1. COMPNANOCOMP final publishable summary report

Executive summary

The COMPNANOCOMP project aimed at the development of multiscale simulation methodology and software for predicting the morphology (spatial distribution and state of aggregation of nanoparticles), thermal (glass temperature), mechanical (viscoelastic storage and loss moduli, plasticity, fracture toughness and compression strength), electrical and optical properties of soft and hard polymer matrix nanocomposites from the atomic-level characteristics of their constituent nanoparticles and macromolecules and from the processing conditions used in their preparation.

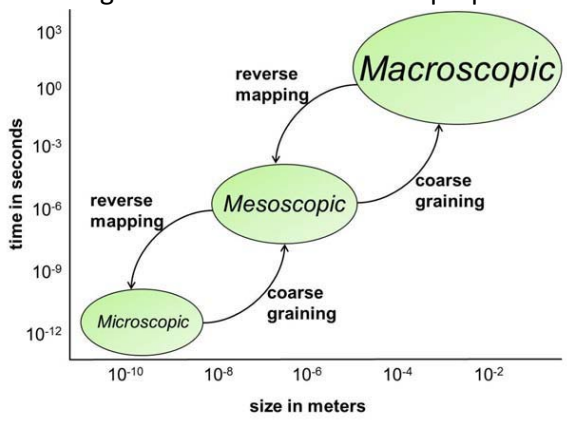

Figure 1. Bridging several length and time scales

The hierarchical simulation methodology and software to be developed was validated against two main categories of systems: silica-filled natural and synthetic rubbers and carbon nanotube filled thermoset resins.

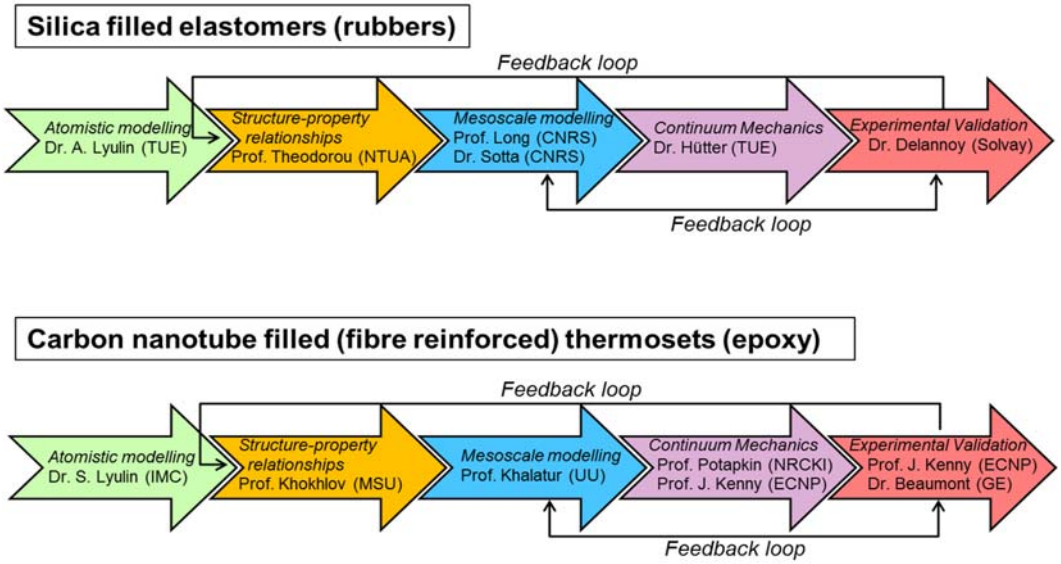

Figure 2. Time and length scale collaborations in the chain

The COMPNANOCOMP initiative consists of two collaborative projects being executed by an EU consortium (8 partners distributed in 6 work packages WP1 to WP6) and a Russian consortium (4 partners) under the FP7 framework and the Federal Russian government.

Project objectives

The central goal of this project is the development of a multiscale simulation methodology and software for reliably predicting the morphology (spatial distribution and state of aggregation of nanoparticles), network formation by cross-linking, thermal (glass temperature), mechanical (viscoelastic storage and loss moduli, stress-strain relations), electrical (conductivity) and optical (scattering) properties of rubbery and glassy polymer matrix nanocomposites from the atomic-level characteristics of their constituent nanoparticles and macromolecules and from the processing conditions used in their preparation. Inputs to the simulation will be the chemical nature, volume fraction, size, and surface treatment of the nanoparticles, and the chemical nature, molar mass, network formation and architecture of the macromolecules.
The developed modelling and simulation methodology should be linking the microscopic, mesoscopic and macroscopic levels in a rigorously predictive and computationally tractable way with a minimum of empirical, physically non-meaningful fitting parameters to address the structure and properties of industrially highly relevant nanocomposite materials.
The hierarchical simulation methodology and software to be developed was validated against two main categories of systems: silica-filled natural and synthetic rubbers and carbon nanotube filled thermoset resins.
The detailed objectives of each work package are listed below.

Work Package 1 (WP1) of the COMPNANOCOMP project aimed at developing a hierarchy of molecular modelling approaches for predicting the thermal, rheological, and mechanical properties of nanocomposites consisting of a soft polymer (melt or rubber) matrix and spherical solid nanoparticles, with special attention to the silica-filled natural rubber "green tyre" materials produced and characterized by Solvay in WP3. It is distinguished from WP2, with which it closely interacts, in that it is based on an explicit molecular representation of the polymer chains. Three interconnected levels of representation are invoked in WP1 to bridge the formidable spectrum of length scales and time scales governing the materials under investigation: A detailed (atomistic, united-atom) representation, in which both polymer chains and nanoparticles are modelled as chemically explicit assemblages of atoms or small groups of atoms, and their behaviour is tracked with molecular dynamics; a coarse-grained Field Theory-inspired representation, cast in terms of freely jointed chains for the polymer and single spherical entities for the nanoparticles and equilibrated with a specially designed Monte Carlo technique; and an even coarser network representation for the polymer in terms of chain ends, crosslink, entanglement, adsorption, and grafting points.

The main project objective of **Work Package 2** (WP2) was to simulate the effective mechanical and electrical properties of polymer nanocomposites. A toolbox should be developed that allows the user to specify the materials and their interactions, and calculate the desired mechanical or electrical properties, respectively. This goal should be achieved by formalizing a multiscale strategy.

Work Package 3 (WP3) aimed at finding the right correlation between the modelling results and experimental data provided by the industrial partners Rhodia/Solvay and General Electric (GE). The modelling results should be verified on reinforcement and electrical properties of practically relevant nanocomposite systems: silica filled rubber (Rhodia) and CNT filled

thermosets (ECNP/GE). Feedback from experimental studies serves as input for improvement of the modelling codes and software.

The main goal of **Work Package 4** (WP4) was the integration of EU and Russian research efforts in the framework of the project, establishing close scientific collaboration between the participants, and building up corresponding educational programs through the exchange of researchers between EU and Russian partners. Such a synergetic approach allows one not only to carry out fundamental research but also to train highly qualified young scientists working in the area of computer modelling of polymer nanocomposites. The exchange of the researchers in the frame of the project was facilitated by the existing contacts between Moscow State University, Eindhoven University of Technology, Institute of Macromolecular Compound St. Petersburg and University of Ulm.

Work Package 5 (WP5) was responsible for the dissemination of the project results to the public at large– via presenting the results from this project at scientific meetings and publishing in highly ranked scientific journals. Another prime objective is to explore new material combinations opening potential new market (e.g. truck tires and conductive thermosets) based on the accurate predictions of mechanical and electrical properties of the modelling software package.

The prime objective **of Work Package 6** (WP6) is the management of the EU work according to the rules and regulations laid down in the Grant Agreement closed between the EC and the consortium and the coordination of work with RU-COMPNANOCOMP. The project management concerns financial, contract and intellectual property management of the project.

Summary of results

The main goal of **Work Package 1** (WP1) has been to understand the reinforcement of polymer-matrix nanocomposites by filler particles, in particular, how the chemical constitution of their components influence macroscopic (structural and mechanical) properties of the resulting nanocomposite. A hierarchical bottom-up approach has been developed involving atomistic Molecular Dynamics (MD), Field Theory-inspired Monte Carlo (FT-i MC) and coarse-grained Brownian Dynamics coupled with kinetic Monte Carlo (BD/kMC) simulations. In parallel, calculations based on Self Consistent Field theory and Transition State Theory (SCF/TST) have provided insight into the slow adsorption/desorption kinetics of end-constrained polymer strands.

Atomistic MD simulations of crosslinked (1,4) cis-polyisoprene (PI) - silica films have been conducted. The PI samples have been prepared by introducing realistic coupling and covering agents in order to quantify the influence of specific chemical features on the local structure (local density and segmental ordering) and local segmental dynamics. The results have been reported for various degrees of cross-linking and film thicknesses.

At the FT-i MC level, polymer chains are represented as freely jointed sequences of Kuhn segments. Nanoparticles (e.g. SiO2) are modelled as structureless spheres interacting with each other and with the Kuhn segments through Hamaker potentials. For polymer-polymer

interactions, however, an effective energy function is used, which prevents large departures of the local polymer density from its value in the bulk melt everywhere in the system. Many-particle simulations at this level have been conducted, indicating aggregation of bare silica particles in high molar mass PI melt.

By randomly linking chains at the Ft-i MC representation level, initial configurations for network simulations of slip-spring models have been created, where cross-links, entanglements, chain ends, and lumped polymer beads, each standing for ca. 5 Kuhn segments, are the degrees of freedom of the polymeric matrix. Our BD/kTST methodology is cast in terms of these degrees of freedom, collectively referred to as "nodal points". From the thermodynamic point of view, the system under study is fully described by a Helmholtz energy function which accounts for the entropic springs connecting nodal points, non-bonded interactions (derived from an appropriate equation of state, e.g. the Sanchez-Lacombe) and Hamaker interactions between nodal points – nanoparticles and nanoparticles – nanoparticles. Brownian simulations at this level, operating at the length scales of up to 1 μm and time scales up to 1 ms, account for changes in segmental mobility induced by the nanoparticles and track elementary events of chain slippage across entanglements, chain adsorption/desorption from surfaces and chain disentanglement/re-entanglement. They have been validated against the rheological properties of long-chain PI melts.

A method has been formulated, based on combining self-consistent field theory with dynamically corrected transition state theory, for estimating the rates of adsorption and desorption of end-constrained chains (e.g., by cross-links or entanglements) from a polymer melt onto a solid substrate, needed in the BD/kMC approach. This method has been tested on a polyethylene/graphite system, where it was parameterized based on atomistically detailed molecular simulations. For short-chain melts, which can still be addressed by molecular dynamics simulations with reasonable computational resources, this SCF/TST approach gives predictions of the adsorption and desorption rate constants which are gratifyingly close to molecular dynamics estimates.

Within **Work Package 2** (WP2) an approach has been developed that describes both the elastic and the dissipative moduli of reinforced elastomers, with good agreement with experimental data. Furthermore, the pure elastomer has been examined and modelled in more detail, and very good qualitative agreement with the real behaviour in the linear and plastic regime of deformation has been found, including the reproduction of Payne effect and shear-banding below Tg and after yield. The mechanism underlying plasticization in polymers can be considered understood, which is essential for understanding silica-filled elastomers. To link and transfer such knowledge with macroscopically relevant mechanical behaviour of the composite, a concurrent multiscale model has been developed successfully.

Furthermore, a multiscale methodology has been developed for generating atomistic structures of epoxy resins, that have been used subsequently in atomistic MD simulations of highly crosslinked epoxies filled with multiwall carbon nanotubes (MWCNT). Most importantly, the effect MWCNTs on the glass transition temperature has been addressed. To study the effect of adding nanotubes to elastomers on the stress-strain behaviour, DPD simulations have been performed. As for the electrical conductivity of CNT-filled thermosets, detailed experimental studies have revealed the significant improvement of electrical properties in simple DGHEBA/DETA epoxy systems with CNTs, especially when aligning the

CNT with an applied AC electric field, without migration of the CNTs. A model to simulate the alignment time of CNTs with electric field has been validated, and a model has been developed for the estimation of electrical properties based on FEM calculations. Finally, attention has been paid to (i) the relation between final electrical and mechanical properties and CNTs parameters for DGEBA/DETA epoxy nanocomposites, and (ii) the CNTs damaging in relation with nanocomposites processing conditions.

Work Package 3 provided experimental feedback on the two systems: (1) silica-filled elastomers and (2) CNTs or silica filled epoxy systems reinforced with carbon fibre.
Spherical silica particles of different sizes (15 and 50 nm in diameter) have been synthetized by Solvay to provide the COMPNANOCOMP consortium with some analytical filled elastomer samples. The synthesis route has been optimized to guarantee a very narrow distribution of size.
Dispersion of the fillers within the polymer matrix has also been developed and works nicely for the 50 nm case. The 15 nm spherical particles seem to be more complex to disperse.
Nice mechanical properties have been measured for the 50 nm samples. The origin of the quality of the reinforcement is still to be understood and will be the subject of different collaborations after the end of the COMPNANOCOMP project between Solvay and CNRS or TUE.
Another goal of this work package was the improvement of mechanical and electrical performance of Carbon fibre composites for aerospace and wind energy applications.
Nanofilled matrices using CNTs (for aerospace applications) and silica (for wind energy applications) have been used to improve the performance of carbon fibre reinforced composites.
In aerospace application different typologies of CNTs have been used in different concentrations in order to find the best solution for electrical and mechanical properties improvement. In particular for electrical properties also the alignment in RTM6 resin has been tested.
In wind energy application three types of silica nanoparticles have been used and also in this case specific work to optimise the content was performed
The dispersion of nanoparticles and the infusion of nanoparticles are the most important processing steps. In the case of CNTs three roll milling approach has been used since with RTM6 was revealed the best processing technology. In the case of silica nanoparticles rotational mixing has been adopted. In both case good dispersion of fillers has been achieved.
Improvements in electrical and mechanical performance of carbon fibre composites have been achieved in aerospace application, and in particular the electrical conductivity through the thickness direction has been improved of one order of magnitude.
In the case of wind energy an improvement of mechanical performance is achieved thanks to the use of silica filled epoxy in carbon fibre composites.
An exhaustive characterization of matrices and composites properties in terms of mechanical and electrical behaviour has been performed in order to supply to Russian partners good experimental data for modelling validation.
Finally a study of possible alternative solution to improve the electrical properties of carbon fibre epoxy composites has been performed.

Potential impact of results

The final result from **WP1**, a joined effort of NTUA and TUE, will be a set of verified and validated codes implementing the interconnected molecular simulation strategies outlined above and capable of predicting the structure, dynamics, and viscoelastic properties (storage modulus *G*', loss modulus *G*") of nanocomposites consisting of spherical solid particles in soft amorphous polymer matrices, starting from the molecular characteristics of the polymer chains and filler particles. This will be of great value in nanocomposite materials design.

The extended model developed by the LPMA in **WP2** allows for a physical description of reinforcement mechanisms of nano-filled elastomers and simulation of the non-linear (plastic yield, strain hardening,…) behavior of confined polymers. When implemented in a concurrent dynamic two-scale model (developed by TUE), it will allow for quantitative predictions regarding mechanical properties of filled elastomers, and thus contribute to the conception and realization of more efficient rubbers (rolling resistance, resistance to tear and wear, ...) and to shortening development times of new products.
The simulation approaches and models developed by UU for multiscale modelling of CNT-filled nanocomposites are expected to provide both a qualitative description of basic phenomena and the optimization and quantitative prediction of nanocomposite materials properties, including the description of microstructural evolution and chemistry-driven problems. An improved understanding of these materials at multiple length scales obtained by modelling will give helpful insights into improving their performance.
The models for electrical properties and for alignment of CNTs developed by ECNP will be very useful for optimizing the materials and process design at industrial level. Both models are very easy to use and the current experimental validation shows a good reliability with experimental results.

The new liquid moulding based process for the production of nanoparticles filled fibre reinforced composites, developed by ECNP within **WP3**, offers an useful and easy method to minimize the filtration of nanoparticles due to carbon fibre lamina which is recognized as a key problem in infusion processes with nanofilled resin.
The developed by Solvay new method to synthesize spherical particles of silica of different chosen radii can be of high importance in the analytical understanding of the role of morphology in the mechanical properties of filled elastomers. Solvay hopes that this understanding will foster new developments of original morphologies that the company will sell in a near future. The new method will also be used in other research projects.

Dissemination activities

Large number of manuscripts have been prepared and published in high ranked scientific journals (see the table below). Several more manuscripts are under preparation and will be submitted for publication after the project is officially terminated.

Scientific journal	***Title and authors***
Book "Supercomputer Technologies in Science and Educations", Moscow: MSU, **2012**, p. 184-195	P. G. Khalatur, A. R. Khokhlov, A. A. Gavrilov, *"Unusual forms of self-assembly in the polymer world"*
Soft Matter, **2013**, 9, 4067-4072	A. A. Gavrilov, A. V. Chertovich, P. G. Khalatur and A. R. Khokhlov, *"Effect of nanotube size on mechanical properties of elastomeric composites"*
Macromolecules, **2013**, 46, 4670-4683	G. G. Vogiatzis and D. N. Theodorou, "S*tructure of polymer layers grafted to nanoparticles in silica-polystyrene nanocomposites"*
Macromolecules, **2013**, 46, 4684-4690	A. A. Gavrilov*,* A. V. Chertovich, "*Self-Assembly in Thin Films during Copolymerization on Patterned Surfaces*"
Macromolecules, **2013**, 46, 6357-6363	S. V. Lyulin, A. A. Gurtovenko, S. V. Larin, V. M. Nazarychev, A. V. Lyulin, "*Microsecond Atomic-Scale Molecular Dynamics Simulations of Polyimides"*
J. Chem. Phys., **2013**, 139, 224901-10	A. A. Gavrilov, Y. V. Kudryavtsev, A. V. Chertovich, *"Phase diagrams of block copolymer melts by dissipative particle dynamics simulations"*
Macromolecules, **2014**, 47, 387−404	G. G. Vogiatzis and D. N. Theodorou, "*Local Segmental Dynamics and Stresses in Polystyrene–C60 Mixtures"*
J. Chem. Phys, **2014**, 140, 114903-14	D. V. Guseva, P. V. Komarov and A. V. Lyulin, *"Molecular-dynamics simulations of thin polyisoprene films confined between amorphous silica substrates"*
Polymer Science, Ser. A, **2014**, 56(1), 90-97	A. A. Gavrilov, A. V. Chertovich, *"Computer simulation of random polymer networks: Structure and properties"*
Soft Matter, **2014**, 10, 1224-1232	S. V. Lyulin, S. V. Larin, A. A. Gurtovenko, V. M. Nazarychev, S. G. Falkovich, V. E. Yudin, V. M. Svetlichnyi, I. V. Gofman and A. V. Lyulin, *"Thermal properties of bulk polyimides: Insights from computer modeling versus experiment"*
RSC Advances, **2014**, 4, 830-844	S. V . Larin, S. G. Falkovich, V. M. Nazarychev, A. A. Gurtovenko, A. V. Lyulin, S. V. Lyulin**,** *"Molecular-dynamics simulation of polyimide matrix pre-crystallization near the surface of a single-walled carbon nanotube"*
Macromolecules, **2014***,* 47, 6964 - 6981	D. N. Theodorou, G. G. Vogiatzis and G. Kritikos, *"Self-Consistent-Field Study of Adsorption and Desorption Kinetics of Polyethylene Melts on Graphite and Comparison with Atomistic Simulations"*

During the reporting period the researchers presented actively their results (11 poster presentations and 24 oral presentations) at many internationally reworded conferences and symposiums, with a large part of invited talks.

Two partners of COMPNANOCOMP – Jean Yves Delannoy (Solvay) and Denka Hristova-Bogaerds (DPI) participated at the kick-off meeting of the European Materials Modelling Council (EMMC) on 5 November 2014 in Brussels. EMMC targets to unite the modelling community in Europe and to bring into commercialization many models and codes developed within the EU funded modelling projects. Therefore COMPNANOCOMP partners can also try, via EMMC, to probe possible ways for exploitation of the selected exploitable results from the project.

Exploitation of results

The following results from the project are selected for further exploitation:

- New liquid moulding based process for the production of nanoparticles filled fibre reinforced composites
- Software Complex for multiscale computer simulations of polymer composites
- Field theory-inspired Monte Carlo code for chain conformation and interactions around nanoparticles
- Network-based kinetic Monte Carlo code for simulation of deformation

European-Russian collaboration

Contribution of the RU partners to the EU project:

- Providing modelling insight on the experimental results of ECNP (KI and IMC)
- Contribution of RU researchers to the EU PhD theses (at TU/e and UU)
- Tutorial for the RU software given to the EU partners
- Providing input for the ESS report

Contribution of the EU partners to the RU project:

- Providing requested information to the RU reports
- Providing experimental data (from ECNP) for the validation of the RU modelling

General:

- Large number of joined EU-RU publications
- Joined EU-RU workshops and meetings
- Joined EU-RU coordinators discussions
- New EU-RU lab created at the Institute of Macromolecular Compounds (IMC) in St. Petersburg (head Prof. Jose Kenny from ECNP), with the financial support of Russian "Megagrant"

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Project website: www.compnanocomp.eu

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