

PROJECT FINAL REPORT

Final Publishable summary report



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Project acronym: NANOMODEL

Project title: Multi-Scale Modeling of Nano-Structured Polymeric materials: From Chemistry to Materials Performance

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Name, title and organisation of the scientific representative of the project's coordinator¹:

Horst Weiss, Head of Molecular Modeling, Polymer Research BASF SE

Tel: : +49 621 60 22 44 5

Fax: +49 621 60-66 22 44 5

E-mail: horst.weiss@basf.com

Project website address:

<https://www.nanomodel.eu/>

¹ Usually the contact person of the coordinator as specified in Art. 8.1. of the grant agreement

Executive Summary

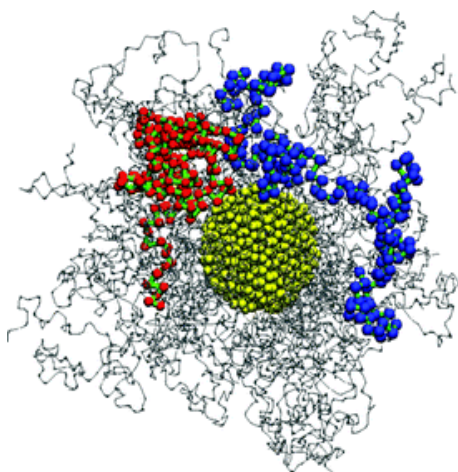
The FP7 project NanoModel - Multi-Scale Modeling of Nano-Structured Polymeric materials: From Chemistry to Materials Performance (Grant Agreement number: 211778) has finished smoothly in accord with the planning as outlined in Annex I to the Grant Agreement. There were no fundamental structural changes necessary. The goal – the sustainable development of validated multiscale modeling methods and tools for rational nanocomposite design- has been reached. This involved synthesis, modeling method development, validation and to a certain extent the development of new materials. The focus of the project was on understanding, design and performance of nanocomposites consisting of surface modified nanoparticles(NP) embedded in technically relevant polymer matrices. In particular, silica, hematite, barium titanate and yttrium europium vanadate particles embedded in polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(butylene terephthalate) (PBT) and polyamide (PA66) were synthesized, characterized, dispersed, characterized again, tested and simulated on length scales from atomistic simulation to constitutive modelling by finite element methods (FEM). To this end, it was necessary to combine expertise from synthesis, testing, processing and simulation (both method developers and application scientists). To ensure sustainability of simulation methods developed, important method developments were integrated into a commercially available modelling software system. To facilitate fruitful collaboration among and across expert areas, the project consisted of three layers –basic method & software development, model systems preparation with characterization and testing and the validation against each other. The concept was successful due to a vivid exchange within and between the three layers.

In a comparative study, the different approaches mentioned above, were validated. It was shown, by direct comparison with neutron scattering results, that the applied simulation strategies describe the structure of the nanocomposites well. New synthesis approaches were developed to create very well defined and characterized nanocomposites with fully dispersed nanoparticles. In detailed analysis, the ordering of the polymer around the nanoparticle could be described, and also the dynamics. The dynamics of free polymer chains in the vicinity of the NP is slowed down both in grafted and ungrafted samples, which has consequences for the processing. Also, reasonable estimates of the mechanical performance together could be obtained and rationalized. Rules for successful stable dispersion of surface modified nanoparticles in polymer matrices could be developed, which is important for commercialization. In our systems, no specific “nano-effect” boosting the mechanical performance of nanocomposites could be detected. Under regular conditions relevant for industrial usage, we could not find extraordinary performance of composites filled with nanoparticles compared to conventional fillers. Thus, since the materials properties of nanocomposites generated throughout the project did not show interesting new effects leading to new application, it was not justified to file any patent. This is, however, consistent with the fact that nanocomposites commercially still do not play a role as materials. The toolbox developed and validated in this project, however, is not restricted to these systems. Since they are available in a commercial package, the tools will be applied in the future to further promising concepts for development of light weight performance materials. In particular the newly developed MD-FEM coupling scheme and the Fti-MC method are important steps towards a rational materials development, since they allow for modelling and simulation of complex materials with high chemical detail.

The project was by its nature multidisciplinary, involving chemists, physicists, mathematicians, chemical and mechanical engineers and software developers from industry and academia. 12 publications are meanwhile published, more than 60 presentations were given, 2 publications are submitted and 6 in preparation. The MD-FEM coupling development is transferred to a DFG SPP project (1369) for further development. There was intensive collaboration among the young team consisting of 13 PhD students (among them 2 females), 10 Postdocs (2 females), 3 Diploma theses students and 2 undergraduates from 11 countries.

Summary description of project context and objectives

Polymers are indispensable materials for mankind. They appear as polyolefins, epoxies, polyesters, polyamides etc., with applications in construction, commerce, transportation, and entertainment across the globe. Estimates of global polymer production range from 250 billion pounds to more than 400 billion pounds (approximately 114–181 billion kg) annually. In the majority of their diverse applications, polymeric materials are not chemically or molecularly homogenous but are multicomponent systems. By adding fillers, such as minerals, ceramics, metals, or even air, materials scientists can generate an infinite variety of materials with unique physical properties and competitive production costs. [*Polymer Nanocomposites*, ed. Karen I. Winey and Richard A. Vaia, *MRS BULLETIN VOLUME 32* (2007) www.mrs.org/bulletin] In the past, mainly micron sized inorganic filler particles to reinforce polymeric materials have been used, and they can be traced back to the early years of the composite industry. The design of such conventional composites has been focused on maximizing the interaction between the polymer matrix and the filler. [*Molecular Mechanisms of Failure in Polymer Nanocomposites*, D. Gersappe, *PRL* 89(5), 58301 (2002) and references cited therein] This is commonly achieved by shrinking the filler particles to increase the surface area available for interaction with the matrix. With the emergence of synthetic methods that can produce nanometer sized fillers, resulting in an enormous increase of surface area, polymers reinforced with nanoscale particles should show vastly improved properties. Yet, experimental evidence suggests that a simple extrapolation of the design paradigms of conventional composites cannot be used to predict the behaviour of nanocomposites. The origin of these differences between conventional and nanocomposites is still unknown. This, unfortunately, **precludes yet any rational design**. However, nanomaterials fabricated by dispersing nanoparticles in polymer melts are considered to have the potential for performances exceeding traditional composites by far. [A. Balazs et al., *Science* 2006, 314,1107; *Polymer Nanocomposites*, ed. Karen I. Winey and Richard A. Vaia, *MRS BULLETIN VOLUME 32* (2007)] Though some property improvements have been achieved in nanocomposites, nanoparticle dispersion is difficult to control, with both thermodynamic and kinetic processes playing significant roles. It has been demonstrated that dispersed spherical nanoparticles can yield a range of multifunctional behaviour, including a viscosity decrease, reduction of thermal degradation, increased mechanical damping, enriched electrical and/or magnetic performance and control of thermomechanical properties. Especially the decrease in viscosity is advantageous for injection-molding operations: lower injection times are required or, alternatively, the processing temperature can be lowered with higher dimensional stability. It is expected that the developed materials fulfil future demands in precision molding of thin-walled products with high demands on dimensional stability. One of the thermomechanical properties of a polymer profoundly susceptible by nanofillers is the glass transition temperature (T_g). [*Controlling the thermochemical properties of polymer nanocomposites by tailoring the Polymer-Particle Interface*, S. Kumar et al., *J. of Polymer Science, Part B: Polymer Physics*, Vol. 44, 2944-2950 (2006), and references cited therein] It has been reported that a polymer's T_g can change by as much as $\pm 30^\circ\text{C}$ due to the addition of nanofiller. This is particularly relevant because the elastic modulus, hardness, conductivity, and various other physical properties change by several orders of magnitude in the vicinity of T_g . Facile tuning of nanocomposite T_g could thus allow us to control the usable temperature range of these materials. Again, the physics underpinning this behaviour remains unresolved, primarily due to the poor understanding of the effects that particle/matrix interactions have on the composite behaviour.



The situation: particles embedded in a polymer matrix and grafted with polymer chains. For the design of nanocomposites, we have to know what the effect is of

Polymer Matrix: crystallinity, polydispersity, molecular weight

Particles:

size, chemical nature, surface treatment

Grafting agents:

chemical nature, grafting density, molecular weight, polydispersity

This project aimed at overcoming these deficiencies by a twofold strategy. First of all, multi-scale modelling nowadays complements experiments to elucidate structure-property relationships. This project brought together a critical mass of scientists, from atomistic to finite-element modelling. **The goal was to develop, implement and validate methods to compute the mechanical, thermochemical and flow behaviour of nano-filled polymeric materials – based on the chemistry of selected model systems.** It was –and is– indispensable to combine all scales of modelling since it is well known that materials' properties depend critically on processes occurring some orders of magnitude below the macroscale which is in particular valid for nano-filled polymers. Here, where chemistry, physics and materials sciences meet, the very structure of matrix, nanoparticles and their interphase critically determine the performance of the whole material. Especially the role of the interphase (structure and dynamics) is difficult to investigate experimentally. By now it is merely evident that the size of the nanoparticles, the radius of gyration of the polymer matrix, the grafting density and the molecular weight of the grafted polymer has to be in a certain range to get dispersed particles and a “nano-effect”. No deeper insight into the underlying mechanisms was available.

We therefore applied state-of-the art techniques to study the detailed structure of matrix, nanoparticles and interface region, and we developed beyond state of the art methods. Structural characterization of the nanocomposites has been carried out with small angle neutron scattering (SANS), the method of choice here. Overview-snapshots to analyze the particle dispersion have been taken with sophisticated Transmission Electron Microscopy (TEM) techniques. By detailed comparisons of computed structures and experimental ones, we calibrated our methods to explore new composites. To this end, model systems were synthesized. In order to have full control on the very composition of these composites, new synthesis strategies for the grafting have been developed [Synthesis of polymer/silica hybrid nanoparticles using anionic polymerization techniques; Hübner, E.; Allgaier, J.; Meyer, M.; Stellbrink, J.; Pyckhout-Hintzen, W.; Richter, D.; *Macromolecules*, 43 (2010) 2, 856 – 867]

These model systems were unique in a sense that it was for the first time that the mechanical performance of nanocomposites was determined where the structure of the interface between particle and matrix was elucidated at the same time by neutron scattering and by molecular simulation. Results and conclusions are discussed in the S&T section below.

Along, and this was the second part, the project brought together all necessary partners to develop nanocomposites based on commercial particles (Epidoris, FriMat, BASF) and commercial polymers (PMMA, PS, PBT, PA66) relevant for the automotive industry. The composites were carefully prepared, characterized and tested, and the results were compared to simulation results to develop structure-property relationships (QSPR). In all cases, the intention was to exploit promising new materials and to increase the competitiveness of European industry by developing validated predictive models aimed at reducing the efforts required for the development of new materials, including newly emerging

nanostuctured materials, for flexible production of knowledge-based products. In particular, modelling tools were developed and applied to understand, design and improve nanocomposite materials.

From a scientific point of view, this goal could not be achieved without significant advances in simulation technology. From a project management point of view, to achieve sustainability, it was necessary to

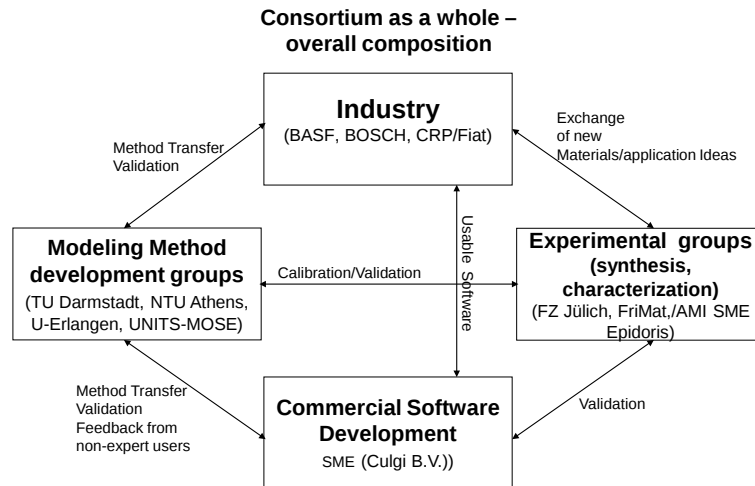
- Validate the methods
- Create “usable” software in terms of support, robustness, efficiency, ease of use etc.

Validation required exhaustive comparison with well characterized model systems. “Usable” software required support after the lifetime of the project; that could only be achieved having a commercial software vendor on board. In the case of the NanoModel project, this was the SME CULGI B.V, a specialist for Soft Matter Simulation software. CULGI BV is an active and highly regarded partner in the scientific simulation community and was ideally suited to pick up the methods developed within the core method developement group within the project. This very strong group was formed by Prof. Müller-Plathe (TU Darmstadt), Prof. Theodorou (NTU Athens), Prof. Fermeglia (MOSE, Trieste), and Prof. Steinmann (Univ. Erlangen); the enumeration reflects the modeling scale from atomistic/coarse graining to FE modeling. The CULGI-team actively participate in the development of integrated suitable simulation software like builders, atomistic and mesoscale tools, and the coupling of Molecular Dynamics and Finite Element Methods into the commercial software package CULGI. These methods are on the market now. As market, we do not only consider modeling colleagues from other industries and academia, but also material scientists who want to support their development with modeling. Thus, the hands-on trainings sessions were open and actively used by all project partners.

The model systems for validation and new materials for application testing were provided by the groups of Prof. Richter (FZ Jülich), Prof. Schurtenberger and Dr. Dietsch (AMI/FriMat), and the SME Epidoris (formerly Gritche Technologies). Jülich has strong expertise in scattering techniques and syntheses of clean model compounds, and was responsible for the synthesis (also deuterated species) and characterization (e.g. with SANS) of model systems. The FriMat/AMI -group had large expertise with the difficult task of nanoparticle dispersion and characterization. Epidoris, on the other hand, supplied the project with commercially available particles from their broad nanoparticle portfolio, in collaboration with AMI/FriMat.

Newly developed modeling techniques were immediately applied in understanding the application testing results. This feedback-loop, on the other hand, stimulated new ideas for modeling methods etc. A good example of this feedback was the investigation of particle dispersion stability. Experiment and simulation agreed after 24 months on the important factors ensuring stability. This is well documented in the project reports and will be published. This exchange inspired the development of a new method by NTUA, the Fti-MC, which helped the interpretation of neutron scattering results from FZ Jülich.

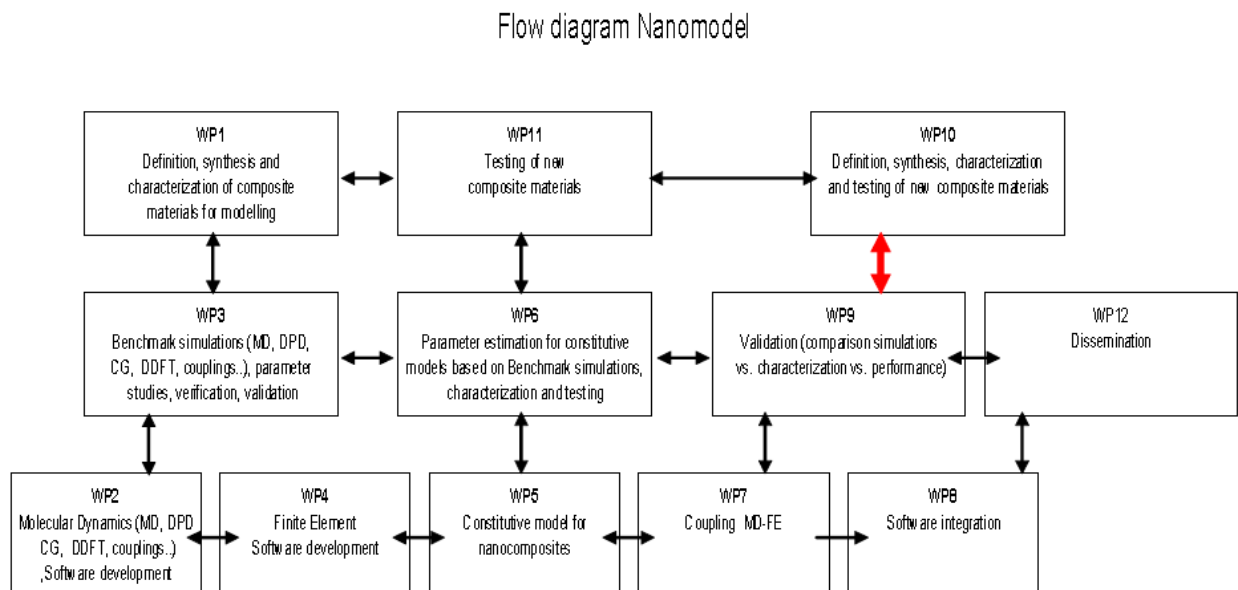
Thus, there was an intensive exchange of ideas, results, methods and materials among the partners – all with one goal: to enhance the development process of new nanostructured materials. Industry served here as a mediator between modeling and materials development with project members from both fields. The consortium structure is sketched below.



Overall composition of the consortium

At the same time, several value chains were created through the composition of the consortium. Obviously, the industry partners formed a consistent chain from materials production to end consumer products. Secondly, we had a true multiscale modeling chain ranging from chemistry to materials properties. Third, the combination of basic research know-how (e.g. matching conditions for SANS analysis) together with deep formulation know-how generated well characterized and finally well understood new materials. Finally, to ensure sustainability of developed modeling methods besides the usual publication of methods in scientific journals, and to help others to improve their materials development process, the simulation methods are available to the public in form of a user-friendly commercial software package with full support after the lifetime of the project.

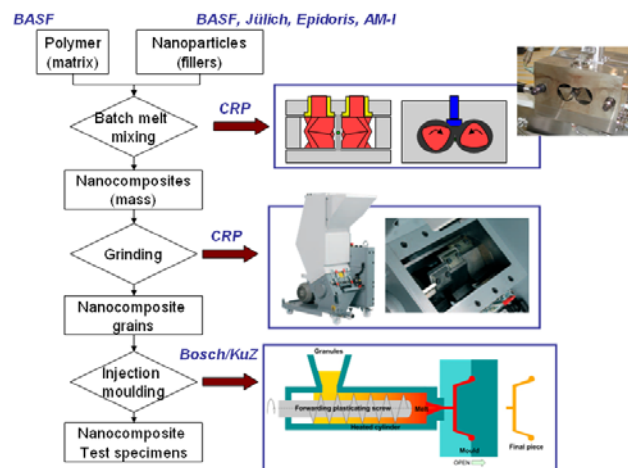
The Pert – Diagram below summarized the project structure and illustrates the relationship between Work Packages in model systems, validation and software layer.



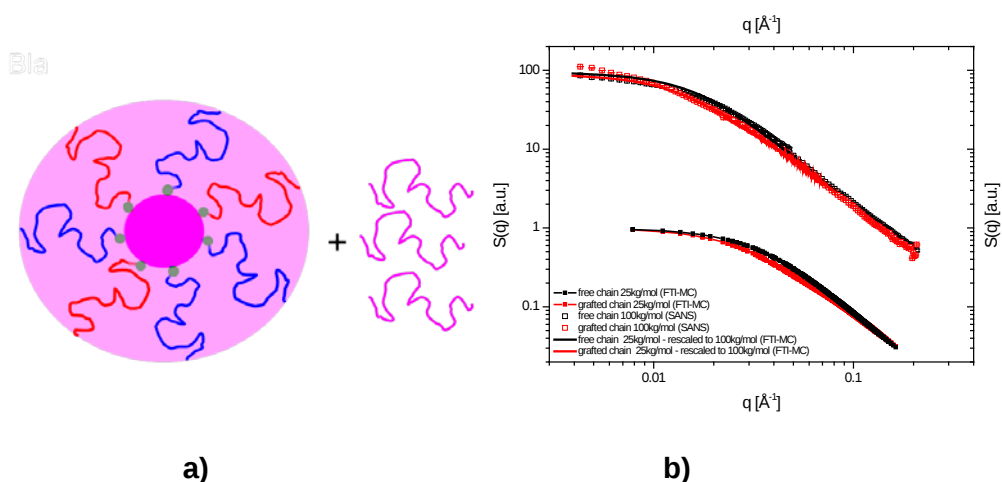
Description of main S & T results/foregrounds

The goal of NanoModel was the sustainable development of validated multiscale modeling methods and tools for rational nanocomposite development. This involved synthesis, modeling method development, validation and to a certain extent the development of new materials. To this end, it was necessary to combine expertise from synthesis, testing, processing and simulation (both method developers and application scientists). To ensure sustainability of simulation method development, important method developments were integrated into a commercially available modelling software system. **To facilitate fruitful collaboration among and across expert areas, the project consisted of three layers – basic method & software development, model systems preparation with characterization and testing and the validation against each other.** The concept was successful due to a vivid exchange within and between the three layers. The main results of the three layers are presented and summarized below.

Model systems layer (WP1,10,11): workflows for nanocomposite synthesis, characterisation and testing between academic and industrial groups from synthesis to characterization, processing and testing were established and worked excellently.



The synthesis and the analytical characterization of the model system (silica grafted with PS (variations of molecular weight and grafting density) in PS matrix) and all needed linear matrix polymers was completed on time after month 18. A beyond state-of-the-art functionalization of nanoparticle surfaces has been published (Huebner, E. et al., *Macromolecules*, 43(2):856–867, Jan. 2010). With finishing the synthesis of the model systems in month 18, the filler material for blending has been distributed to CRP for blending and mechanical testing (CRP, Bosch) in the requested amounts of about 10g per model system. The characterization of the pure core silica by Small Angle Neutron Scattering (SANS) revealed a core-shell-like structure with a high polydispersity of about 30% and an average overall radius of 7.7nm (Meyer, M.; Aachen, RWTH, Diploma Thesis, 2009). Based on these results and theoretical predictions a generalized model function was developed, which described the scattering of the grafted particles in terms of shell thickness, grafting density, molecular weight of the graft and in dependence of the surrounding media. The resulting shell thicknesses of the model systems in solution (toluene) as well as in the polymeric matrix (100kg/mol polystyrene) have been successfully compared to simulations of the partners BASF (DPD simulations) and NTUA (FTI-MC simulations). Also, the characterization results are in good agreement with theoretically derived scaling laws. In addition, the first direct small angle neutron scattering (SANS) investigation on the chain conformation of grafted chains was performed, which compare quantitatively to the form factor of the grafted chains extracted from FTI-MC simulations by NTUA. Both methods thus give a consistent picture of the important interphase structure. Further analysis in the future will be necessary to fully connect these important results to macroscopic behaviour of the resulting composite.



In **a)** a scheme the double contrast condition is shown. The h/d-composition of the random block-co-polystyrene matrix (100kg/mol) is chosen to match the scattering length density of the silica core and the polystyrene shell in average. The corona consists of fully deuterated and protonated polystyrene with a molecular weight of about 100kg/mol, which are randomly distributed within. At these conditions the only scattering contribution arises from the contrast between the polymer chains in the corona and reveals their conformation. In Graph **b)** the results from the experimental setup described before is shown. The open squares are the scattering data of the corona chains (red) in comparison to the one of free polystyrene (black). The dotted lines are extracted from FTI-MC simulations by NTUA with a molecular weight of 25kg/mol of grafted and free chains, which are rescaled to 100kg/mol (red and black line).

AMI performed the synthesis of both silica and silica coated iron oxide particles via sol gel methods. The surface modification of the obtained particles was ensured via covalent bonding of silane coupling agents or physical adsorption of block copolymer for their integration in PMMA or PS matrices via in-situ or ex-situ integration methods. The integration of hematite spindle type particles within a PS-P2VP blockcopolymer matrix was published within the Nanomodel framework (M.R. Hammond, H. Dietsch, O. Pravaz and P. Schurtenberger, *Macromolecules* 2010). In the past 18 months, AMI coworkers focused on the integration strategies and characterization as well as the upscaling of silica-coated hematite nanoparticles for their incorporation within a commercial polymeric matrix of PMMA (Altuglas). A highlight is the fact that TPM-Silica coated particles could be integrated with limited aggregation within a polymeric matrix using classical melt processing techniques. Injection moulding oriented the ellipsoidal shaped nanofillers within the commercial PMMA, but no improvement in terms of mechanical properties even at weight fraction as large as 10 wt% was observed. SME partner Epidoris supplied nanoparticles with a precise and well characterized morphology, size distribution, surface chemistry and shape (e.g. 50nm mono-dispersed silica, for which original synthesis was developed ab initio by Epidoris during the project, and 30nm and 50nm BaTiO_3 treated with different dispersant agents). Epidoris worked closely with AMI on scale-up. CRP performs the function of compounder, using industrially relevant methods (batch melt mixing and extrusion) and material characterisation (DSC, rheology and optical microscopy). CRP compounded most of the nanometric fillers. The resulting products were analysed in CRP, as thoroughly described in meeting proceedings and in deliverable 3.1, 11.1 and 11.2. CRP also performed the important function of distributing polymer, nanoparticle and nanocomposite samples to different partners in the model layer. The figure above illustrates the workflow for nanomaterial production through industrially relevant methods. The mechanical characterization of the nanocomposites developed in the project was performed by the partner Robert Bosch GmbH. Due to the fact that only very small material quantities in the range of some grams are prepared, special sample preparation and characterization procedures had to be adopted. Micro-samples with dimensions of $1/12^{\text{th}}$ of the standard specimens are injection moulded on a micro-injection moulding machine.

The mechanical testing machine allowed for mechanical strain (room temperature) and optical strain (elevated temperature) measurements. The influence of the sample geometry

on the mechanical properties was studied by comparing different sample geometries. It was concluded that the different processing conditions enforced by the different geometries (e.g. faster cooling of micro-samples) can induce differences in the micro-structure of the polymer leading to different macro-mechanical properties. As a consequence all the materials should be compared on the same sample geometry. The materials were characterized by tensile tests and dynamic scanning calorimetry. Other characterization analyses that were performed by the partner Bosch were thermo-gravimetric analysis, viscosity measurements, microscopic analysis and dynamic mechanical analysis.

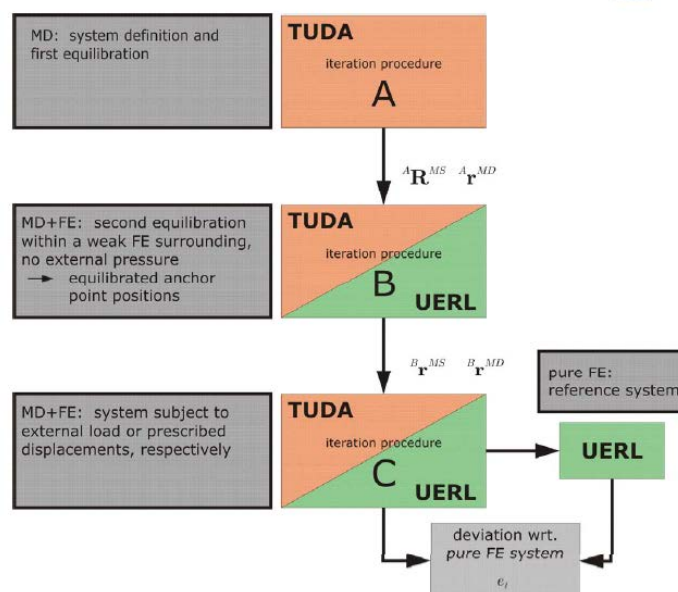
Software development layer (WP 2,4,5,7,8)

Within the 2nd period, the ambitious plan of a concurrent coupling of continuum mechanics with particle based methods has been realized successfully. Advancing the work of the first period of the NanoModel project, a first prototype of a staggered algorithm to couple the continuum based Finite Element (FE) method (responsible partner UERL) with the particle based Molecular Dynamics (MD) technique (responsible partner TUDA) has been developed and tested: To do so, the two main parts of the coupling procedure, namely the FE and MD part, have been adapted as follows: in the MD part, the necessary number of degrees of freedom has been reduced by coarse graining, i.e. groups of atoms are considered as single super atoms. Furthermore, the periodic boundary conditions (PBC), which avoid surface effects in the MD simulation box, have been replaced by stochastic boundary conditions (SBC), combined with a DPD thermostat. Using a certain probability function in the boundary domain, a part of the super atoms in that region is tethered via a harmonic interaction potential to so-called anchor points. These additional artificial particles transfer information (forces and positions) from the MD region to the FE domain and vice versa. The main advantage of this approach is the spatial fixing of the anchor points during the MD run, thus there is no dynamic coupling to FE required. From our point of view a fully dynamical coupling seems technically impossible due to the enormous difference in time and length scales in FE and MD. This has been proved within a diploma thesis supervised by UERL. The rigid frame of anchor points enclosing the MD domain is coupled to the FE domain by using the Arlequin method which is based on an energy blending of the different domains. After each FE run, the positions of anchor points are updated and act as modified boundary conditions to the MD box, while after each MD computation step the time average of forces exerted on the anchor points by the “real” super atoms form a different boundary condition for the FE part. After a certain number of iteration steps between MD and FE domains the system reaches equilibrium, i.e. except for thermal movements of the super atoms, the system does not deform any more. The suitability of this newly developed algorithm has been shown with the help of a crystal system, a system consisting of pure polystyrene and a polystyrene system with a nano particle inside. This work has been done within a very fruitful cooperation between TUDA, UERL and Culgi B.V., who eventually embedded all relevant program codes into the Culgi scientific computing framework. With that tool at hand, the usage of the algorithm has become more convenient and available to the public. Suitable constitutive models for the description of the FEM part have been developed in close collaboration between TU Erlangen and Bosch. TU Darmstadt implemented and evaluated methods to compute elastic constants to parameterize these models, although it was found that this is not practical yet because of computational effort. Thus, tools like reverse engineering and sensitivity analysis were mainly employed, although structural details like interphase thickness were estimated based on molecular simulation (BASF, NTU Athens, FZ Jülich).

A flow diagram illustrating the algorithm is shown below. For a more refined description of the approach, we have to refer to the project documents (reports to milestone 13 and 14, and to the meanwhile published results [Pfaller S, Possart G, Steinmann P, Müller-Plathe F, Böhm MC, Rahimi M: *A comparison of staggered solution schemes for coupled particle-continuum systems modeled with the Arlequin method*, *Computational Mechanics*, published online on November 16th, 2011, DOI 10.1007/s00466-011-0657-7; Rahimi M, Karimi-Varzaneh HA, Böhm MC, Müller-Plathe F, Pfaller S, Possart G, Steinmann P: *Nonperiodic stochastic*

boundary conditions for molecular dynamics simulations of materials embedded into a continuum mechanics domain, *The Journal of Chemical Physics* 134, 154108 (2011)]

Adapted algorithm

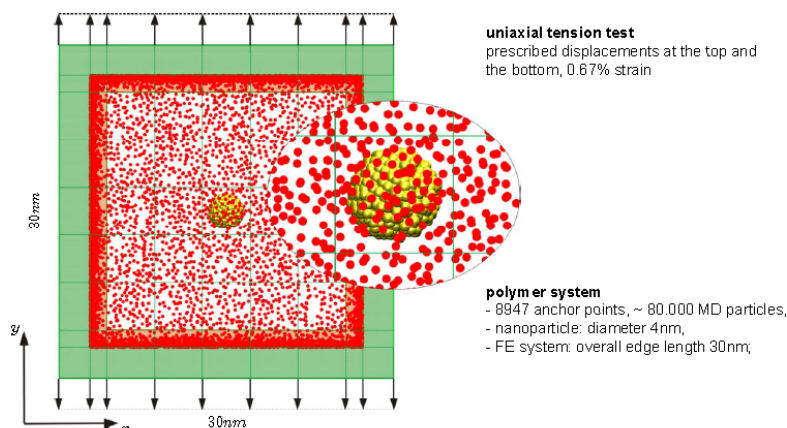


Milestone report 13

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A coupling algorithm between MD (Molecular Dynamics) and FEM (Finite element modelling) allows for the computation of forces externally exerted on a nanocomposite. In the example below, the nanocomposite consists of one particle embedded in a polymer matrix. The particle is described by MD, the surrounding matrix also by MD, but embedded into a continuum described by FEM:

The enhanced coupling algorithm is applied to a polystyrene system with a nanoparticle inside. The MD system contains approximately 80.000 super atoms which are coupled to the FE system by 8947 anchor points. The diameter of the nanoparticle is 4nm. The FE system consists of 604 hexagonal finite elements and 936 nodes, the displacements are prescribed at the outmost nodes in y-direction.



Milestone report 13

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NTUA, BASF, TU Darmstadt, Mose-Trieste and Culgi have adopted a multiscale approach to study the structure and dynamics of silica-polystyrene nanocomposite systems. Four levels of description were employed: an atomistic one, several coarse grained ones where each "superatom" or bead represents e.g. a monomeric unit or a meso or racemo diad of styrene monomers, parametrized using Iterative Boltzmann Inversion (Coarse Grained Monte Carlo, CG-MC), or DPD, and a third one (developed by NTU Athens) describing the system at a length scale comparable to that of the Kuhn length, by exploiting the polymer mean field approximation (Field Theory – inspired Monte Carlo, FT-i MC), and a micromechanical

approach based on mesoscale morphologies. The first two levels of modelling are closely connected, via forward and reverse mapping schemes. Initial configurations have been subjected to CG-MC simulations, where polymeric chains were e.g. treated as chains of diads and nanoparticles as solid spherical Hamaker interaction sites. Based on atomistic molecular dynamics trajectories of the equilibrated structures, local packing and dynamics were addressed by calculating pair distribution functions, bond orientational autocorrelation functions and H-NMR spectra. The third level of modeling (FT-i MC) has enabled simulations of micrometer-sized domains of the nanocomposite system, wherein the nanofillers are represented as solid spheres (interacting via Hamaker integrated potentials) and the polymer chains as freely jointed sequences of Kuhn segments. Based on the positions of Kuhn segments, prediction of Small Angle Neutron Scattering (SANS) patterns was achieved and found to be in excellent agreement with results available from experimental partners (Forschungszentrum Jülich). Moreover, brush heights and scaling laws of grafted polymer layers have been studied and validated, in favorable agreement with existing literature findings and other simulation approaches (Dissipative Particle Dynamics simulations, DPD) undertaken by project partners (BASF SE). Trieste-Mose together with Culgi performed mesoscale simulations with parameters obtained from the multiscale procedure on PS based model system, and the relevant morphology was used to predict the corresponding macroscopic properties by FEM. The protocols developed for the model systems were applied to other systems identified by the consortium as interesting for applications, such as PMMA, Nylon 66, and PBT SiO₂ based nanocomposites. A pseudo core-shell model to account for interface phenomena in the multiscale procedure was developed and tested on unmodified spherical and cylindrical nanoparticles based nanocomposites.

Synopsis: Validation of methods and development of structure-property relations

In the following, the results of the comparative studies are presented. First, the model compounds are listed, and then the “commercial ones” follow.

List of model systems

The model systems comprise a series of nanocomposites based on a Polystyrene matrix with narrow molecular weight distribution with molecular weight $M_n = 97700$ g/mol, Polydispersity index 1.07. It is referred to as 100K PS. The fillers are polymer (Polystyrene) grafted silica particles extensively described in delivery reports 1.1 and 1.2. Fillers are all spherical; systems are listed below in table 1:

Nanocomposite	Internal Code	Filler content wt% filler	Filler (core) diameter (nm)	chemistry grafting agent	graft Mol. Weight (Mn, g/mol)	Polydispersity-index (PDI) polymer graft	grafting density (chains/nm**2)
PS 100k + SiO2 (EHII.123/125) 0.5mass% (EU04-028) annealed	EU04-028	0,5	16	PS	20500	1,11	0,82
PS 100k + SiO2 (EHII.115) 0.5mass% (EU04-030) not annealed	EU04-030	0,5	16	PS	20500	1,07	0.31
PS 100k + SiO2 (EHII.115) 0.5mass% (EU04-030) annealed	EU04-030	0,5	16	PS	20500	1,07	0.31
PS 100k + SiO2 (EHII.115) 5mass% (EU04-032) annealed	EU04-032	5	16	PS	20500	1,07	0.31
PS 100k + SiO2 (EHII.123/125) 5.0mass% (EU04-033) annealed	EU04-033	5	16	PS	20500	1,11	0,82
PS 100k + SiO2 (EHII.105/114) 0.5mass% (EU04-051) annealed	EU04-051	0,5	16	PS	102900	1,02	0,51
PS 100k + SiO2 (EHII.105/114) 1.0mass% (EU04-052) annealed	EU04-052	1	16	PS	102900	1,02	0,51
EHII.158		0,3	16	PS	2000	1,08	0,51

Table 1: overview of model nanocomposites

List of nanocomposites based on commercial polymer grades

The polymer matrix of the nanocomposites was in most cases a commercial polymer: polymethylmetacrylate (PMMA, Altuglas TP 727), polystyrene (PS 148G), polybutyleneterephthalate (PBT, Ultradur B4500) and polyamide (PA, Ultramid A27E). In the case of the nanocomposites with polyamide matrix the material could not be processed properly, since the material foamed during the process (please see Milestone 8 for more

details on the preparation of the polyamide nanocomposites). Therefore the polyamide nanocomposites are not included in this report.

Table 2 shows an overview of the commercial polymers used as matrix in the composites and Table 2 up to Table 4 an overview of the nanocomposites. Table 2 refers to the nanocomposites with PS matrix, Table 3 to the ones with PBT matrix and Table 4 to the one with PMMA matrix. The first column contains a code used along this report for each material. Moreover the internal code used in the project by the partners is also given. The tables contain also the information about the filler type, filler content and geometry as well as the preparation method.

Table 2: Overview of commercial polymer matrix materials

Code in this report	Polymer	Trade name	Provider
PMMA-0	PMMA (Polymethylmet acrylate)	Altuglas TP 727	Altuglas International, Arkema Group
PS-0	PS (Polystyrene)	PS148G	BASF SE
PBT-0	PBT (Polybutylenete rephthalate)	Ultradur B4500	BASF, SE

Table 3: Overview of nanocomposites with PS as matrix

Code in this report	Internal code	Polymer matrix	Filler type, surface functional. (Provider)	Filler content	Filler geometry	Composite preparation method (prepared by)
PS-1	EU04-016	PS, PS 148G	SiO ₂ -OH (bare) (Epidoris SAS)	1wt%	spherical $r_p \approx 20\text{nm}$	Melt mixing (CRP / FIAT)
PS-2	EU04-013	PS, PS 148G	SiO ₂ , Type-I * (Epidoris SAS)	0.5wt%	spherical $r_p \approx 10\text{nm}$	Melt mixing (CRP / FIAT)
PS-3	EU04-014	PS, PS 148G	SiO ₂ , Type-II * (Epidoris SAS)	0.5wt%	spherical $r_p \approx 10\text{nm}$	Melt mixing (CRP / FIAT)

*Surface functionalization of the fillers Type-I and Type-II:

Type-I: GPTMS - 3- glycidoxypropyltrimethoxysilane in ethanol solution with 10% water

Type-II: GPTMS - 3- glycidoxypropyltrimethoxysilane in pure ethanol

Table 4: Overview of nanocomposites with PBT as matrix

Code in this report	Internal code	Polymer matrix	Filler type, surface functional. (Provider)	Filler content	Filler geometry	Composite preparation method (prepared by)
PBT-1	EU04-047	PBT, Ultradur B4500	BaTiO ₃ - <i>Butylglycol</i> (BASF SA)	0.5wt%	spherical	Melt mixing (CRP / FIAT)
PBT-2	EU04-048	PBT, Ultradur B4500	BaTiO ₃ - <i>Butylglycol</i> (BASF SA)	1wt%	spherical	Melt mixing (CRP / FIAT)
PBT-3	EU04-043	PBT (Ultradur B4500)	SiO ₂ -AMEO (Epidoris SAS)	1wt%	spherical $r_p \approx 25\text{nm}$	Melt mixing (CRP / FIAT)

PBT-4	EU04-044	PBT (Ultradur B4500)	SiO ₂ -AMEO (Epidoris SAS)	2wt%	spherical $r_p \approx 25\text{nm}$	Melt mixing (CRP / FIAT)
PBT-5	EU04-045	PBT (Ultradur B4500)	SiO ₂ -PO Silan (BASF SA)	1wt%	spherical $r_p \approx 7.5\text{nm}$	Melt mixing (CRP / FIAT)

Table 5: Overview of the nanocomposites with PMMA as matrix

Code in this report	Internal code	Polymer matrix	Filler type, surface functional. (Provider)	Filler content	Filler geometry	Composite preparation method (prepared by)
PMMA-1	EU04-018	PMMA, Altuglas TP727	SiO ₂ -OH (bare) (Epidoris SAS)	1wt%	spherical $r_p \approx 20\text{nm}$	Melt mixing (CRP / FIAT)
PMMA-2	EU04-001	PMMA, Altuglas TP727	SiO ₂ , Type-I * (Epidoris SAS)	0.5wt%	spherical $r_p \approx 10\text{nm}$	Melt mixing (CRP / FIAT)
PMMA-3	EU04-003	PMMA, Altuglas TP727	SiO ₂ , Type-I * (Epidoris SAS)	1wt%	spherical $r_p \approx 10\text{nm}$	Melt mixing (CRP / FIAT)
PMMA-4	EU04-005	PMMA, Altuglas TP727	SiO ₂ , Type-II * (Epidoris SAS)	0.5wt%	spherical $r_p \approx 10\text{nm}$	Melt mixing (CRP / FIAT)
PMMA-5 a / b / c / d ($r_p = 15 / 20 / 28 / 34\text{nm}$)	50/51/52/48-0.5-PMMA // PMMA-silica-AMI-inSitu-2009	PMMA prepared by in-situ polymerization (AM-Institute)	SiO ₂ , TPM-coated (AM-Institute)	0.5wt%	spherical, $r_p \approx 15\text{nm}$, $r_p \approx 20\text{nm}$, $r_p \approx 28\text{nm}$, $r_p \approx 34\text{nm}$	In-situ polymeriz. (AM-Institute)
PMMA-6 a / b / c / d ($r_p = 15 / 20 / 28 / 34\text{nm}$)	50/51/52/48-1.0-PMMA // PMMA-silica-AMI-inSitu-2009	PMMA prepared by in-situ polymerization (AM-Institute)	SiO ₂ , TPM-coated (AM-Institute)	1wt%	spherical, $r_p \approx 15\text{nm}$, $r_p \approx 20\text{nm}$, $r_p \approx 28\text{nm}$, $r_p \approx 34\text{nm}$	In-situ polymeriz. (AM-Institute)
PMMA-7 a / b ($r_p = 28 / 34\text{nm}$)	PMMA-silica-AMI-solvent-2010	PMMA, Altuglas TP727	SiO ₂ , TPM-coated (AM-Institute)	0.5wt%	spherical, $r_p \approx 28\text{nm}$, $r_p \approx 34\text{nm}$	Solvent integration (AM-Institute)
PMMA-8 a / b ($r_p = 28 / 34\text{nm}$)	PMMA-silica-AMI-solvent-2010	PMMA, Altuglas TP727	SiO ₂ , TPM-coated (AM-Institute)	1wt%	spherical, $r_p \approx 28\text{nm}$, $r_p \approx 34\text{nm}$	Solvent integration (AM-Institute)
PMMA-9 a / b ($r_p = 28 / 34\text{nm}$)	PMMA-silica-AMI-solvent-2010	PMMA, Altuglas TP727	SiO ₂ , TPM-coated (AM-Institute)	5wt%	spherical, $r_p \approx 28\text{nm}$, $r_p \approx 34\text{nm}$	Solvent integration (AM-Institute)
PMMA-10 a / b ($r_p = 28 / 34\text{nm}$)	PMMA-silica-AMI-solvent-2010	PMMA, Altuglas TP727	SiO ₂ , TPM-coated (AM-Institute)	10wt%	spherical, $r_p \approx 28\text{nm}$, $r_p \approx 34\text{nm}$	Solvent integration (AM-Institute)
PMMA-11	PMMA-hemat-AMI-solvent-2010	Altuglas TP727	TPM-silica-hematite (TPM-SiO ₂ -Fe ₂ O ₃)	0.5wt%	ellipsoidal dimensions**	Solvent integration (AM-Institute)
PMMA-12	PMMA-hemat-AMI-solvent-2010	Altuglas TP727	TPM-silica-hematite (TPM-SiO ₂ -Fe ₂ O ₃)	1wt%	ellipsoidal dimensions**	Solvent integration (AM-Institute)
PMMA-13	PMMA-hemat-AMI-solvent-2010	Altuglas TP727	TPM-silica-hematite (TPM-SiO ₂ -Fe ₂ O ₃)	5wt%	ellipsoidal dimensions**	Solvent integration (AM-Institute)
PMMA-14	PMMA-hemat-AMI-solvent-2010	Altuglas TP727	TPM-silica-hematite (TPM-SiO ₂ -Fe ₂ O ₃)	10wt%	ellipsoidal dimensions**	Solvent integration (AM-Institute)

*Surface functionalization of the fillers Type-I and Type-II:

Type-I: GPTMS - 3- glycidoxypropyltrimethoxysilane in ethanol solution with 10% water
Type-II: GPTMS - 3- glycidoxypropyltrimethoxysilane in pure ethanol

** Dimensions: hematite core: long axis $\approx$ 272nm, short axis $\approx$ 65nm; silica thickness $\approx$ 18nm
(see Milestone 7)

Dispersion of nanoparticles

It was one of the goals of this project to work out strategies for stable dispersion of nanoparticles under “industrial” conditions, which means by cheap extrusion or melt mixing procedures. Obviously, the surface chemistry of the nanoparticles is crucial, and systematic variations of grafting agents and grafting densities have been carried out. The success of the dispersion (by melt mixing, solvent mixing) has been monitored by TEM and SAXS measurements as described in the above cited delivery and milestone reports. The model systems highlight the effect of variations of grafting density, molecular weight and particle loadings. Results are collected in Table 6. Stable dispersion could be achieved for grafted molecular weights of 20.000 g/mole as well as for 100.000g/mole if the grafting density was sufficiently high and the particle loading is not too high (!). NP grafted with PS chains of $M_n = 2000$ g/mole could not be stably dispersed. It was (see delivery report 1.1) impossible to achieve a higher grafting density than 0.5 there, which was not sufficient to stabilize the particles even at very low loadings (0.3 wt.% NP). It is remarkable to compare EU004-032 and EU004-033. The only difference is the grafting density. Increasing the grafting density from 0.3 to 0.8 makes the difference between stable and non-stable dispersion.

These systems have been studied also by mesoscale simulation. The results are reported in detail in delivery report 3.3. As a brief summary, the following results were obtained:

By direct comparison between atomistic simulation and DPD (a mesoscale simulation technique) (milestone report 10), and on direct comparison with SANS data (delivery report 1.2) it was shown that DPD is capable of reproducing structural features of nanocomposites. This gave confidence that with DPD techniques, a direct estimate of stable nanoparticle dispersion is possible. The work was carried out within WP3, see delivery report 3.3. It could be clearly shown that insufficient particle coverage by the grafting chain as in EHII.158 is responsible for particle agglomeration. The DPD calculations were used to predict suitable grafting schemes and resulting nanocomposite morphologies, which were then used to compute mechanical properties (see below).

As a qualitative result, it seems that the grafting density **together** with molecular weight is the crucial parameter or, to build up a QSAR model, the main descriptor. It is, however, not straight forward to assess the suitable combination of both factors. The applied simulation techniques can provide this information. It is possible to predict the right combination. The model systems were athermal systems, i.e. the chemical nature of the graft was identical to the matrix. Compatibility was solely determined by entropic effects. Obviously, as shown by comparisons of 20K and 100K grafts, there is no “minimal” molecular weight for successful dispersion grafts. If the grafting density is sufficient, relatively low molecular weight grafting agents are sufficient for stable dispersion. The good understanding and control of the different steps: nanoparticle syntheses, surface chemistry, colloidal stability and the integration methods within different polymeric matrix, allowed us to produce very well-defined and characterized nanocomposites. An overview can be found in Milestone 8 report.

Table 6: Effect of grafting density, molecular weight & particle loadings on nanoparticle dispersion

	Internal Code	Polymer matrix chemistry	Matrix Mol. Weight (Mn, g/mol)	Polydispersity index (PDI) polymer matrix	Filler content w % filler	Filler geometry	inorganic filler content [w %]	Filler (core) diameter (nm)	dispersion method	stable dispersion in nanocomposite (yes/no)	characterization method to prove dispersion in nanocomposite	chemistry grafting agent	graft Mol. Weight (Mn, g/mol)	Polydispersity index (PDI) polymer graft	grafting density (chains/nm ²)
Nanocomposite															
PS 100K + SiO ₂ (EH1123/125) 0.5mass% (EU04-028) annealed	EU04-028	PS 100K	97700	1.07 (FZ Jülich)	0.5	spherical	0.083	16	melt mixing (CRP)	yes	TEM	PS	20500	1.11	0.82
PS 100K + SiO ₂ (EH11115) 0.5mass% (EU04-030) not annealed	EU04-030	PS 100K	97700	1.07 (FZ Jülich)	0.5	spherical	0.1715	16	melt mixing (CRP)	yes	TEM	PS	20500	1.07	0.31
PS 100K + SiO ₂ (EH11115) 0.5mass% (EU04-030) annealed	EU04-030	PS 100K	97700	1.07 (FZ Jülich)	0.5	spherical	0.1715	16	melt mixing (CRP)	yes	TEM	PS	20500	1.07	0.31
PS 100K + SiO ₂ (EH11115) 5mass% (EU04-032) annealed	EU04-032	PS 100K	97700	1.07 (FZ Jülich)	5	spherical	1.715	16	solvent mixing (Jülich)	no (some aggregates)	TEM	PS	20500	1.07	0.31
PS 100K + SiO ₂ (EH1123/125) 5.0mass% (EU04-033) annealed	EU04-033	PS 100K	97700	1.07 (FZ Jülich)	5	spherical	0.83	16	solvent mixing (Jülich)	yes	TEM	PS	20500	1.11	0.82
PS 100K + SiO ₂ (EH1105/114) 0.5mass% (EU04-051) annealed	EU04-051	PS 100K	97700	1.07 (FZ Jülich)	0.5	spherical	0.035	16	solvent mixing (Jülich)	yes	TEM	PS	102900	1.02	0.51
PS 100K + SiO ₂ (EH1105/114) 1.0mass% (EU04-052) annealed	EU04-052	PS 100K	97700	1.07 (FZ Jülich)	1	spherical	0.07	16	solvent mixing (Jülich)	yes	TEM	PS	102900	1.02	0.51
EH1158		PS 100K	97700	1.07 (FZ Jülich)	0.3	spherical	0.23346	16	solvent mixing (Jülich)	no	TEM	PS	2000	1.08	0.51

Thermochemical properties

As already stated in the introduction, it was claimed that nanoparticles allow for tuning of thermochemical properties, namely influencing T_g of amorphous polymers.

In the course of our modelling investigations, we found some evidence that nanoparticles influence the local dynamics of polymer chains in their neighbourhood.

The Darmstadt and Athens groups carried out atomistic Molecular Dynamics (MD) simulations of a composite consisting of an ungrafted or a grafted spherical silica nanoparticle embedded in a melt of 20-monomer atactic polystyrene chains. The **structural** properties of the polymer in the vicinity of a nanoparticle have been studied. The nanoparticle modifies the polymer structure in its neighborhood. These changes are pronounced for higher grafting densities and larger particle diameters. Mass and number density profiles show layering of the polymer chains around the nanoparticle, which extends to ~2 nm. In contrast, the increase in the polymer's radius of gyration and other induced ordering (alignment of the chains parallel to the surface and orientation of backbone segments) are shorter-ranged. The infiltration of free polystyrene chains into the grafted chains region is reduced with increasing grafting density. Therefore, the interpenetration of grafted and free chains at high grafting densities, which is responsible for the mechanical anchoring of nanoparticles in the polystyrene matrix, is less than what would be desirable for a well-reinforced composite (delivery report 3.2, and paper [The interface of grafted and ungrafted silica nanoparticles with a polystyrene matrix: Atomistic molecular dynamics simulations, T.V.M. Ndoro, E. Voyiatzis, A. Ghanbari, D.N. Theodorou, M.C. Böhm, F. Müller-Plathe, *Macromolecules* **44**, 2316-2327 (2011), and references cited therein]).

Furthermore, Darmstadt group investigated the local **dynamics** of chains in nanocomposites on the same system. The chain and segmental dynamics of free and grafted 20-monomer atactic polystyrene chains, surrounding a silica nanoparticle, have been investigated employing atomistic molecular dynamics simulations. The effect of the nanoparticle curvature and grafting density on the mean square displacement of free polystyrene chains and also on the mean relaxation time of various intramolecular vectors was investigated as a function of separation from the surface. **Confinement, reduced surface curvature, and densification resulted in a reduction of the mean square displacement and an increase in the mean relaxation time of the C α -H bond vector and chain end-to-end vector in the vicinity of the surface.** Depending on the property investigated, the thickness of the interphase, i.e., the distance beyond which the polymer has bulk behaviour, varies between 1 and 3 nm, corresponding to 1-3 radii of gyration of the bulk polymer. Therefore, the presence of a surface has a significant influence on the dynamics of the surrounding polymer chains, especially the ones in the interfacial region. [Interface and Interphase Dynamics of Polystyrene Chains near Grafted and Ungrafted Silica Nanoparticles, Tinashe V. M. Ndoro, Michael C. Böhm, and Florian Müller-Plathe *Macromolecules* in press (2011) and references cited therein].

Although it is obvious that there is an effect of nanoparticles on the interfacial dynamics, and thus the local glass transition temperature, it was unclear to which extent this effect macroscopically shows. The usual argumentation [e.g. *The effect of silica on the thermomechanical properties of polystyrene*, E. Kontou, G. Anthoulis, *Journal of Polymer Science* **105**, 1723 (2007)] is that the high number density of nanofillers at loadings around very few weight% creates that much interface that the effect is macroscopic. The work of the Darmstadt group cited above however indicates that the effect decays after 1-3 radii of gyration. The thickness of the interface layer for the “real” model composites from table 1 has been determined by experiment (SANS, delivery report 1.2) and simulation (milestone report 10 for an overview). Since the agreement between simulation and experiment was good, it is justified to discuss the interfacial structure and its consequences based on simulation. In the following table 7, the brush height of the model systems, the estimated particle-particle distance and T_g are shown.

Comparison for nanocomposite Tg should be made with Tg of the unfilled polymer which is 107 °C. Experimental details can be found in delivery report 3.1. For the filled polymers (between 0.5 and 5 wt%), Tg is virtually unaffected. Tg of the composites is 107-108 °C, which means that the nanoparticles have no effect on Tg at least for our model system.

To rationalize the absence of an effect, it is instructive to discuss the effective particle-particle distance. The table contains estimates for the brush height based on SANS and two mesoscale methods, one of which developed within the project (Fti-MC, Athens group), the other (DPD) validated by BASF, MOSE-Trieste and Culgi within the project. All three methods coincide in that the layer thickness (brush height) is of the order of 10 - 15 nm for the present systems. Assuming a regular distribution, it can be estimated that the particle-particle surface distance is approximately 50-60 nm for the 5 wt% sample, and up to 200 nm for the 0.5 wt% sample. This should be compared to the radius of gyration r_g of a 100K PS which is of the order of 10 nm (depending on the solvent; in toluene, it is 11.4 nm according to Fetters et al [L. Fetters et al., *Journal of Physical and Chemical Reference Data* 1994, 23(4),619-640]). Thus, the particles do not interact, they are well separated, and the majority of polymer chains is unaffected by their presence. This is macroscopically reflected in the almost constant Tg. These findings were confirmed when we turned to commercial matrix materials and oligomeric grafting agents. In table 8, results for PS 148K (an industrial polymer grade) are collected. Here, Tg varies between 105 and 106 °C.

Details on the DSC procedure, the original graphs and a thorough discussion can be found in delivery report 11.1. Without going into details, it should be mentioned that similar findings were made for the PMMA composites prepared by solvent integration. Results and discussions can be found in delivery report 11.1.

Table 8: Tg (in °C) for nanocomposites based on a commercial (PS 148G) matrix

Nanocomposite	Internal Code	Polymer matrix chemistry	Matrix Mol. Weight (Mn, g/mol)	Polydispersity index (PDI) polymer matrix	Filler Type	Filler content wt% filler	Filler geometry	Filler (core) diameter (nm)	chemistry grafting agent	Tg
PS-0	PS148G EU04-016 (PS)	PS	85000	5,5						105,4
PS-1	148G+SiO ₂ -OH, 1.0%) EU04-013 (PS)	PS 148G	85000	5,5	SiO ₂ -OH (bare) Epidoris SAS	1	spherical	40	bare silica	106,4
PS-2	148G+SiO ₂ (I), 0.5%) EU04-013 (PS)	PS 148G	85000	5,5	SiO ₂ -OH Type I Epidoris SAS	0,5	spherical	20	GPTMS (γ-glycidoxypolytrimethoxysilane), Ethanol+10% water	105,3
PS-3	148G+SiO ₂ (II), 0.5%) EU04-013 (PS)	PS 148G	85000	5,5	SiO ₂ -OH Type II Epidoris SAS	0,5	spherical	20	GPTMS (γ-glycidoxypolytrimethoxysilane), pure Ethanol	105,6

Table 7: comparison of brush height, particle-particle distance and Tg (in °C) for model systems

Nanocomposite, 100K matrix, 16 nm diameter filler, PS graft	Internal Code	Filler content wt%	inorganic filler content [wt %]	graft Mol. Weight (Mn, g/mol)	grafting density (chains/nm ²)	Tg	estimated brush height avg (nm) DFD	estimated brush height 99% (nm) DFD	estimated brush height avg (nm) FH-MC	estimated brush height 99% (nm) MC	estimated brush height t(av)(i) (nm) SANS	estimated full diameter (core & brush) nm DFD	estimated full diameter (core & brush) nm FH-MC	estimated full diameter (core & brush) nm SANS	estimated particle- particle distance, surface-surface (nm)
PS 100K annealed						107									
PS 100K + SiO2 (EHL123/125) 0.5mass% (E04- 028) annealed	E04-028	0.5	0.083	20500	0.82	107	6.47	14.08	6.93	122	14.99	44.16	40.4	45.98	197
PS 100K + SiO2 (EHL115) 0.5mass% (E04-030) not annealed	E04-030	0.5	0.1715	20500	0.31	108	6.13	13.91	5.85	112	10.99	43.82	38.4	37.98	163
PS 100K + SiO2 (EHL115) 0.5mass% (E04-030) annealed	E04-030	0.5	0.1715	20500	0.31	108	6.13	13.91	5.85	112	10.99	43.82	38.4	37.98	163
PS 100K + SiO2 (EHL115) 5mass% (E04-032) annealed	E04-032	5	1.715	20500	0.31	107	6.13	13.91	5.85	112	10.99	43.82	38.4	37.98	55
PS 100K + SiO2 (EHL123/125) 5.0mass% (E04- 033) annealed	E04-033	5	0.83	20500	0.82	107	6.47	14.08	6.93	122	14.99	44.16	40.4	45.98	67

Mechanical properties

Much has been written about the potential of nanocomposites to boost the mechanical performance of polymeric materials [e.g. *Polymer Nanocomposites*, ed. Karen I. Winey and Richard A. Vaia, *MRS BULLETIN VOLUME 32 (2007)* www.mrs.org/bulletin and references cited in the issue]. It is remarkable that not a single commercial nanocomposite grade exists to the best of our knowledge. This in mind, the project tried to build up a thorough understanding of model and real nanocomposites with particular emphasis on understanding of the role of the interface, and to develop modelling tools to support rational development of high performance materials.

The **characterization** as described in delivery report 11.1 comprises the following **methods**:

- The preparation of micro-samples by injection moulding with small material quantities (<10g) for mechanical testing.
- The thermal characterization of the granulate material as well as of the injection moulded micro-samples in order to determine the relevant characteristic material temperatures (glass transition temperature, melting temperature) by means of differential scanning calorimetry (DSC) as well as to determine the content of inorganic materials (fillers) by means of thermo-gravimetric-analysis (TGA).
- The mechanical characterization by means of tensile tests on the micro-samples to determine the Young's modulus, the tensile strength and elongation at break as well as dynamic-mechanical analysis (DMA) for the determination of the material behaviour under dynamic loading at different temperatures and frequencies.

The **procedure for the analysis** is based on the following aspects:

- The macroscopic properties (e.g. Young's modulus) are always evaluated by comparing the values of the nanocomposites with the ones obtained on the unfilled material as well as comparing the values between nanocomposites with e.g. different filler content but same constituents.
- In the case of the mechanical properties, all the results are collected on injection moulded micro-samples. This enables the direct comparison of the results between materials avoiding differences that might arise due to differences in the sample geometry and processing method.
- The results of the nanostructure characterization (see report of Milestone 8), i.e. of the dispersion state of the nanoparticles in the polymer matrix, are incorporated in the analysis.
- Estimations of the macroscopic properties by means of micro-mechanical modelling are considered in the analysis.

The **results** can be summarized as follows:

- No impact on the macroscopic properties was observed for:
 - o Nanocomposites prepared by melt mixing with PS matrix and spherical silica (SiO₂) nanoparticles (composite with 1 mass % bare nanoparticles, composites with 0.5 mass % PO silane and 0.5% AMEO-functionalized nanoparticles respectively).
 - o Nanocomposites prepared by melt mixing with PBT matrix and spherical barium titanate (BaTiO₃) nanoparticles (0.5 and 1mass %).
 - o Nanocomposites prepared by melt mixing with PBT matrix and spherical PO-silane functionalized silica nanoparticles (1mass %). The analysis of the nanostructure shows large aggregates for this material.

- A considerable embrittlement of the material (strong reduction in the elongation at break) was observed for the following nanocomposites:
 - o Nanocomposites prepared by melt mixing with PMMA matrix and spherical TPM-coated silica nanoparticles.
 - o Nanocomposites prepared by in-situ polymerization with PMMA matrix and spherical TPM-coated silica nanoparticles.
 - o Nanocomposites prepared by solvent integration with PMMA matrix and spherical TPM-coated silica nanoparticles.
- An increase in Young's modulus was observed for
 - o Nanocomposites prepared by melt mixing with PBT matrix and spherical AMEO-functionalized silica (SiO₂) nanoparticles (1 and 2% filler mass content). The results of an estimation with a micro-mechanical model show that the potential in increasing the Young's modulus by adding only 1 mass% of spherical silica micro-sized particles is almost negligible. It can not be excluded that the trend in the increase of Young's modulus might be supported by the fact that the particles are nano-sized. Considering the standard deviation of the measurements however it should be remarked that the effect is not dominant. The analysis of the nanostructure shows small aggregates and a homogeneous dispersion of nanoparticles and aggregates. Further analysis of the mechanical properties should be performed in order to conclude if the increase in Young's modulus is due to a nano-effect.
 - o Nanocomposites prepared by solvent integration with PMMA matrix and spherical TPM-coated silica nanoparticles. The results of the nanostructure characterization showed a very well dispersion of the nanoparticles in the matrix, which is an important prerequisite for enhancing the macroscopic material properties. In the mechanical measurements a trend in an increasing Young's modulus with higher filler content can be observed. The micro-mechanical analysis suggests however that the stiffening effect might be only due to the addition of a certain amount of stiff particles and not to the fact that the particles are nano-sized.
 - o Nanocomposites prepared by solvent integration with PMMA matrix and ellipsoidal TPM-silica-hematite nanoparticles.
 The results of the nanostructure characterization (report of Milestone 8) showed a homogeneous dispersion of the nanoparticles in the matrix. Moreover the nanostructure analysis showed that while after the synthesis in the laboratory the orientation of the ellipsoidal inclusions was approximately isotropic; in the micro-samples the nanoparticles were oriented due to the injection moulding process. The glass temperature of the nanocomposites is more reduced the higher the nanoparticle content is. In the mechanical measurements the nanocomposites with higher filler content (2.7 and 6.3%) showed an increased Young's modulus compared to the unfilled material. Micro-mechanical calculations idealizing the nanoparticle suggest however that the stiffening effect might be mainly due to the addition of a certain amount of stiff particles and that the nano-effect might be very low. Further analysis will be performed in order to evaluate the system.

The characterization work reported here was performed within WP-11.

Overall, no significant mechanical enhancement could be detected that is not expected by a trivial mixing rule adding a stiff compound (the mineral filler) to a polymer. Three examples are discussed below to illustrate this point. The full set of materials is described in delivery reports 3.1. and 11.1.

We start with a comparison of the mechanical behaviour of the “model systems”

Example 1: Nanocomposites with PS 100K matrix and PS grafted SiO₂ nanoparticles, “model systems table 1”

It is for the first time that the mechanical performance of nanocomposites (model systems listed in table 1) was determined where the structure of the interface between particle and matrix was elucidated at the same time by neutron scattering and by molecular simulation. As discussed in detail in delivery report 1.2 and in milestone report 10, the scaling behaviour of the grafted chains could be determined. The grafted chains clearly show a Gaussian behaviour, which means that there is no strong repulsion of the matrix to the grafted chains leading to a clear separation between grafting shell and matrix; instead, matrix and shell are mixed and in the same state. This, in turn, would mean that there is no particular interphase created at least under athermal conditions in the case of our PS model systems. This, together with the large particle-particle distance as estimated in table 7, would result in mechanical properties not significantly influenced by low concentration fillers as in the model systems.

In the following table 9, the characterization results are collected and compared to simulation estimates of the effective particle diameter.

Table 9: Composition and mechanical properties of PS nanocomposites

Nanocomposite, 100K matrix, 16 nm diameter silica filler, PS graft	Internal Code	Filler content w % filler	stable dispersion in nanocomposite (yes/no)	graft Mol. Weight (Mn, g/mol)	Polydispersity index (PDI) polymer graft	grafting density (chains/nm ²)	Elastic modulus [MPa]@23°C, 1%/min, mechanical	tensile strength [MPa]@23°C, 1%/min, mechanical	Elastic modulus [MPa]@23°C, 1%/min, optical	tensile strength [MPa]@23°C, 1%/min, optical	Elastic modulus [MPa]@40°C, 1%/min, optical	tensile strength [MPa]@40°C, 1%/min, optical	elongation at break [%]@40°C, optical	estimated full diameter (core & brush) nm DPD	estimated full diameter (core & brush) nm MC	estimated full diameter (core & brush) nm SANS	estimated particle-particle distance, surface-surface (nm)
PS 100k annealed							2872	67,2	2969	52	2852	46	2				
PS 100k + SiO ₂ (EHL115) 0.5mass% (EU04-030) annealed	EU04-030	0,5	yes	20500	1,07	0,31	2753	55,1	2801	53	3234	45	2	43,82	38,4	37,98	163
PS 100k + SiO ₂ (EHL115) 5mass% (EU04-032) annealed	EU04-032	5	no (some aggregates)	20500	1,07	0,31	2815	51,5	3134	48	2970	44	2	43,82	38,4	37,98	55
PS 100k + SiO ₂ (EHL123/125) 5.0mass% (EU04-033) annealed	EU04-033	5	yes	20500	1,11	0,82	2596	47,9	3414	47	2799	43	3	44,16	40,4	45,98	67
PS 100k + SiO ₂ (EHL105/114) 0.5mass% (EU04-051) annealed	EU04-051	0,5	yes	102900	1,02	0,51			2906	52	2851	46	3				
PS 100k + SiO ₂ (EHL105/114) 1.0mass% (EU04-052) annealed	EU04-052	1	yes	102900	1,02	0,51			3032	52	3015	46	3				

There are noticeable differences between the two methods (optical vs. mechanical measurements), in particular for EU0-033. The mechanical detection finds a Youngs modulus of 2596 MPa@23°C, whereas with an optical detector, the value is 3414 MPa@23°C. Overall, the error bars for the mechanical tests on the 1/12 micro species (as discussed in delivery report 3.1) are in the order of 5%. Within these error bars, the results do not significantly deviate from the expected behaviour. In the following figures 1 and 2, Youngs modulus and tensile strength are plotted with error bars.

Figure 1: **Young's modulus measured in tensile tests at T=23°C (grey) and T=40°C (yellow), optical strain measurements**

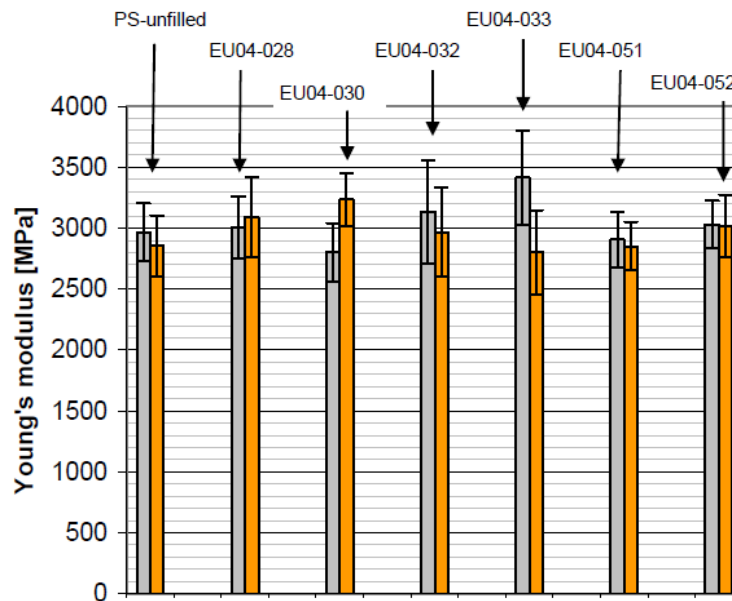
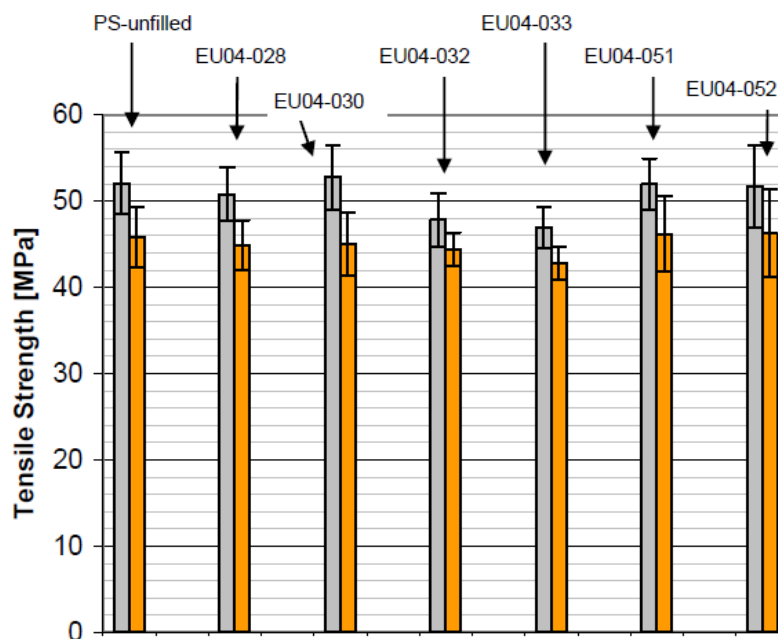


Figure 2: **Tensile strength measured in tensile tests at T=23°C (grey) and T=40°C (yellow), optical strain measurements**



Within error bars, there are no significant differences between the different nanocomposites. There is not even a clear trend between 23°C and 40°C behaviour. The insignificance of the well dispersed nanofillers can be rationalized by the large particle-particle distances. In the last columns, the effective size of the particles is listed as determined by SANS (neutron scattering) and by two mesoscale simulation methods, one of which (Fti-MC) developed within this project. It is found that the overall effective diameter of the grafted (20 K PS graft, EU04-33) nanoparticles is approximately 40-45 nm. A rough estimate of the surface-surface distance gives at a particle loading of 5 wt% a distance of approximately 70 nm, still 6 times the radius of gyration of a 100K PS in toluene. Thus, most of the polymer chains are almost bulk polystyrene and not affected by the interface around the nanoparticles.

In WP3, micromechanical simulations to compute the linear elastic properties of the model systems have been carried out. Work was done in collaboration between CRP and Culgi. Results are explained in detail in delivery report 3.3.

The morphologies of the nanocomposites were computed with DPD, a coarse graining of 4 styrene units per bead was applied.

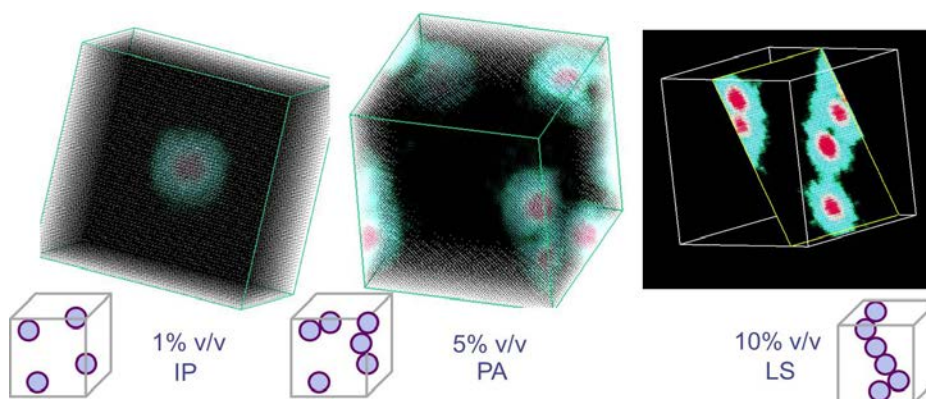
Table 10 lists the model systems for which the mechanical properties were estimated via FEM calculations using the nanocomposites morphologies as obtained for DPD Culgi (DPD 1:4) simulations.

Table 10. Model systems for which the mechanical properties were estimated via FEM calculations using the nanocomposites morphologies as obtained for DPD Culgi (DPD 1:4) simulations.

System		System	
19	PS 100kDa m_{wg} : 20 kDa ρ : 0.5 chains/nm ² c : 1 wt%	23	PS 100kDa m_{wg} : 20 kDa ρ : 0.7 chains/nm ² c : 5 wt%
20	PS 100kDa m_{wg} : 20 kDa ρ : 0.5 chains/nm ² c : 5 wt%	24	PS 100kDa m_{wg} : 20 kDa ρ : 0.7 chains/nm ² c : 10 wt%
21	PS 100kDa m_{wg} : 20 kDa ρ : 0.5 chains/nm ² c : 10 wt%	25	PS 100kDa m_{wg} : 20 kDa ρ : 1 chains/nm ² c : 1 wt%
22	PS 100kDa m_{wg} : 20 kDa ρ : 0.7 chains/nm ² c : 1 wt %	26	PS 100kDa m_{wg} : 20 kDa ρ : 1 chains/nm ² c : 5 wt %

Systems 19-21. Figure 3 shows the FEM cells for systems 19-21, while Table 11 lists the corresponding calculated Young modulus values E_C and the enhancement factor E_F , defined as $E_F = E_C/E_M$, where E_M is the Young modulus of the pristine PS matrix.

Figure 3 FEM cells for systems 19 (left), 20 (middle), and-21 (right) of Table 10. Below each panel the schematic representation of a prototypical morphology is portrayed: IP = isolated nanoparticle; PA = primary aggregates; LS = long strings.



System	Vol % NP	E_C (GPa)	E_C/E_M
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19	1	2.59	1.03
20	5	2.94	1.17
21	10	3.45	1.37

Table 11: Young modulus E_c and enhancement factor EF for nanocomposites systems 19-21 of Table 10 as obtained from FEM calculations using Culgi DPD morphologies.

It is evident that the model captures the overall characteristics of the test results quite well. Since the model works with elastic properties of the bulk materials in the linear regime, it is evident that no particular interfacial properties play a role here. The computed increase of stiffness is due to the incorporation of the stiff filler. Without assuming particular interfacial properties, the overall mechanical behavior of the nanocomposites could be predicted. This again confirms that the interface between grafting shell and matrix does not create a new interphase with novel properties in these systems.

This, however, is the case if the grafting chemistry and polymer matrix chemistry are similar or, in our case, identical. In order to evaluate if interfacial property tuning would allow for significant changes of mechanical properties of the nanocomposite, micromechanical modeling has been carried out. This work is described in detail in delivery report 5.2., and it was part of the constitutive modeling approach in this project.

Both the viscoelastic and elastic material properties of the nanocomposite model system as well as a micromechanical approach for the prediction of the macroscopic elastic properties were analyzed.

It was shown that the nanocomposite model system (polystyrene PS 100k filled with polystyrene grafted silica nanoparticles) shows no pronounced viscoelastic behavior at room temperature, the material is mainly elastic. Furthermore the temperature dependence of the nanocomposite dynamic mechanical properties is very similar to the one of the unfilled material. The micromechanical model analyzed for the evaluation of the composite elastic properties is a three phase analytical model which considers the interface region between nanoparticle and bulk matrix as a continuous and homogeneous phase. It is based on the so called "double-inclusion" model. The analytical model was evaluated by means of numerical homogenization on representative volume elements. This evaluation was performed for a characteristic set up (in terms of volume fraction and phase properties) for nanocomposites. The results show a good agreement between the analytical and the numerical homogenization.

Moreover the analytical model was used in order to estimate the properties of one example of the model system nanocomposite. In this case the interface properties were assumed. It was shown the effect of the integration of the nanoparticle in the matrix on the macroscopic properties by varying the ratio of interface modulus to bulk matrix modulus. Furthermore the effect of the ratio of interface region to the nanoparticle radius was analyzed. This study allows an evaluation of the enhancement potential by adding the spherical nanoparticles. **In case of spherical nanoparticles the fillers have to be very small (< 10nm radius) and the interfacial region surrounding the nanoparticles has to be considerably stiffer (factor 10) than the bulk matrix in order to have a significant effect on the mechanical properties. This is different to our systems where the interface has more or less identical properties as the matrix. With polymers, it will be difficult to fulfill those requirements.**

The analytical model enables an estimation of the effect of the nanostructure parameters (phases properties, geometrical arrangement) on the macroscopic material properties, thus enabling a better understanding of the behavior and hence the deduction of the key parameters to influence it.

It was planned to compute the interfacial properties for the present systems by molecular simulation (WP 6, delivery report 6.2) as an input for micromechanics and constitutive modeling to close the loop of a true multiscale modeling of our systems, but here we did not succeed with predictions. Approaches and formalisms to compute elastic coefficients such as the Poisson ratio, the shear modulus as well as the bulk modulus have been developed and tested for different systems, mainly by TU Darmstadt with support from NTU Athens. The

developed methods, based on molecular dynamics simulations, have been designed for applications on any type of system. An anisotropic polystyrene bulk has been chosen as an example to test the different developed methods. The obtained results indicate that for the polymeric systems considered, several realizations are required to obtain an averaged volume element suitable for the local evaluation of elastic coefficients. Specifically, the Poisson ratio and bulk modulus require smaller volume elements than the shear modulus. The determination of the Young's modulus is possible for larger volume elements. It can be obtained indirectly from the combination of two other elastic coefficients assuming local isotropy. The high computational cost is caused by finite-size effects and local anisotropies in the samples that lead to fluctuations in the elastic coefficients larger than (the expected) surface influence. Once the computational conditions for numerically stable calculations of elastic coefficients have been established in bulk systems, a reliable locally resolved mechanical description of the nanocomposite systems is therefore possible. Further computations with the noise level within a predefined acceptable range are currently underway for the nanocomposite systems of interest. Extensive computational simulations have to be performed to obtain a resolution allowing an analysis of the interphase influence on elastic coefficients.

Finally, on the level of constitutive modeling, partner Univ. Erlangen developed a working constitutive model based on methodology recently introduced by Miehe et al. [*Finite Viscoplasticity of Amorphous Glassy Polymers in the Logarithmic Strain Space*, Miehe C, Goektepe S, Diez M, *International Journal of Solids and Structures* 46, 2009, p.181-203]] is a successful model for the modelling of amorphous glassy polymers. The modular structure of this model makes it very attractive especially for the numerical implementation. In delivery report 5.1, the Miehe model has been adapted to model the influence of different types of nano-fillers mixed into bulk amorphous glassy polymers.

The proposed modified model was successfully validated against the model systems and applied to the system which is described in example 3. It was planned – and has to be left for a DFG project that has started now to continue the successful co-work of TU Darmstadt and Univ. Erlangen- to employ this model for the continuum part of the coupled FEM-MD approach that was successfully implemented within this project.

Example 2: Nanocomposites with PBT matrix and BaTiO₃ and SiO₂ nanoparticles

Polybutyleneterephthalate (PBT) is an important semi-crystalline engineering polymer. The commercial polymer Ultramid B4500 from BASF was used. The following composites were prepared and characterized:

Table 12: Composition and mechanical properties of PBT nanocomposites

Nanocomposite	Internal Code	Polymer matrix chemistry	Matrix Mol. Weight (Mn, g/mol)	Polydispersity index (PDI) polymer matrix	Filler Type	Filler content wt% filler	Filler (core) diameter (nm)	stable dispersion in nanocomposite (yes/no)	chemistry grafting agent	Elastic modulus [MPa]@23°C, 1%/min	tensile strength [MPa]@23°C, 1%/min	elongation at break [%]
PBT-0	Ultramid B4500 (PBT)	Polybutyleneterephthalate, PBT	28500	2,6						1639 +/- 85	61	13,9
PBT-1	4500+BaTiO ₃ /Butylglycol, EU04-048 (PBT)	PBT 4500	28500	2,6	BaTiO ₃ -Butylglycol, BASF	0,5	8	yes	80% BaTiO ₃ , 20 % Butylglycol	1594 +/- 76	61	
PBT-2	4500+BaTiO ₃	PBT 4500	28500	2,6	BaTiO ₃ -Butylglycol, BASF	1	8	yes	80% BaTiO ₃ , 20 % Butylglycol	1642 +/- 92	60	
PBT-3	EU04-43	PBT 4500	28500	2,6	SiO ₂ -AMEO, Epidoris SAS	1	50	yes	(3-aminopropyltriethoxysilane) AMEO	1609 +/- 116	55,4	11,9
PBT-4	EU04-44	PBT 4500	28500	2,6	SiO ₂ -AMEO, Epidoris SAS	2	50	yes	(3-aminopropyltriethoxysilane) AMEO	1586 +/- 85	53,6	10,54
PBT-5	EU04-45	PBT 4500	28500	2,6	SiO ₂ -PO Silane, BASF	1	15	no	Aerosil 380, Propylenoxydetrimer-silane	1522 +/- 56	55,3	13,22

The analyses on the nanocomposites with PBT matrix give the following results:

The mechanical behaviour of the nanocomposites with BaTiO₃ nanoparticles is very similar to the one of the unfilled PBT. No considerable changes in Young's modulus, tensile strength or elongation at break are observable by adding the barium titanate nanofillers. The mechanical behaviour of the nanocomposites with SiO₂ nanoparticles

is also similar to the one of the unfilled PBT. The following characteristics however were observed:

While the Young's modulus of the nanocomposite with PO-Silane functionalized silica nanoparticles (PBT-5) is approximately the same as the one of the unfilled material, the nanocomposites with AMEO-functionalized nanoparticles show a certain trend in an increase of the Young's modulus. Considering the standard deviation of the measurements it has to be remarked that the effect is not dominant, not all the samples show an increased Young's modulus, nevertheless a trend is observable. The nanocomposite PBT-3 with 1% of SiO₂-AMEO nanoparticles shows an increase of the Young's modulus (of the mean value) of approx. 9%, while the nanocomposite PBT-5 with the same amount of fillers but PO Silane functionalized shows approximately the same value of Young's modulus as the matrix. In this respect it is interesting to make an estimation of the expected increase in Young's modulus by adding 1% of spherical micron-sized instead of nano-sized fillers. Using the Mori-Tanaka model [Mori, T.; Tanaka, K.: *Average Stress in Matrix and Average Elastic Energy of Materials with Misfitting Inclusions. Acta Metallurgica* (21), pp. 571-574.], assuming the elastic values of the silica nanoparticles from literature [Schürmann, H.: *Konstruieren mit Faser-Kunststoff-Verbunden*, Springer-Verlag Berlin Heidelberg 2007: model parameters are given in delivery report 11.1] and taking the elastic modulus of the matrix as the one measured on the unfilled PBT, the micromechanical model predicts for a material with 0.5% volume content (calculated from the mass content and the material densities) of micron-sized spherical silica nanoparticles a Young's modulus that is only 1% higher than the one of the matrix. While in the experimental characterization an increase in Young's modulus of 9% is observed, in the micromechanical computation the increase in Young's modulus by adding only 1 mass % of spherical silica micro-sized particles is almost negligible. Thus it cannot be excluded that the trend in an increase of Young's modulus observed in the experimental characterization might be due to the fact that the particles are nano-sized. Nevertheless, as mentioned before, the effect is not dominant considering the standard deviation of the measurements. Moreover it is interesting that the nanostructure characterization performed by the Adolphe-Merkle Institute and presented in the report of Milestone 8 shows that the material with PO Silane functionalized nanoparticles (PBT-5) has very large aggregates of the nanoparticles in specific zones of the matrix, the nanoparticles and the polymer are almost phase separated (report of Milestone 8). The materials with AMEO-functionalized nanoparticles (PBT-3 and PBT-4) show some aggregates of the nanoparticles but a reasonable distribution of nanoparticles / aggregates in the matrix (report of Milestone 8). The results of the nanostructure characterization are consistent with the ones of the macroscopic mechanical characterization inasmuch as the material with large aggregates (PBT-5) does not show an increase in Young's modulus compared to the nanocomposites with smaller and well distributed aggregates.

Example 3: Nanocomposites with PMMA matrix and ellipsoidal TPM- SiO₂-Fe₂O₃ nanoparticles

Based on the argument that the missing "nano-effect" at low particle loadings is a consequence of the large particle-particle distance, it was decided to investigate the effect of non-spherical fillers. PMMA (commercial Altuglas TP727, see milestone report 8 for details) from Arkema Altuglass was chosen as matrix material.

The following composites were prepared and characterized:

Table 13: Composition and mechanical properties of nanocomposites with PMMA matrix and ellipsoidal TPM- SiO₂-Fe₂O₃ nanoparticles

Nanocomposite	Internal Code	Polymer matrix chemistry	Matrix Mol. Weight (Mn, g/mol)	Polydispersity index (PDI) polymer matrix	Filler Type	Filler content wt% filler	Filler (core) diameter (nm)	stable dispersion in nanocomposite (yes/no)	chemistry grafting agent	Elastic modulus [MPa]@23°C, 1%/min	tensile strength [MPa]@23°C, 1%/min	elongation at break [%]
PMMA-0	PMMA TP727 (unfilled)	PMMA TP727 (unfilled)	crosslinked							2040	59	
PMMA-11	PMMAhemat-AMI-solvent-2010	PMMA, Altuglas TP727	crosslinked	N/A	TPM-silica-hematite (TPM-SiO ₂ -Fe ₂ O ₃)	0,3	272/65 core, silica layer 18	yes	3-(trimethoxysilyl) propylmethacrylate	2339	58	18
PMMA-12	PMMAhemat-AMI-solvent-2010	PMMA, Altuglas TP727	crosslinked	N/A	TPM-silica-hematite (TPM-SiO ₂ -Fe ₂ O ₃)	0,6	272/65 core, silica layer 18	yes	3-(trimethoxysilyl) propylmethacrylate	2371	58	27
PMMA-13	PMMAhemat-AMI-solvent-2010	PMMA, Altuglas TP727	crosslinked	N/A	TPM-silica-hematite (TPM-SiO ₂ -Fe ₂ O ₃)	2,7	272/65 core, silica layer 18	yes	3-(trimethoxysilyl) propylmethacrylate	2662	59	14
PMMA-14	PMMAhemat-AMI-solvent-2010	PMMA, Altuglas TP727	crosslinked	N/A	TPM-silica-hematite (TPM-SiO ₂ -Fe ₂ O ₃)	6,3	272/65 core, silica layer 18	yes	3-(trimethoxysilyl) propylmethacrylate	2607	58	21

The results of the nanostructure characterization (see report Milestone 8) showed a homogeneous dispersion of the nanoparticles in the matrix. Homogeneous nanoparticle dispersion is a requisite for the enhancement of macroscopic properties. While after the synthesis in the laboratory the orientation of the ellipsoidal inclusions was approximately isotropic, the nanostructure analysis on micro-samples showed that the nanoparticles are oriented due to the injection-moulding process (see report of Milestone 8). In the mechanical measurements the nanocomposites with higher filler content, i.e. PMMA-13 (with 2.7% measured filler content) and PMMA-14 (with 6.3% measured filler content) showed an increased Young's modulus compared to the unfilled material. In contrast to the nanocomposites prepared also by solvent integration but containing TPM-coated silica nanoparticles, the elongation at break of the nanocomposites with TPM-silica-hematite nanoparticles is not reduced compared to the one of the unfilled PMMA. In order to make a rough estimation of the expected increase in Young's modulus by adding spherical and micron- instead of nano-sized fillers an estimation with a micro- mechanical model, with the Mori-Tanaka model was performed. For this purpose the nanoparticle is idealized as being made out of silica only. The aspect ratio of the nanoparticle is ~4 (272:65 nm, table 13). The elastic values of the silica nanoparticles are again taken from literature, and the elastic modulus of the matrix corresponds to the one measured on the unfilled PMMA. Details can be found in delivery report 11.1. The calculation is performed for two extreme cases of filler orientation. In the one case, it is assumed that the fillers are all unidirectionally oriented, whereas in the other case, the filler orientation is assumed to be fully isotropic. Assuming that the nanoparticles are unidirectionally oriented, the measured Young's modulus is lower than the estimated one for the nanocomposites PMMA-11, PMMA-12 and PMMA-14 (0.3%, 0.6% and 6.3% of mass content). In case that the nanoparticles are isotropically oriented, the measured Young's modulus is more or less equal to the estimated one. These results do not support the idea that the stiffening effect is mainly due to a "nano-effect". In the case of the nanocomposite PMMA-13 (2.7% mass content of nanoparticles) the measured Young's modulus is in both cases higher than the estimated one: assuming an isotropic nanoparticle orientation the measured Young's modulus is approx. 11% higher than the estimated one, assuming a unidirectional nanoparticle 5% higher. The effect, however, could be attributed to experimental uncertainties. Results are collected in tables 14 & 15.

Table 14: Estimation of the Young's modulus with a micro-mechanical model assuming that the filler are unidirectionally oriented, comparison with measured Young's modulus.

Material	Filler content		Nanocomposite		
	mass	volume	Calculated Young's Modulus	Measured Young's Modulus	Difference of Measured w.r.t. Calculated Modulus*
	[-]	[-]	[MPa]	[MPa]	[%]
PMMA-11	0.003	0.001	2352	2339	-0.56
PMMA-12	0.006	0.003	2375	2371	-0.15
PMMA-13	0.027	0.013	2535	2662	5.03
PMMA-14	0.063	0.030	2824	2607	-7.67

Table 15: Estimation of the Young's modulus with a micro-mechanical model assuming that the filler are fully randomly oriented, comparison with measured Young's modulus

Material	Filler content		Nanocomposite		
	mass	volume	Calculated Young's Modulus	Measured Young's Modulus	Difference of Measured w.r.t. Calculated Modulus*
	[-]	[-]	[MPa]	[MPa]	[%]
PMMA-11	0.003	0.001	2338	2339	0.03
PMMA-12	0.006	0.003	2347	2371	1.04
PMMA-13	0.027	0.013	2407	2662	10.61
PMMA-14	0.063	0.030	2515	2607	3.66

These three examples are sufficient to illustrate our findings throughout the whole project: the mere introduction of large interfacial areas into a polymer matrix is not sufficient to alter the mechanical performance. Well dispersed particles of different kinds, grafted with oligomers up to large polymers, with particle sizes between 8 and 250 nm were introduced into amorphous (PS, PMMA) and semi-crystalline (PBT; we failed with Polyamide) polymer matrices. The effect was an incremental increase of Young's modulus, and in many cases embrittlement. Both effects are well known. No particular "nano-effect" was found. Thus, since the materials properties of nanocomposites generated throughout the project did not show interesting new effects leading to new application, it was not possible to file any patent. This is, however, consistent with the fact that nanocomposites commercially still do not play a role as materials.

Rheological properties

Mackay and co-workers [A. Tuteja, P. M. Duxbury and M. E. Mackay, *Macromolecules* **40** (26), 9427-9434 (2007)] have reported that nanocomposites exhibiting reduced viscosity and multifunctional performance enhancements may be fabricated using simple processing procedures. These phenomena are elucidated by analysis of the effects of dispersed organic (fullerene) nanoparticles on the flow properties of polystyrene, demonstrating that simple spherical nanoparticles can induce a range of unexpected behaviour due to nanoscale effects. In general, multifunctional performance improvements including enhanced mechanical, electrical, magnetic and thermal degradation properties as well as reduced viscosity are promoted when simple design guidelines are followed. Specimens produced using the rapid precipitation method (which produces well-dispersed samples) exhibit viscosity decrease under flow conditions. On the contrary, if the sample is prepared using the

solvent evaporation method, large aggregates of fullerenes are present in the system, causing an increase in the viscosity. This provides two design parameters for achieving a viscosity reduction in nanocomposites: the polymer must be entangled and the interparticle half-gap must be less than the polymer size. It should also be pointed out that the shape of the nanoparticles is extremely important, since only spherical nanoparticles have been shown to provide a viscosity decrease so far.

In the molecular simulation approach of the Athens group within the project, the systems considered are dispersed fullerenes (C60 molecules) in atactic polystyrene matrix. The aim is to present the atomistic model used and to validate the predicted dynamics with existing experimental evidence. The objective of this work (see delivery report 2.2. for details) is to shed some light on the phenomena that cause a non-Einstein decrease of viscosity and accelerate the dynamics in polymeric nanocomposite systems when the dimensions of the nanoparticles are small compared to those of matrix chains. The characteristics of the system under investigation, such as the chain length of the matrix, the volume fraction and the size of the nanoparticles and the operational variables, are comparable to the experimental ones. Equilibration of the systems at a coarse-grained level is carried out using connectivity-altering Monte Carlo moves, which are capable of treating long-chain systems. The configurations are then subjected to a reverse-mapping procedure in order to restore important missing atomistic details due to coarse-graining. The detailed description is at the level of a united-atom model. Only such a detailed level can elucidate all possible mechanisms resulting in accelerated dynamics. The resulting structures have been subjected to extensive molecular dynamics runs. The original plan for this deliverable was to conduct topological analyses of chain entanglements in silica/atactic polystyrene melt nanocomposites, since entanglements are thought to be important for rheological properties. The computational tools required for the entanglement analyses planned are at hand in the form of the CReTA algorithm and code, developed at NTU Athens. However, we chose to adopt a different and, in our opinion, more illuminating approach to understanding rheological properties through simulations than envisioned in the original plan for the deliverable. This new approach was to characterize the dynamics by direct atomistic molecular dynamics simulations of well-equilibrated fullerene – atactic polystyrene nanocomposite systems in the molten state, which have been chosen to match as closely as possible the molecular constitution and composition of the systems studied experimentally in the recent work of Mackay and collaborators. Such a direct comparison between computed and measured dynamics is more useful for understanding and controlling rheological properties than carrying out the entanglement analysis, which would only give clues on topological aspects of the problem.

The system was equilibrated with coarse grained MC techniques as applied in WP 3, and with back-mapping techniques as further developed in WP 2 and applied in WP3, mapped onto an united atom representation of the system to study the local dynamics of the segments in the melt and close to the fullerenes. Since these are extremely demanding simulations, they are yet not finished, and a clear statement if the effect observed by Mackay can be confirmed by simulation cannot be given yet (see delivery report 2.2).

On the experimental side, partner CRP carried out routinely rheological characterizations of the nanocomposites listed in tables 2-5. The results are described in detail in delivery report 11.2.. The two requirements for viscosity reduction cited above, namely that the polymer must be entangled and the interparticle half-gap must be less than the polymer size was only partially fulfilled. The polymers were clearly entangled, but the interparticle gap was larger in our systems with the exception of the POSS systems since POSS (Polyhedral Oligomeric Silsesquioxane) nanoparticles have diameters comparable to fullerenes. Assuming a regular dispersions, particles with a diameter of 3 nm like POSS have at volume fractions of 1Vol% a surface – surface distance of approximately 10 nm, which is comparable to the radius of gyration of a technical polymer. The distance s is estimated as

$$s = d * ((0.74/V_f)^{(1/3)} - 1),$$

Vf volume fraction of nanoparticles, d NP diameter, assuming a dense packing with maximum volume fraction of 74 Vol%.

As described in milestone report 7, however, we failed to disperse POSS particles both in PMMA and in PA66. In all experiments, the POSS particles purchased from Aldrich formed aggregates.

For the successfully dispersed nanocomposites, characterization of the rheological properties was carried out by CRP. The methods and handling is described in delivery report 11.2. Briefly, the rheological characterization was carried out on a TA Instruments ARES oscillating rheometer equipped with a convection oven operation with N₂ gas and using a plate-plate geometry (d = 25mm). The samples were loaded in granule form to the heated plates and pressed to a 0,5 to 1,0 mm thick disk by the means of a melt ring adapter. The frequency sweep analysis were carried with a dynamic oscillating strain of 0.5%, inside the linear viscoelastic region. The frequency range used was between 0.3 and 100 rad/s, with logarithm spacing between data points. The frequency sweeps were repeated over a temperature range from 160° C to 250° C to allow for time-temperature shift analysis and the building of mastercurves.

For the “model systems” (table 1), the following zero shear viscosities and plateau moduli were obtained:

Table 16: zero shear viscosities and plateau moduli of PS nanocomposites

Nanocomposite, 100K matrix, 16 nm diameter filler, PS graft	Internal Code	Filler Type	Filler content wt% filler	Filler geometry	stable dispersion in nanocomposite (yes/no)	characterization method to prove dispersion in nanocomposite	chemistry grafting agent	graft Mol. Weight (Mn, g/mol)	Polydispersity index (PDI) polymer graft	grafting density (chains/nm ²)	zero-shear viscosity [Poise]	plateau modulus [dyn/cm ²]	estimated particle-particle distance, surface-surface (nm)
PS 100k annealed PS 100k + SiO ₂ (E-H1115) 0.5mass% (EU04-030) not annealed	EU04-030	SiO ₂ -PS (FZ Jülich)	0,5	spherical	yes	TEM	PS	20500	1,07	0,31	1,41E4@190°C	1,06E6@150°C	
PS 100k + SiO ₂ (E-H1115) 0.5mass% (EU04-030) annealed	EU04-030	SiO ₂ -PS (FZ Jülich)	0,5	spherical	yes	TEM	PS	20500	1,07	0,31	1,70E4@190°C	1,28E6@150°C	163
PS 100k + SiO ₂ (E-H1115) 5mass% (EU04-032) annealed	EU04-032	SiO ₂ -PS (FZ Jülich)	5	spherical	no (some aggregates)	TEM	PS	20500	1,07	0,31	1,58E4@190°C	1,27E6@150°C	55
PS 100k + SiO ₂ (E-H1123/125) 5.0mass% (EU04-033) annealed	EU04-033	SiO ₂ -PS (FZ Jülich)	5	spherical	yes	TEM	PS	20500	1,11	0,82	1,44E4@190°C	1,15E6@150°C	67
PS 100k + SiO ₂ (E-H1105/114) 0.5mass% (EU04-051) annealed	EU04-051	SiO ₂ -PS (FZ Jülich)	0,5	spherical	yes	TEM	PS	102900	1,02	0,51	1,64E4@190°C	1,05E6@150°C	
PS 100k + SiO ₂ (E-H1105/114) 1.0mass% (EU04-052) annealed	EU04-052	SiO ₂ -PS (FZ Jülich)	1	spherical	yes	TEM	PS	102900	1,02	0,51	1,75E4@190°C	1,20E6@150°C	

By trend, the nanocomposites show an increase in zero shear viscosity as expected. The same trend was observed for the nanocomposites with PBT and PMMA matrix and various fillers. These results gave no new insights and we refer to report 11.2 for further discussions.

Potential impact and main dissemination activities and exploitation of results

Awareness and wider societal implication

Nanotechnology is the basis for the next industrial revolution. However, the true potential of nanotechnology is not yet exploited exhaustively. Currently, the creation of new business opportunities in this domain does not show the same industrial dynamics as other, more mature industrial branches. This can be attributed to the following peculiarities of nanotechnology related research and industrial sectors:

1. The knowledge required for economic exploitation of nanotechnology enhanced materials and products is extraordinarily high. Europe has to face fragmented research and technology and innovation initiatives.
2. The large depth of knowledge needed on different aspects related to life sciences, chemistry and microelectronics leads to the need for a different profile of manager from the typical entrepreneurs traditionally working in other industrial branches. Nanotechnology requires fully networked poles or clusters of technology that support research to innovation cycles.
3. At its present state of development, nanotechnology is an enabling technology rather than a product. It operates mostly with unstructured value chains in which technology strategies have little chance to meet market needs. There is need for clear market drivers.
4. Because of the emphasis on new applications and markets for nano-inventions, established companies are unlikely to enter this domain, since it requires different approaches from those successfully applied in the past. Therefore, it is more likely than new start-up companies de-rived from other industrial branches aim at the exploitation of a given nanotechnology and its applications. There is a need for a dynamic and updated framework based on industrial fore-sight.
5. In the public perception, nourished often by publications in the media which lack of scientific evidence, nanotechnology is still associated with an unusually high level of risk. As a consequence, even large companies consider it wise to exploit nanotechnology in new, independent small companies -in particular start-ups- as part of their strategic risk and image management or even choose not to disclose the nano content on which the product appeal is based. Europe must address the crucial issue of safety with an evidenced-based approach.

NanoModel was mainly dealing with aspect 1, the technology and innovation aspect for a very specific application which is nanocomposites. The transfer potential of this project lies in the build-up of sound structure – property relationships and in the dissemination of validated simulation technology to speed-up development times and to reduce number of experiments. Improved understanding, however, will help to support the crucial safety aspects addressed under aspect 5.

The evolution of polymer nanocomposites has reached the stage at which these materials show great potential for application in a wide range of industries. Over the past ten to fifteen years there has been astonishing growth in the number of publications and patents in the field. The most recent information suggests that these materials are still on the steep part of the technology S-curve. Because nanocomposites greatly expand the available properties of materials, they are likely to find uses in a variety of fields. Initial applications are expected to be found in fields that make use of high-technology materials to meet demanding specifications, such as automotive, aerospace, and biomedical applications, with nanocomposites later spreading into commodity materials. One of the main hurdles that must

be overcome to reach this stage is the lack of validated models, which would allow precise predictions of structure-property relations. One of the key-learnings of NanoModel, however, is that it takes much more than structure-property relationships to yield commercially relevant materials. The good news is that we have further developed the tools to look into the innermost details of those materials, which sooner or later will lead to success. **Our concept, the introduction of isolated spherical nanoparticles by simple melt mixing or solvent evaporation has not led to “nano-effects” for mechanical properties. The main conclusion here is to concentrate on dispersion of smaller particles (we tried to disperse POSS, with no success) below 5 nm, and/or to work with aspherical particles to facilitate percolation of interphase.** There still is demand since the existing examples with clays [*Polymer-layered silicate nanocomposites: an overview*, Peter C. LeBaron, Zhen Wang, Thomas J. Pinnavaia, *Applied Clay Science* **15** (1999), 11–29] work by strong interaction with the crystal-phase (modifying it), in a difficult to commercialize way.

Previous research had demonstrated a range of novel mechanical, thermodynamic, and flow related properties for polymer nanocomposites. An overview of the state of the art is given in [Nanoparticle polymer composites: Where two small worlds meet; A. C. Balazs, T. Emrick, and T. P. Russell, *Science* **314**, 1107 (2006)]. Some recent findings were:

- melt state composites drive nanoparticles into surface cracks, suggesting a way to create self-healing systems [*Using nanoparticles to create self-healing composites*; J. Y. Lee, G. A. Buxton, and A. C. Balazs, *Journal of Chemical Physics* **121**, 5531 (2004)]
- nanoparticles eliminate the “shark-skin” instability in polymer extrusion and control the dewetting of thin polymer films [*A novel processing aid for polymer extrusion: Rheology and processing of polyethylene and hyperbranched polymer blends*; Y. Hong, J. J. Cooper-White, M. E. Mackay, et al., *Journal of Rheology* **43**, 781 (1999)]
- interaction of particles with block copolymers can be used to control the spatial distribution of the particles [*Entropically driven formation of hierarchically ordered nanocomposites*; J. Y. Lee, R. B. Thompson, D. Jasnow, et al., *Physical Review Letters* **89** (2002)], allowing a wide range of optical or electrical properties [*Proximity effects in self-organized binary particle-block copolymer blends*; M. R. Bockstaller and E. L. Thomas, *Physical Review Letters* **93** (2004)]
- varying nanoparticle properties forces a transition in the morphology of a block copolymer melt [*Binary hard sphere mixtures in block copolymer melts*; R. B. Thompson, J. Y. Lee, D. Jasnow, et al., *Physical Review E* **66** (2002)]
- nanoparticles that localize at the interface stabilize bicontinuous phases in mixtures [*Colloidal jamming at interfaces: A route to fluid-bicontinuous gels*; K. Stratford, R. Adhikari, I. Pagonabarraga, et al., *Science* **309**, 2198 (2005)]
- nanoparticles significantly alter phase separation kinetics and can arrest domain coarsening [*Compatibilizing bulk polymer blends by using organoclays*; M. Si, T. Araki, H. Ade, et al., *Macromolecules* **39**, 4793 (2006)]
- nanoparticles can reduce viscosity [*Nanoscale effects leading to non-Einstein-like decrease in viscosity*; M. E. Mackay, T. T. Dao, A. Tuteja, et al., *Nature Materials* **2**, 762 (2003)] and can reduce or increase T_g [*Controlling the thermomechanical properties of polymer nanocomposites by tailoring the polymer-particle interface*; A. Bansal, H. C. Yang, C. Z. Li, et al., *Journal of Polymer Science Part B-Polymer Physics* **44**, 2944 (2006)]

Taken collectively, these results show the great potential of properly designed nanoparticles to control both structure and kinetics at the micro- and meso-scales. With the development of validated multiscale methods within this project we are now in a position to

- provide the missing link that will allow many of the predicted novel features of nanocomposites to be reproduced in industrial systems
- greatly streamline the process for discovering previously unknown properties of nanocomposites that can provide technological advantages.
-

Industrial Applications

The increased ability to control materials properties through the addition of nanoparticles will prove beneficial in a number of different industries. Recent estimates put the global rate of polymer production in the range of 110 to 180 billion kg per year [*Polymer nanocomposites*; K. I. Winey and R. A. Vaia, *MRS Bulletin* **32**, 314 (2007)]. Market surveys estimate the global consumption of polymer nanocomposites at tens of millions of kg (~\$250 million) and forecast a potential annual growth rate of 24%, leading to a market of \$500-800 million within five years [Winey and Vaia]. The most effective path for introducing this new technology in industry will be to first target high value sectors, where the enhanced properties of nanocomposites can play a critical role. At a later stage we see these benefits being extended to commodity materials. We have identified three high technology areas where nanocomposites have strong promise: automotive, aerospace, and biomedical.

The use of high-performance plastics in automobile manufacture has shown a steady increase in recent decades, such that average plastic content has increased from 6.0% of total vehicle weight in 1994 to 8.3% in 2004 [*Driving efficiency*; A. H. Tullo, *Chemical & Engineering News* **84**, 12 (2006)]. This ongoing trend will continue to enhance the need for well designed nanocomposites. They offer several advantages including an increase in rate of production, lower manufacturing costs (both economic and energy), enhanced environmental and thermal stability, and lower weight [*Polymeric nanocomposites for automotive applications*; J. M. Garces, D. J. Moll, J. Bicerano, et al., *Advanced Materials* **12**, 1835 (2000)]. To ensure that the modelling tools developed under this proposal are aligned with the needs of industry we have integrated representatives from several levels of the automotive industry in the team. As discussed above, an important impact of nano-inclusions is to reduce melt viscosity, improving the injection-molding process. **In particular the methods developed by NTU Athens (Fti-MC) together with their atomistic codes will help here.** However, the full benefits of nanocomposites span the timeline of automobile production and operation. Due to the electrical conductivity of nanocomposite based automotive parts, such as bumpers, coats can be applied by electrostatic spray, removing the need for an additional primer coat and reducing volatile emissions. Nanocomposites also offer significant reductions in weight (~50-80% over metals and ~25% over traditional filled plastics). Reducing vehicle weight is crucial to energy efficiency, since ~90% of the energy used in an automobile's life cycle is from fuel consumption. The percent decrease in fuel consumption is commonly estimated to be half of the percent decrease in vehicle weight. Lightweight materials, in particular together with e-mobility, have become extremely important recently.

Aerospace applications provide some of the most demanding physical, chemical, electrical, thermal, and mechanical property requirements, making this an inviting area for the use of nanocomposites [*Challenges and opportunities in multifunctional nanocomposite structures for aerospace applications*; Y. Baur and E. Silverman, *MRS Bulletin* **32**, 328 (2007)]. Currently, typical approaches to meet these requirements incorporate large-scale conducting materials (such as foils and grids). The size and weight of these components can complicate maintenance and repair. When properties can be enhanced by a small added amount of nanoparticles, a much lower trade-off can be achieved. Typical challenges in the aerospace field include the need to maintain chemical stability in adverse environments, minimum distortion in widely varying temperatures, the need to allow high localized heat flux for power dissipation, and the need for electrically conducting polymer materials to control static discharge, electrical bonding, and other issues. In addition, fuel accounts for roughly 50% of the operation costs of a commercial airplane, while the cost of launching payloads into Earth orbit is roughly \$20,000/kg [Baur and Silverman]. Thus, any reduction in material weight will have a significant economic impact.

In biomedical technology, new biocomposite materials are finding interest for applications such as tissue engineering, bone replacement/repair, dental applications, and controlled drug delivery [*Polymer nanocomposites for biomedical applications*; R. A. Hule and D. J. Pochan, *MRS Bulletin* **32**, 354 (2007)]. Composite materials used in these areas are derived from

biodegradable polymers, (e.g. polysaccharides, polyesters, polypeptides, and proteins) and both organic and inorganic fillers. This field raises new challenges for, in addition to possessing desired mechanical properties, materials must also satisfy biocompatibility, biodegradability, and, in some instances, aesthetic demands. A typical application of nanocomposites is in bone grafting. It is estimated that over one million bone grafting procedures are performed annually in the USA and Europe combined, with a market size of \$1.5 billion to \$2 billion, while the annual number of hip replacements in the USA is around 200,000 [Development of nanocomposites for bone grafting; R. Murugan and S. Ramakrishna, *Composites Science and Technology* **65**, 2385 (2005)]. Nanocomposites are among the most promising bone graft materials, in part due to their similarity with natural bone, which is itself a nanocomposite matrix.

Outreach and exploitation of results

One of the primary reasons for the lack of validated simulation tools for the design of composite materials is the fundamental multiscale nature of the problem. For atomistic simulations, there exist several well developed force field models (e.g. CHARMM, AMBER, Dreiding) that can be used in molecular dynamics and Monte Carlo simulations to obtain physically useful results. For large scale problems, continuum modelling approaches, such as FEM and computational fluid dynamics allow one to predict behaviour using a manageable number of experimentally measurable properties as input. With the coupling of both approaches, one of the main tasks of NanoModel, mainly performed by University of Erlangen and TU Darmstadt, and implementation into a commercially available software system by Culgi BV, a first step has been made to connect both worlds. From a societal point of work, the get-together of both communities was a success in itself. Scientists from mechanical engineering (Erlangen) had their first encounter with molecular simulation, and molecular simulators (Darmstadt) made their first FEM experiences. This is documented not only in joined publications (2 already published, 1 submitted) and a working prototype that is the basis of Culgi's commercial version, **but in 11 joined workshops to disseminate know-know between and among the different communities**. In total, 2 undergraduates were trained on this topic, 3 diploma theses and 2 PhD theses were obtained. It is clear that the method needs some further development due to its novelty. This is ensured by a research grant obtained by DFG priority program 1368 which will support the further research. We have high hopes that the method will become very fruitful for industrial applications in the next time due to the availability of the commercial version. Based on the prototype developed with locally separated MD and FE computations, the integration into CULGI software has been done and presented to consortium members in a workshop at BASF on October 28th 2011. Documentation and installation notes are available upon request, and are submitted as milestone reports 13 and 14.

Modeling Methods & Software

NanoModel developed and enhanced methods and simulation software. To make sure that others can sustainably use the software developed throughout this project, a commercial vendor of simulation software, CULGI BV was integrated into the project right from the start. Thus there now is a **commercial version of software, "CULGI-Software"** marketed by CULGI BV, and a consortium-restricted software (the software provided by the consortium members and the software written within the project for use within the project). Affiliated partner CULGI Ltd (Beijing) was mainly responsible for interface development of the commercial CULGI version, and was involved in dissemination in so far as to assist CULGI BV in dissemination in China.

The **non-commercial consortium software** has been exchanged and used free of charge among consortium members and also the right to use free of cost in future even after the EU project has ended. Using this standalone software developed by individual groups might need training which was provided by the respective consortium member under support of CULGI BV. The commercial software has been available by CULGI to other consortium

members free of charge during the lifetime of the project. CULGI organized trainings, validation and showcases which have been used to validate the commercial as well as the non-commercial software. The events are listed under dissemination activities.

Each project member has unrestricted and royalty-free access to the results of the other project members, especially to the software tools (“**non-commercial consortium software**”) developed within the project. The project members may use the software without restriction and may also adapt or enhance the software after the duration of the project. Additionally, they were trained in **workshops** during the project.

The Computational Material Science and Engineering group (CoMSE) of NTU Athens worked closely with the Technical University of Darmstadt, the University of Erlangen and University of Trieste. The most important contributions in the field of method development from the Athens group have been:

- Adaptation of existing methodologies such as forward / reverse mapping schemes between coarse-grained and atomistic levels and Monte Carlo moves to treat systems with interfaces and systems where there are constraints on the location / motion of polymeric chains
- Development of a novel coarse-grained computational methodology “Field Theory-inspired Monte Carlo” to predict whether aggregation or stable dispersion of nanoparticles inside polymeric matrices is thermodynamically favoured.
- Development of a new computational methodology to compute the local stress in model systems characterized by periodic boundary conditions.

The main results have been summarized and published in two papers and five presentations in scientific conferences. At least two more papers are in preparation and are expected to be submitted soon. **A significant portion of the developed software has been designed to allow smooth interaction with the open-source MD package LAMMPS and will be made available as public domain in the near future. The group is planned to continue working on the field of nanocomposite materials as partner in a new EU-funded project on the field of Nanotechnologies.** Thus, the results obtained and the methodologies developed in the context of NanoModel will be immediately exploited.

The DPD builder developed by BASF has been used to generate structures for BASF and TU Athens, and it will be further developed by BASF. Tools developed in Darmstadt and Athens have been mutually exchanged between those partners, and this will continue, in particular since one of the developers in Athens will take a position at TU Darmstadt.

Industry Modeller, external Modeller & sustainability of method development

For “industry & external modellers”, methods relevant to perform molecular simulation on nanocomposites and materials in general have been implemented, and are thus available to the public on a royalty-bearing basis. The **CULGI software** package has graphical interfaces, builders and simulation engines to construct and simulate properties of nanocomposites (milestone 15, 16 and 17). The capabilities have been in particular evaluated by consortium member MOSE-Trieste, who have shown that e.g. dispersion stability of fillers can be predicted with tools within CULGI (delivery reports 3.2, 3.3, milestone report 10). These simulations have been compared to experimental findings and to benchmark simulations with academic codes within the consortium.

In the three meetings of the EURG (end users reference group), partners from industry (BASF, Bosch and CRP) were trained with the most recent versions of CULGI containing most of the foreground. It is the intention of BASF to continue using CULGI on a commercial basis for its research in soft matter development.

The integrated MD-FEM program has been installed and tested at the BASF site in Ludwigshafen, Germany (workshop, milestone 14), and successfully run. It is planned to explore the potential of the implementation in more detail, and to stay in contact with the developers in Darmstadt and Erlangen. CULGI has made available a standalone software

package that will allow users of the consortium to run the integrated MD-FEM program on their computers. Both the groups in Erlangen and Darmstadt have shown interest to use this package in future research projects. CULGI has no intention at the moment to commercialise the integrated MD-FEM program in its current form. However, for CULGI it was a good exercise to see if we could integrate the external academic codes into our software platform. In addition we will continue to follow the future development of the MD-FE code by the academic partners and assess the possibility to commercialise the code. In addition to working with individual clients, members of CULGI have frequent contact with end users through an internal web forum (www.culgi-scripts-exchange.com) and larger external forums. The latter includes participation in the Industrial Fluid Properties Simulation Collective (<http://fluidproperties.org/>), an international collaboration between industry, academia, and national labs that promotes the validation of modelling tools for use in industrial settings.

Dissemination activities

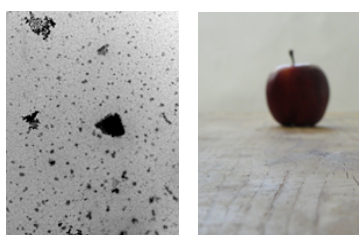
The full list of dissemination activities is given in section 4.2. of the final report.

Besides the usual dissemination activities like publications and scientific presentations in national and international conferences, there were some activities which were very important for the success of the project. As previously mentioned, this project brought together very diverse competencies and communities which finally had to work successfully together. That we succeeded can be seen by the successful coupling of continuum mechanics to molecular simulation techniques. This became possible through a series of joined workshops and meetings and seminars. To introduce experimentalists into simulation methodology and handling, on occasion of **each semi-annual meeting** there was a hands-on training carried out by Culgi BV. For the special necessities of professional modellers in industry, there were three End Users Reference Groups (EURG) meetings (1-2 days) to introduce to the newly implemented features relevant to materials modelling.

During the first day of the first annual user meeting, a scientist (Dr. Javier V. Goicochea) from the related EU project Nanopack participated in the scientific discussions, and Prof. Müller-Plathe in turn presented NanoModel at the Nanopack Workshop at IBM Rüschlikon, Switzerland, at their meeting on 2nd July 2009.

Together with EU project CODICE, a joined NanoModel-CODICE Molecular Modeling course was organized and held by Dr. Kurkal-Siebert from BASF who was member in both projects. Some of the lectures were given by NanoModel researchers. The course took place in *Park Inn Hotel, Mannheim* on 27th – 29th October 2010

A very special introduction into the nano world was organized by O. Pravaz from FriMat/AMI. Olivier Pravaz has collaborated with the Belgian artist Edith Dekyndt in order to attempt to visualize the link and controversy between nature (an apple) and technology (plastic) at the fundamental level of matter, the nanoscale. He has developed a protocol to make possible the uniform dispersion of wood and apple in Plexiglas. At the macroscopic scale, which is the scale of presentation of the "nanocomposite", it is impossible to distinguish one or the other components of the Plexiglas. However, using a transmission electron microscope (TEM), one can reach the nanoscale, which reveals the heterogeneity of the plastic. The artistic installation was presented at the art gallery of Fribourg (Fri-Art: fri-art.ch) <http://www.unifr.ch/scm/de/news/6643/> from February 13th to May 8th 2011.



Culgi finally organized specific training to introduce to multiscale modeling and the methods implemented :

- *Hands-on training sessions were given at the M6 (Erlangen) and M12 (Athens) , M18 (Waiblingen), M24 (Trieste) and M30 (Darmstadt) meeting. Attendee lists are available on request.*
- *From 26-30 October 2009 Volker Bernart (BASF) visited the Culgi Office in Leiden to get training on the usage of Culgi software.*
- *From 11-13 October 2011 Dr. Murat Cetinkaya (BASF) visited the Culgi Office in Leiden to get training on the usage of Culgi software.*
- *On April 2 and 3 Dr. Klein Wolterink gave a two-day tutorial on the usage of the Culgi software during the first EURG meeting hosted by BASF.*
- *On 8 December 2010 Dr. Klein Wolterink and Dr. van Male gave a one-day tutorial on the usage of the Culgi software during the second EURG meeting hosted by Bosch.*
- *On 29 and 30 August 2011 the Culgi team gave a two-day workshop on the usage of the Culgi software during the third EURG meeting hosted by Culgi in Leiden.*
- *Computational , Chemistry Course (Date: 1 – 3 June 2010), Topics: Atomistic, mesoscopic, field-based and hybrid modeling; Mapping techniques; Simulation methods; Culgi, Python and Tcl script writing; Parallel computing.*

The team

Finally, the team. As stated in the mid-term review,

“This project benefit from an experienced scientific core partners, assisted by young, competent researchers, coordinated with competence by the BASF coordinator...An excellent asset of this project is related to the fact that the Human Resources have been very well targeted in involvement of young researchers.....The Gender Equality Actions has been satisfactory progressed. The coordinator has taken interesting actions and delivered documents related to the implications of women in research. ...Actually, in this project there are many researchers - women involved, from almost all partners including coordinator, also from young generation which is a very positive fact.”

The project was indeed carried out by young researchers, as can be seen below by the many PhD students and PostDocs. Most of them were specifically hired for the project. There was vivid exchange among partners, also across communities. There is some hope that the multi disciplinarily of the project will have in impact to their future work.

	Coordinator	WP leader	Experienced Researcher	PhD student	Other	Postdocs
BASF		1 m	1f, 3 m		1m	
TUD		1m	3m	1f, 2m	2f	3 m, 1f recruited for the project
NTUA		1 m	2m	5 m		4 m recruited for the project
ERL		1m	2m	2m	4m,1f	
EPIDORIS		1m			1f	
JUELICH		1m	2m	1m		
Culgi		1m	2m,1f		1f,4m	
CRP		1m	5 m, 3 f		1 m	
AMI		1m		1m	1f	
MOSE-Trieste		1 m	2 f, 1 m	1 f	1f	1 m, 1f
BOSCH		1 f	2 f, 4 m		1 f	
Total	1m	9m, 1f	24m,9f	11m,2f	6m, 7f	8m, 2f

Address of project public website and relevant contact details

Website: <https://www.nanomodel.eu>

NanoModel Mission

The practice of adding micron sized inorganic filler particles to reinforce polymeric materials can be traced back to the early years of the composite industry. With synthetic methods that can produce nanometer sized fillers, resulting in an enormous increase of surface area, polymers reinforced with nanoscale particles should show vastly improved properties. Yet, experimental evidence suggests that a simple extrapolation of the design paradigms of conventional composites cannot be used to predict the behavior of nanocomposites.

The origin of these differences between conventional and nanocomposites is still unknown. This, unfortunately, precludes yet any rational design. This project aims at overcoming these deficiencies by a twofold strategy. This project will bring together a critical mass of scientists, from atomistic to finite-element modeling. The goal is to develop, implement and validate multi-scale methods to compute the mechanical, thermochemical and flow behaviour of nano-filled polymeric materials – based on the chemistry of selected model systems.

-> [project_presentation](#) -> [publications&talks](#)

Sign in to NanoModel

Enter your username and password here in order to log in on the website:

Username:

Password:

[Forgot your password?](#)

Beneficiaries

Logos of project beneficiaries: Universitat Freiburg, Technische Universität Darmstadt, BASF, Eπ, Universität Pavia, Culgi, Bosch, and CRP.

Public part: [link to project presentation](#)
 [link to publication & talks list](#)

Beneficiary Number	Beneficiary	Contact	e-mail address
1 (coordinator)	BASF	Horst Weiss	horst.weiss@basf.com
2	TU-Darmstadt	Florian Müller-Plathe	f.mueller-plathe@theo.chemie.tu-darmstadt.de
3	NTU Athens	Doros Theodorou	doros@chemeng.ntua.gr
4	U-Erlangen	Paul Steinmann	Paul.steinmann@itm.uni-erlangen.de
5	Epidoris	Iacopo Galli	iacopo.galli@epidoris.eu
6	FZ-Jülich	Wim Pyckhout-Hintzen	w.pyckhout@fz-juelich.de
7	Culgi	Jan-Willem Handgraaf	janwillem@culgi.com
8	CRP	Sarah Padovani	sara.padovani@crp.crf.it
9	FriMat/AMI	Herve Dietsch	herve.dietsch@unifr.ch
10	UNITS	Maurizio Fermeglia	Maurizio.fermeglia@dicamp.units.it
11	Robert Bosch GmbH		kurt.hornberger@de.bosch.com