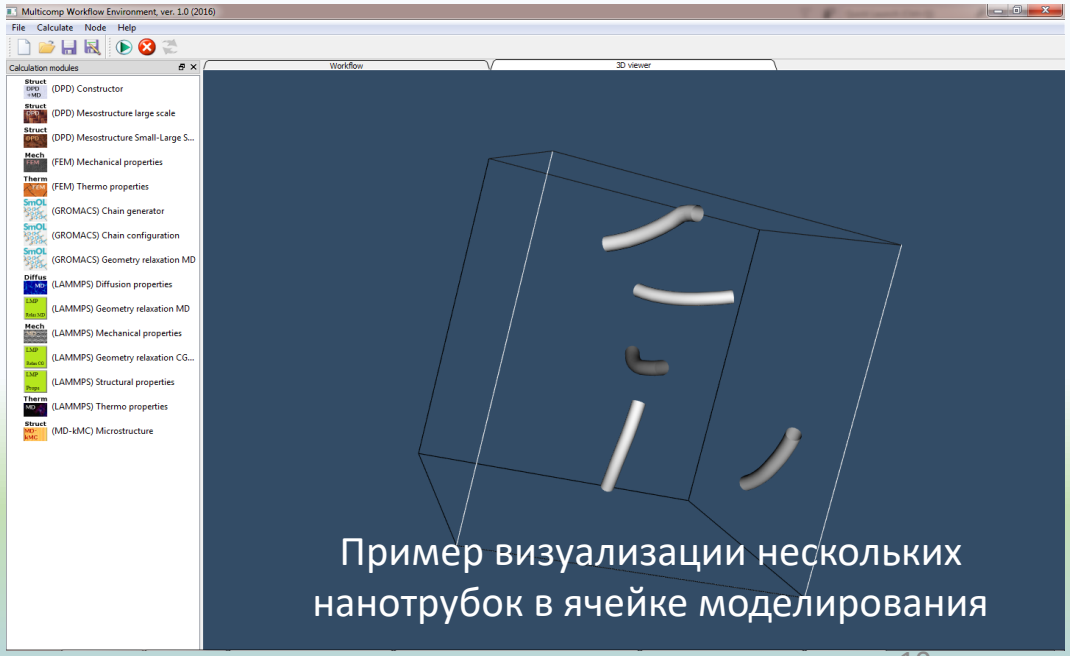
visualization

- The results are displayed using an interactive 1D / 2D / 3D visualization module consisting of 2 blocks: 1D visualization and 2D / 3D visualization.
- Block 1D visualization consists of an embedded window for displaying functional dependencies, a separate form containing a display window and a toolbar, a window for setting display parameters and auxiliary windows.
- The 2D / 3D visualization block consists of a built-in window for displaying 2D / 3D objects and grids and a separate form containing the display window, the main menu and the toolbar.

embeddable window for displaying functional dependencies



embedded 2D / 3D object and mesh display window



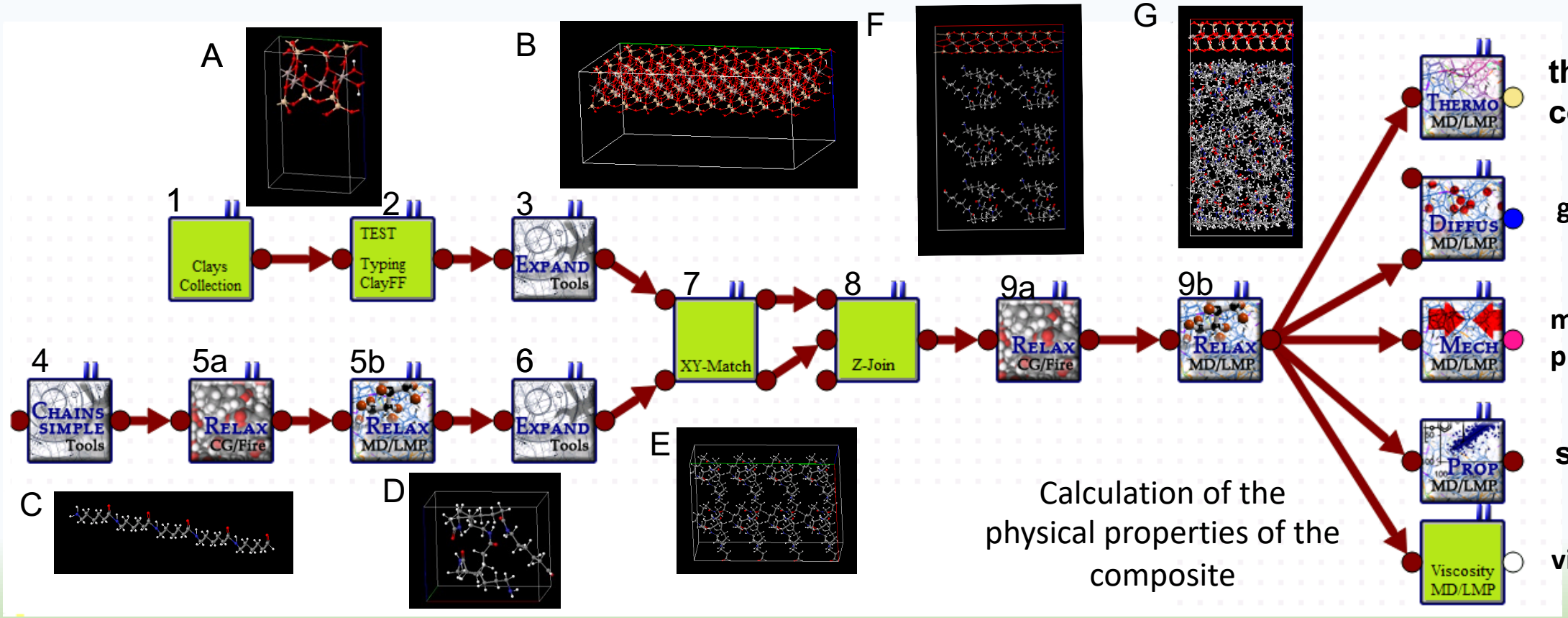
Пример визуализации нескольких нанотрубок в ячейке моделирования

calculation of mechanical properties of organomodified montmorillonite intercalated with polyamide-6

Generation of the atomistic structure of clay nanoparticles

Creation of a composite structure (connection of clay and polymer structures)

filler 15%



Generation of the atomistic structure of a polymer matrix

Elastic moduli obtained by calculation:

EPA6 = 2.8 Gpa EMMT = 232 Gpa Ecomposite = 41 GPa

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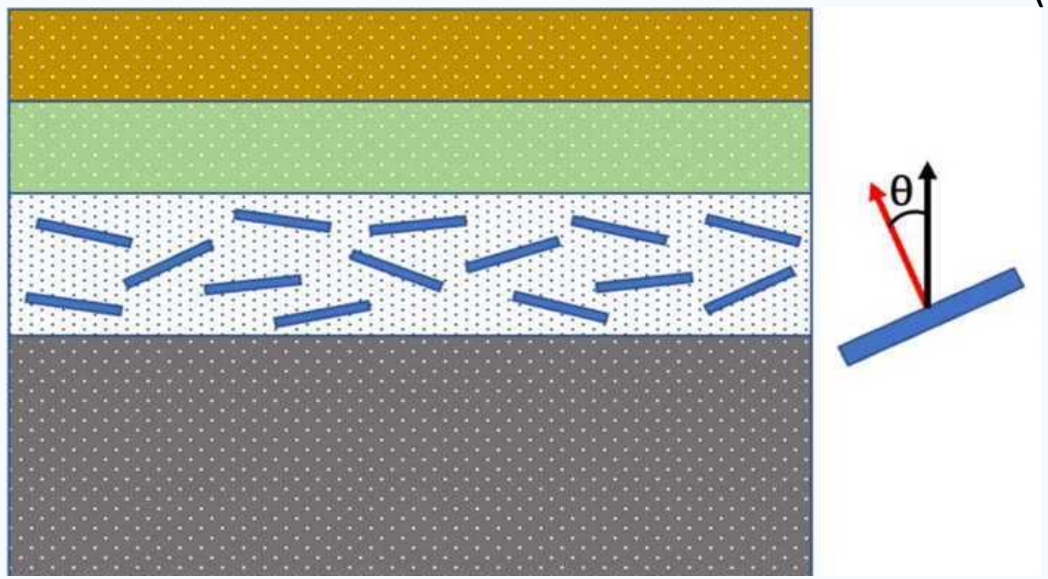
Skomorokhov A. S., Knizhnik A. A., Potapkin B. V. //The Journal of Physical Chemistry B. – 2019. – Т. 123. – №. 12. – С. 2710-2718.

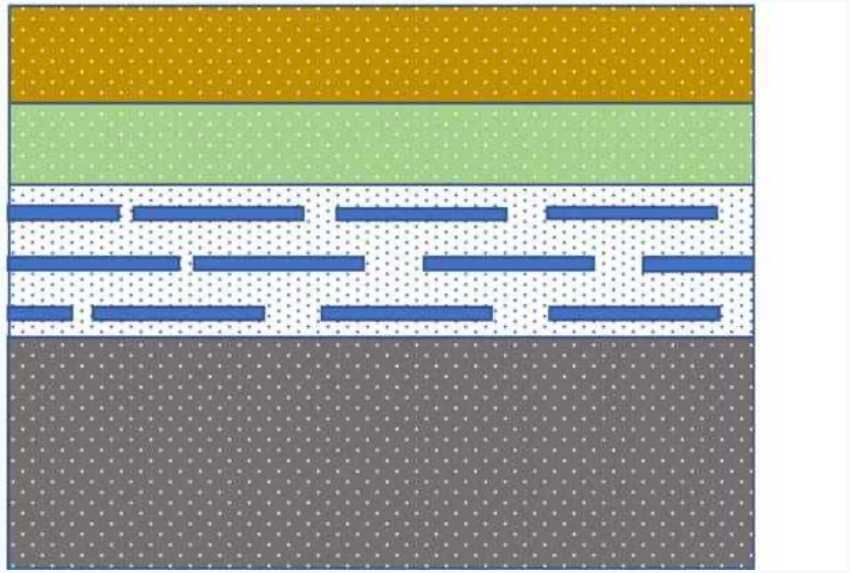
models of a barrier layer based on hybrid organic–inorganic multilayer films

(a)



orientationally disordered filler particles

(b)

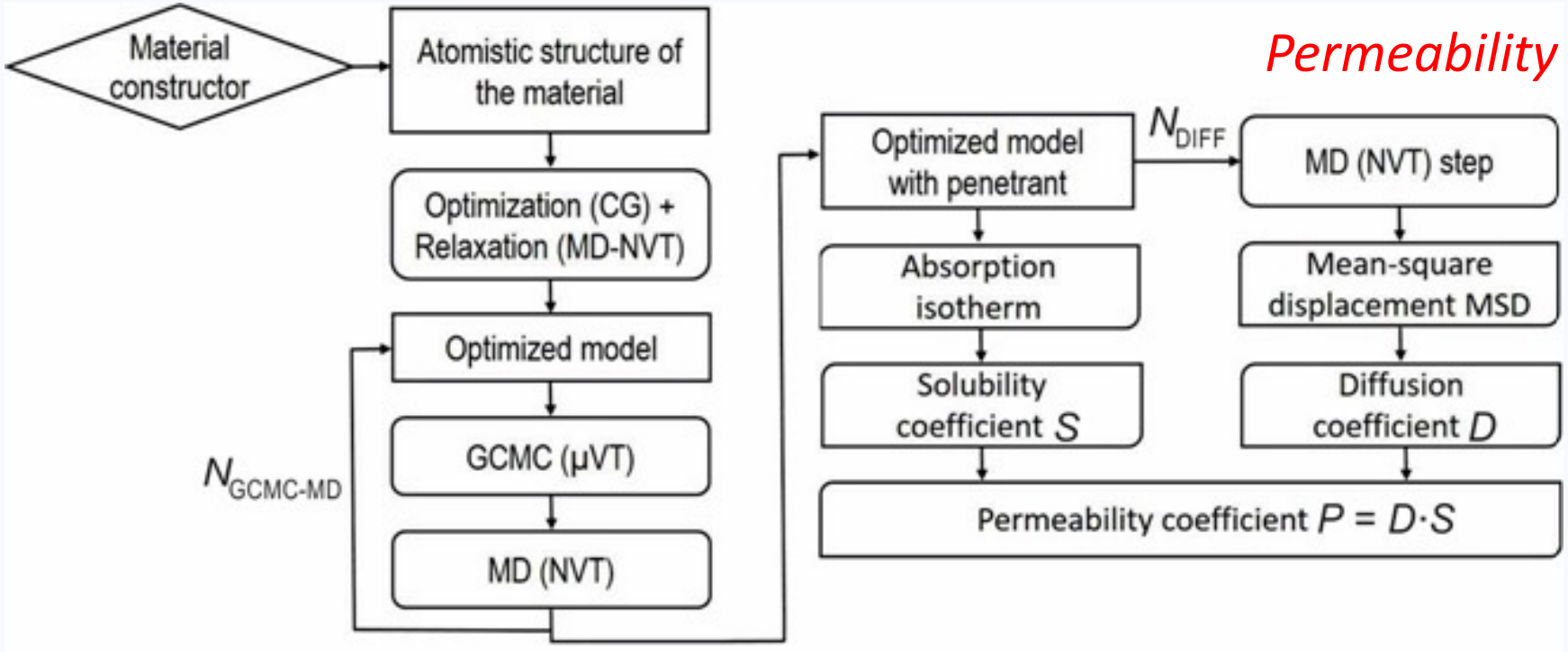


laminate structure with orientationally ordered filler particles

Different colors of the layers schematically show the use of different materials for the formation of the multilayer protective films.

general scheme for calculating permeability using combined MD and GCMC modeling

Module



- The gas barrier properties of PET, PE, PVDF, and PTFE were calculated using the "Permeability" module integrated into the MULTICOMP package.
- All calculations were performed using the PCFF force field [1].
- As a separate issue, we considered the sensitivity of our results to the choice of the valence-force field.
- For this purpose, the solubility of oxygen and water molecules was calculated using VFF COMPASS [2] and DREIDING [3].

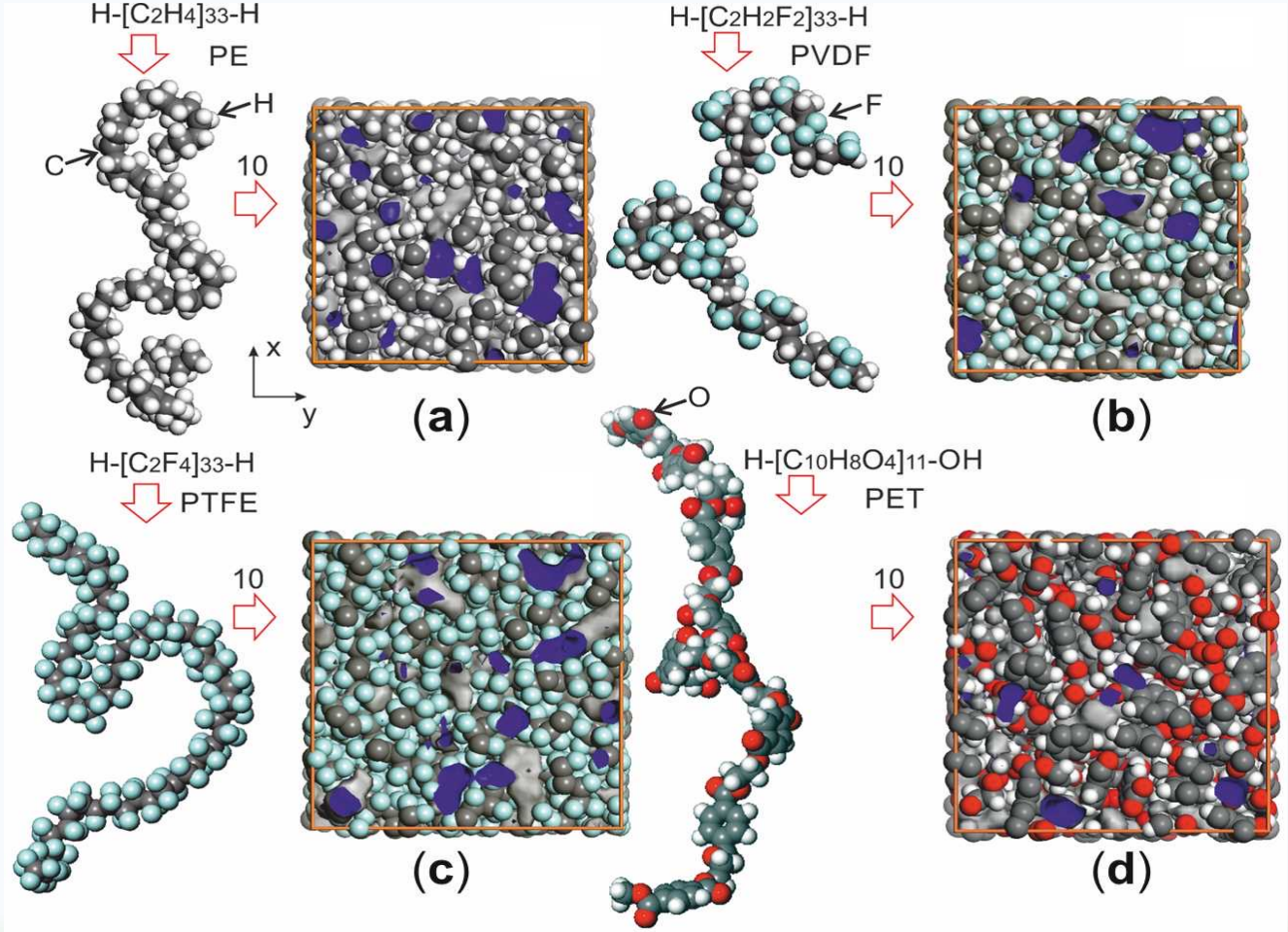
$S = d/dp\ Ncell(p)$

$D = \frac{1}{6} N \lim(t \to \infty)\ d/dt \sum_{(i=1)}^{N} \langle (\mathbf{r}i(t) - \mathbf{r}i(0))^2 \rangle$

$P = D \cdot S$

1. Sun, H. Ab Initio Calculations and Force Field Development for Computer Simulation of Polysilanes. Macromolecules 1995, 28, 701–712.
2. Sun, H. COMPASS: An Ab Initio Force-Field Optimized for Condensed-Phase ApplicationsOverview with Details on Alkane and Benzene Compounds. J. Phys. Chem. B 1998, 102, 7338–7364.
3. Mayo, S.L.; Olafson, B.D.; Goddard, W.A. DREIDING: A Generic Force Field for Molecular Simulations. J. Phys. Chem. 1990, 94, 8897–8909.

chain models of selected polymers



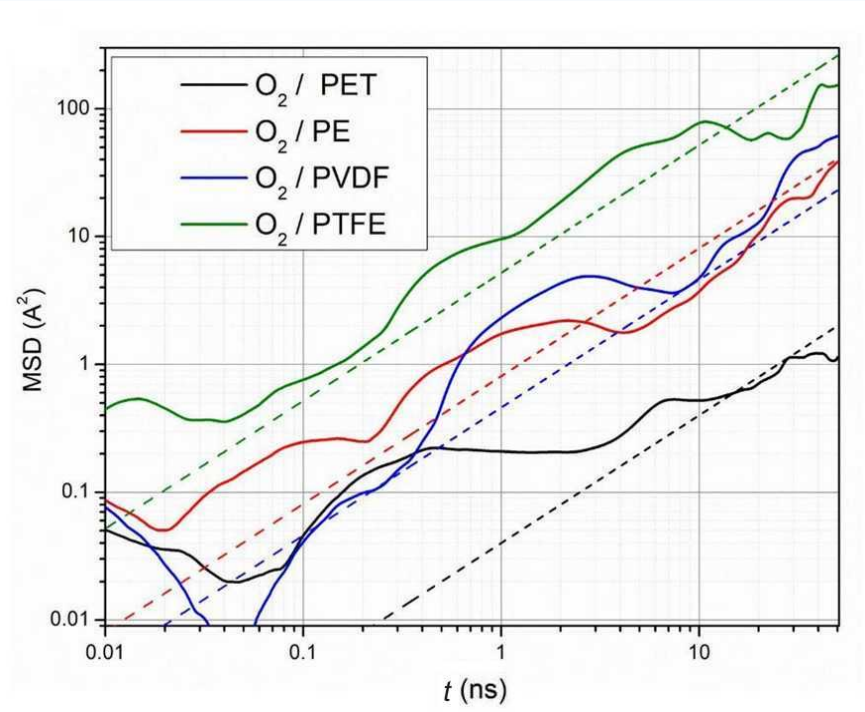
	Material			
Property	PET	PE	PVDF	PTFE
Density (g/cm^3)	1.4 ± 0.05	0.9 ± 0.05	1.8 ± 0.1	2.1 ± 0.1
Free volume fraction	0.13 ± 0.05	0.30 ± 0.05	0.23 ± 0.09	<0.25

- Polymer matrices were prepared using constructor modules (integrated into our previously developed MULTICOMP package) and the Class II Polymer Consistent Force Field (PCFF).
- Polymer chains were constructed using the "Polymer Chain" module.
- The degree of polymerization of the chains was set at to 33 for PE, PTFE, PVDF, and 11 for PET. The length of the polymer chains was chosen so that each chain contains approximately 200 atoms, as this value is sufficient to predict the transport properties of polymers.
- The samples of matrices were then obtained from 10 polymer chains using the "Polymer/Composite Constructor" module.

(a) polyethylene (PE),
(b) polyvinylidene fluoride (PVDF),
(c) polytetrafluoroethylene (PTFE),
(d) polyethylene terephthalate (PET)

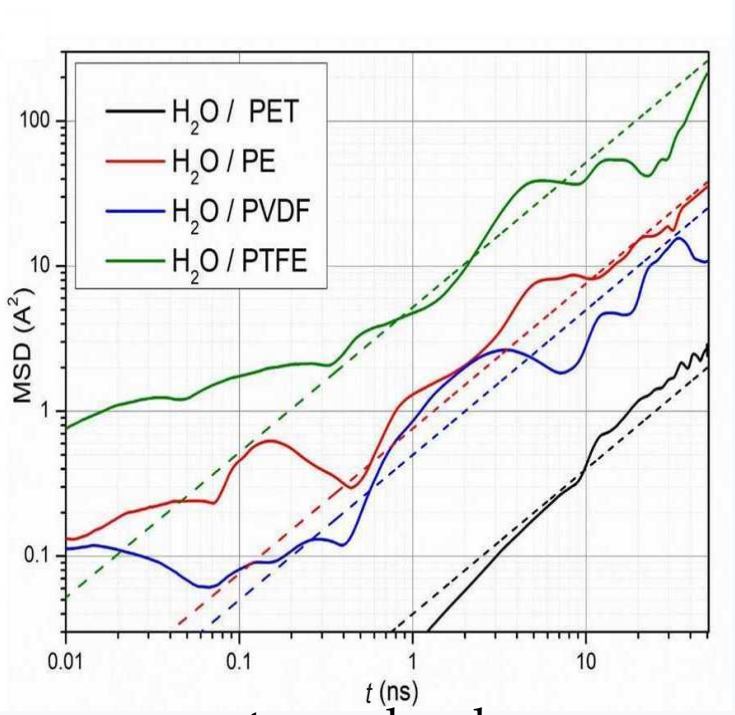
calculated MSD curves for PET, PE, PVDF, and PTFE obtained using the PCFF force field

(a)



oxygen

(b)



water molecules

Diffusion coefficients of oxygen and water molecules

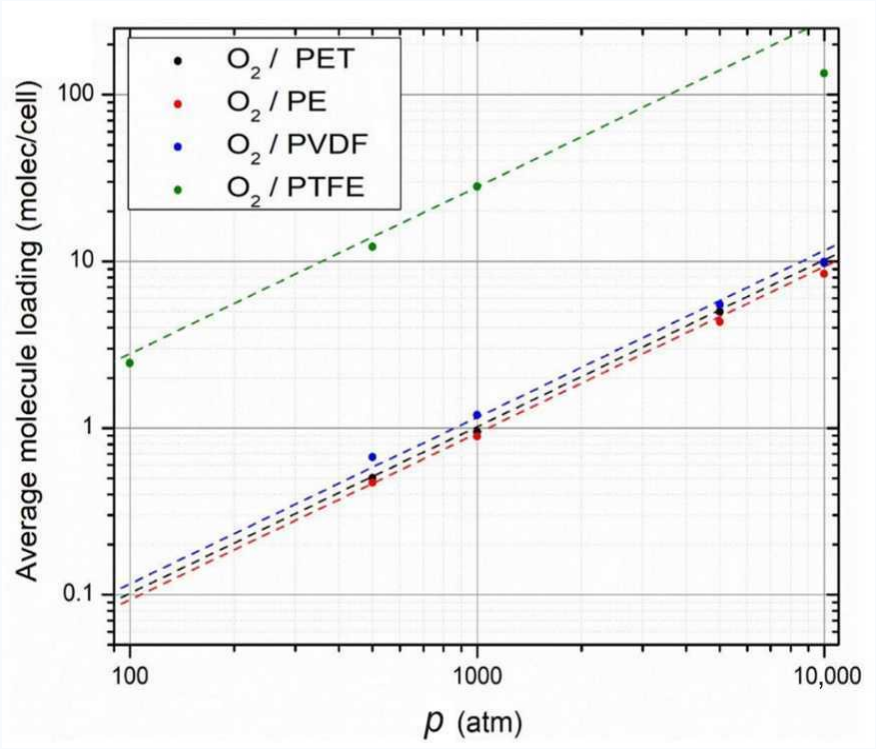
	$D(O_2)$ (cm^2/s)		$D(H_2O)$ (cm^2/s)	
Material	Calculation	Experiment [1]	Calculation	Experiment [1]
PET	$2.0 \pm 0.4 \times 10^{-8}$	$3–80 \times 10^{-9}$	$2 \pm 0.5 \times 10^{-8}$	$0.3–13 \times 10^{-8}$
PE	$2.7 \pm 0.7 \times 10^{-7}$	$0.2–12 \times 10^{-7}$	$3.8 \pm 0.7 \times 10^{-7}$	$0.6–13 \times 10^{-7}$
PVDF	$2.3 \pm 0.4 \times 10^{-7}$	1.7×10^{-7}	$2.5 \pm 1.0 \times 10^{-7}$	$5–8 \times 10^{-7}$
PTFE	$2.6 \pm 0.4 \times 10^{-6}$	1.5×10^{-7}	$2.6 \pm 0.6 \times 10^{-6}$	$1.5–12 \times 10^{-7}$

The observed trend (PTFE > PVDF > PE > PET) of the diffusion coefficients of both O_2 and H_2O molecules is determined by the characteristics of the interaction of dissolved molecules with polymers and the free volume values in the created samples.

1. NIMS Materials Database (MatNavi). Available online: https://mits.nims.go.jp/en/ (accessed on 3 July 2023)

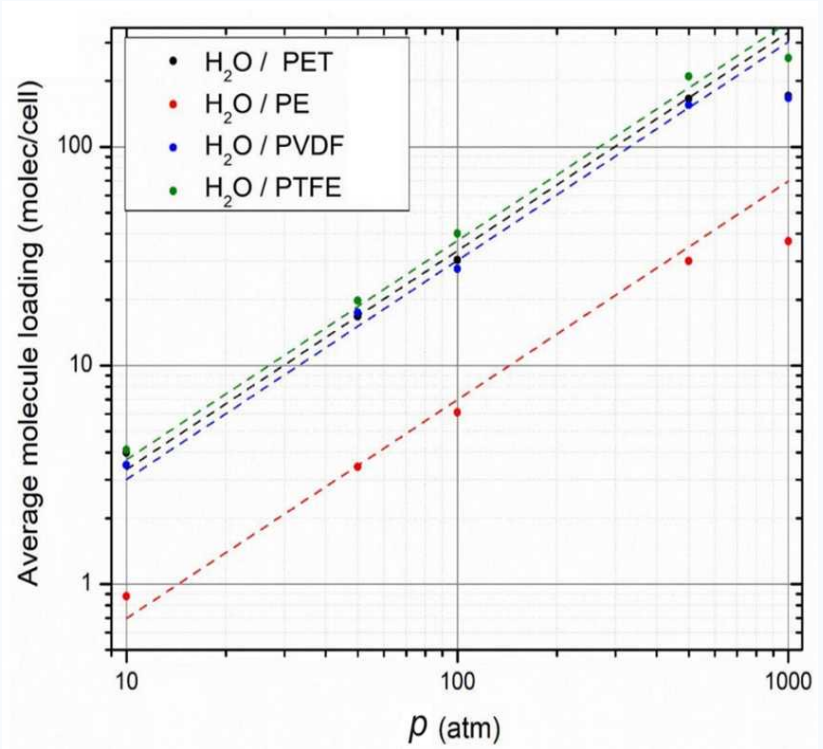
calculated dependencies of the number of oxygen and water molecules in the simulation cell Ncell(p) for PET, PE, PVDF, and PTFE obtained using the PCFF force field

oxygen



(a)

water molecules



(b)

Solubility coefficients of oxygen and water molecules

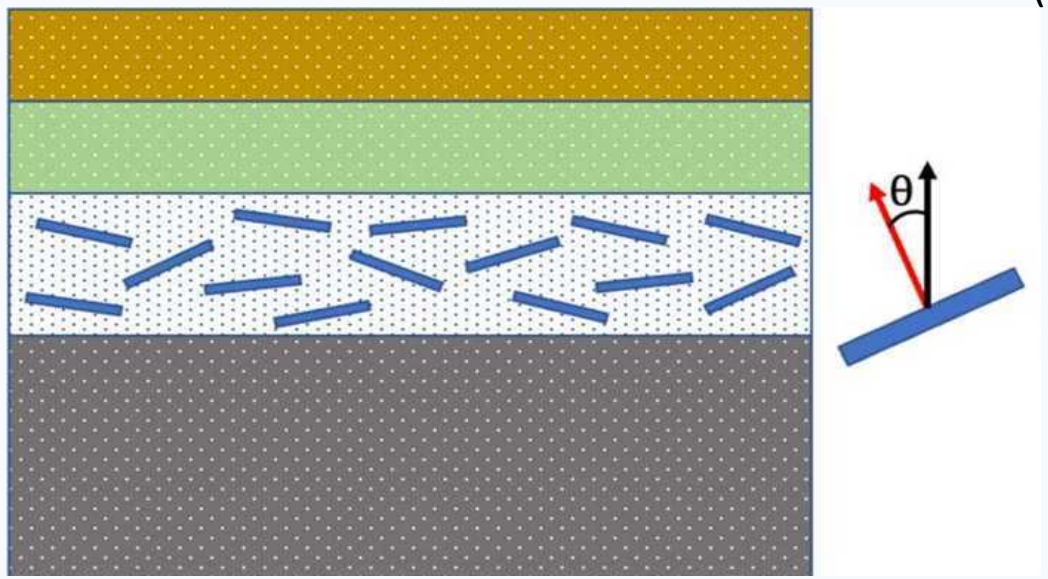
	$S(O_2)$ ($cm^3(STP)/(cm^3Pa)$)		$S(H_2O)$ ($cm^3(STP)/(cm^3Pa)$)	
Material	Calculation	Experiment [84]	Calculation	Experiment [84]
PET	$2.2 \pm 0.8 \times 10^{-8}$	$6–10\times10^{-7}$	$7.2 \pm 0.7\times10^{-6}$	$3–8\times10^{-9}$
PE	$2.0 \pm 1.0\times10^{-8}$	$2–5\times10^{-7}$	$1.5 \pm 2\times10^{-6}$	5.8×10^{-8}
PVDF	$2.5 \pm 1.5\times10^{-8}$	3.6×10^{-7}	$6.5 \pm 0.6\times10^{-6}$	–
PTFE	$6.0 \pm 1.0\times10^{-7}$	$6–9\times10^{-7}$	$8 \pm 1.5\times10^{-6}$	–

permeability coefficients of oxygen and water molecules for PET, PE, PVDF, and PTFE

	$P(O_2)$ (Barrer)			$P(H_2O)$ (Barrer)		
Material	MD-GCMC Simulations	Bicerano Model	Experiment [39,84]	MD-GCMC Simulations	Askadskii Model	Experiment [39,84]
PET	**0.01–0.02**	**0.04**	**0.013–5**	**1–2**	**87**	**100–1300**
PE	**0.2–0.6**	**4.47**	**0.04–5**	**2–12**	**60**	**20–75**
PVDF	**0.07–0.2**	**8.91**	**0.02–1.8**	**8–30**	**193**	**–**
PTFE	**17–22**	**7.65**	**2.5–6**	**10–50**	**328**	**3–8**

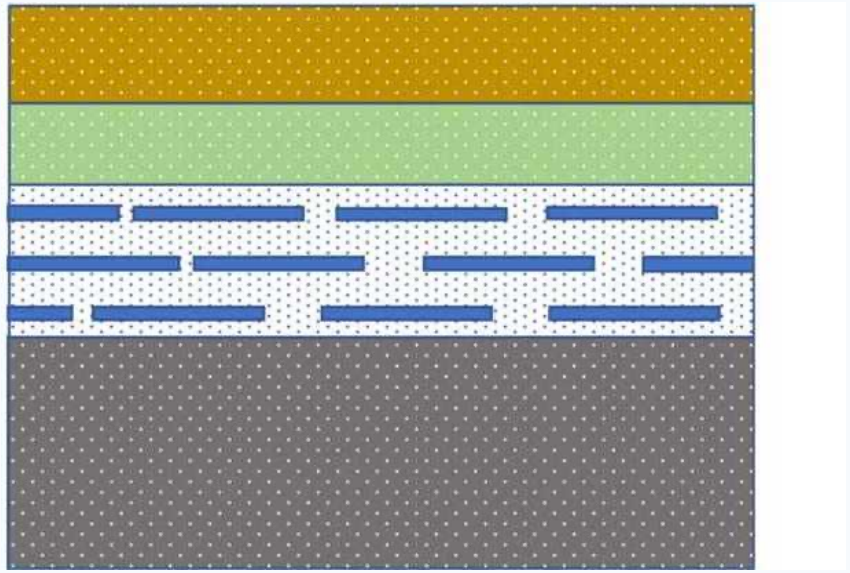
models of a barrier layer based on hybrid organic–inorganic multilayer films

(a)



orientationally disordered filler particles

(b)

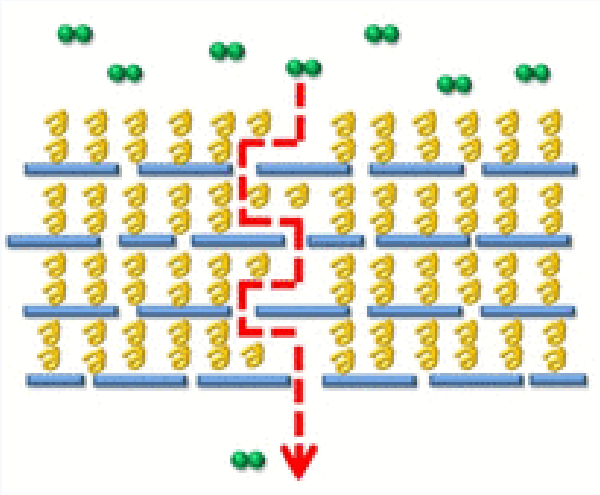


laminate structure with orientationally ordered filler particles

Different colors of the layers schematically show the use of different materials for the formation of the multilayer protective films.

continuous model

- Monte Carlo methods are often used to analyze transport in complex configurations of in-organic layers
- In the initial state, the molecule is located in the first polymer layer near the outer surface of the film, and then the molecule makes microsteps, i.e., random displacements whose value depends on the distance d to the nearest barrier:
- d = ½ max (min (d), dmin)
- The minimum step size dmin depends on the minimum geometric size in the system (e.g., the size of the hole or the thickness of the layered filler). After displacement, the total diffusion time increases by the value
- Δt = d2/6 Di
- The probability of a molecule passing from one polymer layer to another is deter-mined by the ratio of its solubilities:
- wi,i+1 = min(Si+1/Si, 1)
- The model gives the diffusion time τdiff of the molecule throughout the thickness of the multilayer coating. This time is then averaged over the number of attempts for a set of molecules. By comparing the average diffusion times in a multilayer system with inor-ganic fillers, <τdiff>, and without them, <τdiff>free, we can estimate the change in the per-meability of the coating as:
- P/Pfree = <τdiff>free/<τdiff>
- where Pfree is the permeability of the multilayer system without fillers and inorganic layers:
- Pfree =1/(∑i 1/Pifree)

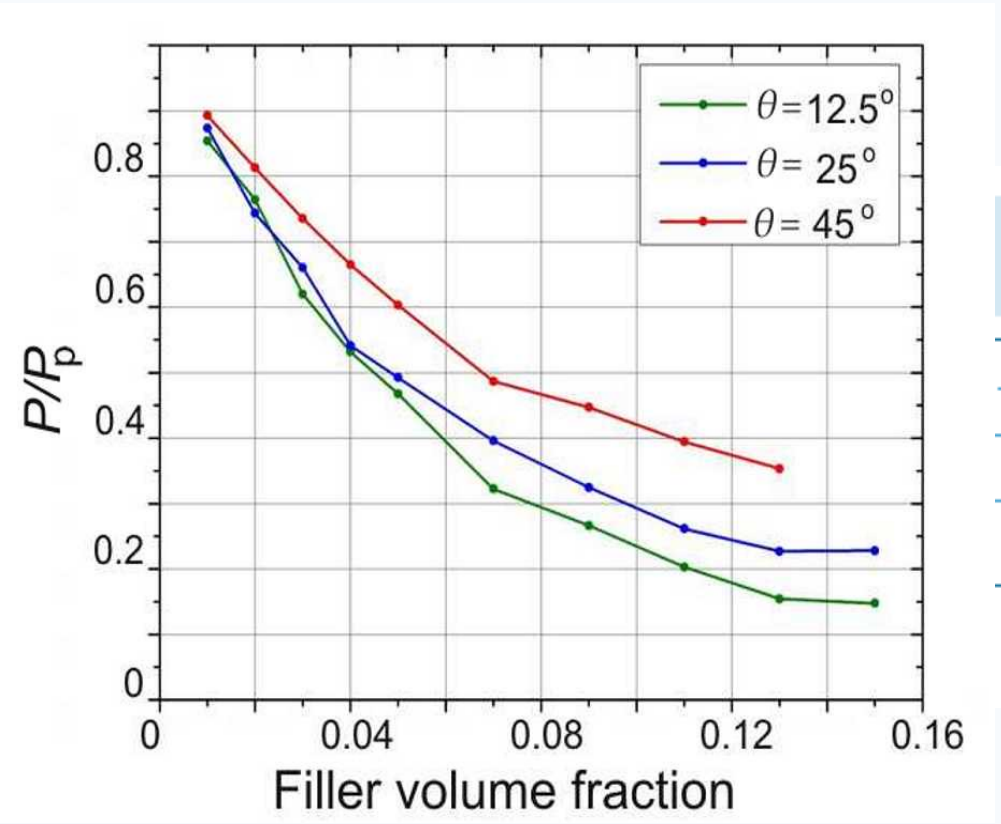


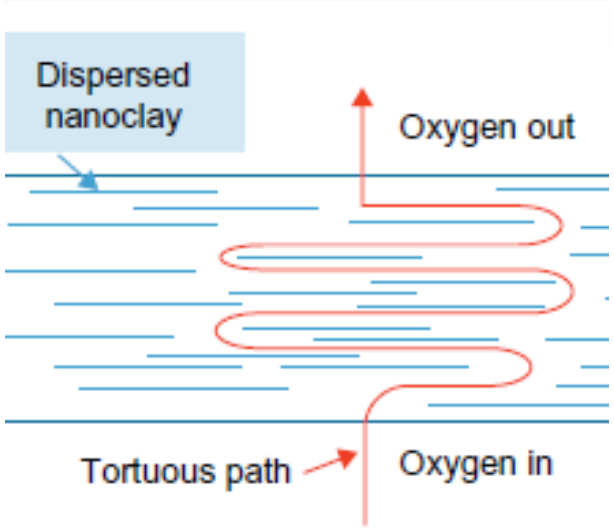
minimum step size dmin depends on the minimum geometric size in the system (e.g., the size of the hole or the thickness of the layered filler)

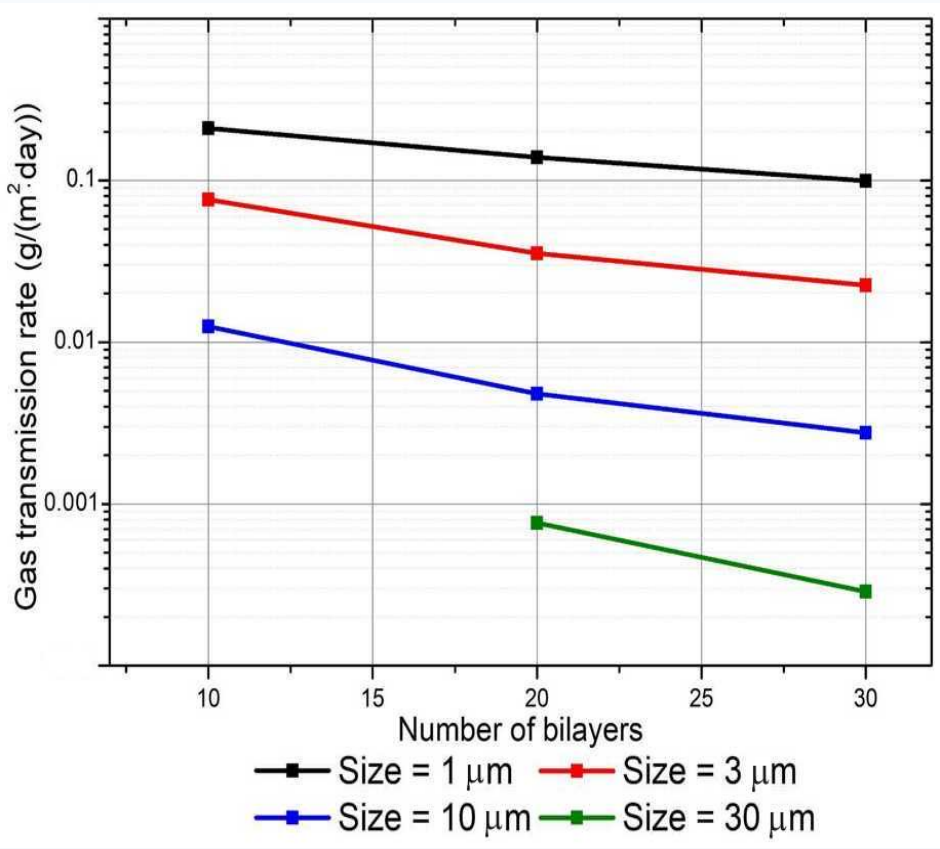
where S_i is the solubility of the current layer and S_{i+1} is the solubility of the layer into which the molecule is trying to penetrate

Pifree = Si·Di is the permeability of the i-th layer of the multilayer system without fillers

results based on the continuous model







The calculated dependence of the ratio of the permeability of the polymer layer with fillers P to the permeability of a pure polymer layer P_p on the filler volume fraction with the aspect ratio of α = 60 at different values of the angle $\theta_{max} = 12.5^\circ$, 25°, and 45

Vapor permeability of the modified protective coating with a clay–polymer laminate layer as a function of the number of laminate bilayers for clay particle sizes of 1, 3, 10, and 30 μm.

conclusion

- A multiscale computational model was developed to predict the barrier properties of multilayer protective films consisting of alternating polymer and hybrid layers containing clay minerals as fillers.
- Oxygen and water molecules were used as penetrant molecules.
- The model combines three levels of calculation, namely continuum, all-atom, and QSPR.
- To quickly parameterize the continuum model, the possibilities of using calculation schemes based on QSPR and full-atom models are were considered.
- Full atomic level of simulations allows us to make good predictions of the oxygen permeability of pure polymers in agreement with the results of the Bicerano model and experimental studies.
- We have obtained evidence that existing QSPR schemes need to be improved to better predict water vapor permeability. In the case of all-atom simulations, it is necessary to make a more accurate choice of the sizes of the polymer samples and to adjust the parameters of the valence -force field responsible for describing the water/polymer interactions.
- Based on the developed methodology, a "*Permeability*" module was created and integrated into the **MULTICOMP** package.
- The "Permeability" module allow the estimation of the transport properties of polymer materials for gas molecules (i.e., diffusion, solubility, and permeability coefficients).
- Using the result obtained and the continuum model, we demonstrate that the maximum effect on the reduction of in permeability from the addition of clay fillers to the polymers is obtained when using minerals in which the filler particles have high aspect ratios. It is also desirable to ensure a high degree of orientational order. We have shown that the product of the aspect ratio of the disk-shaped filler and its volume fraction must be greater than 10 to obtain a noticeable effect in reducing permeability. In addition, this should be combined with the use of polymer matrices with minimal oxygen and water permeability.

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Contact us:
Kintech Lab Ltd.
WWW: http://www.kintechlab.com
E-mail: support@kintech.ru - for general service and product information
info@kintech.ru - for all questions concerning Kintech Lab software
Phone: +7 (499) 704 25 81