Proposal synopsis

Organic-inorganic polymer nanocomposites (PNCs), defined as polymer composites where the inorganic filler size is at least in one dimension less than about 100 nm, have attracted much interest the last 25 years, due to the significant improvement of many of the properties of the polymer matrix (mechanical, thermal, barrier properties etc) at much lower filling factors, as compared to conventional composites. The low filling factors of PNCs are particularly important from the technological point, e.g. for low polymer viscosity during mixing with the nanoparticles and processing. Interestingly, even reduction of polymer melt viscosity by mixing with nanofiller has been reported. In addition, experiments show that we may have simultaneous increase of both stiffness and toughness in a PNC, in contrast to what we know for conventional composites.
Despite many efforts, there is yet no theory to satisfactorily account for the significant improvement of properties in PNCs. It is generally accepted, however, that interfacial effects arising from the large surface to volume ratio of nanoparticles play a significant role for that improvement. In analogy to results of experiments and computer simulations in model systems, we may expect that polymer at the interface and in a few nm thick interfacial layer around the nanoparticles shows different organization, thermal transitions, dynamics and properties, as compared to bulk polymer. As a result, the presence of interfaces and interphases may affect significantly the final properties of PNCs, including the technologically significant ones, such as mechanical properties. A better understanding of this dependence, as a part of the structure-property relationships, i.e. the complex relationships between composition, preparation/processing conditions, structure/morphology, dynamics, and final properties, is essential for a rational, knowledge-based design of materials with predicted properties to meet specific end-use requirements. From the fundamental point of view, on the other hand, the large interface area in PNCs allows studying the polymer interface in bulk samples. Crucial for both, technological applications and fundamental studies, is the quality of dispersion of nanoparticles in PNCs.
Results on thermal transitions and dynamics in PNCs reported in the literature, often discussed in terms of the glass transition (and quantified by the glass transition temperature T_g), measured in experiments by calorimetry (DSC), and the associated segmental α relaxation (dynamic glass transition), followed in experiments by spectroscopic techniques, such as dielectric (DRS) and mechnanical spectroscopy (DMA), are controversial. Dynamics may become faster or show no change even in well dispersed composites. In most of the studies a few nm thick layer of interfacial polymer with restricted mobility is detected around the filler particles, while the rest of the polymer shows bulk dynamics, this behaviour being described in terms of three- and two-layer models or a continuous distribution of T_g*s* as a function of the distance from the particle surface. In addition to this interfacial effect on polymer dynamics in PNCs, there is also a "confinement" effect, which should be properly considered. With that we mean the acceleration of dynamics (reduction of T_g) when the mean distance between the nanoparticles, which decreases with increasing filling factor, becomes comparable to the cooperativity length of the glass transition. Physical ageing (structural relaxation), intimately related to glass transition, has been found to be accelerated in PNCs, a correlation of that to changes in polymer dynamics being, however, a point of controversy. Next to polymer dynamics, nanoparticles may affect significantly also polymer crystallization in the case of semicrystalline thermoplastic matrices. Results reported so far are not conclusive as to whether the nanoparticles control the crystallization process or rather the crystalline lamellae dominate by manipulating the particle dispersion.
The proposed project aims at the preparation, characterization and understanding of interface and interphase properties of organic/inorganic PNCs. NCs based on selected, mostly thermoplastic polymer matrices (poly(methyl methacrylate) (PMMA) and semi-fluorinated PMMA (f-PMMA), polystyrene (PS), poly(hydroxyethyl acrylate) (PHEA), poly(ethylene glycol) (PEG), poly(ethylene terephthalate) (PET), poly(ether ether ketone) (PEEK), as well as the elastomer poly(dimethyl siloxane) (PDMS)) and spherical metal oxide (mainly silica and titania), as well as CNT fillers will be chosen as model systems. They will be prepared by expert groups in abroad in the frame of existing collaborations, using various routes, depending on the combination of polymer and filler. These include generation of oxide nanoparticles by sol-gel processes in the presence of the swollen polymer matrix or simultaneously with polymerization, polymerization in-situ in the presence of preformed filler, and mixing of polymer and filler in the melt or in a common solvent. The strength of polymer-filler interactions will be finely tuned by the selection of the polymer and the filler (e.g. hydrogen bonding interactions are absent in PS/silica, moderate in PMMA/silica and stronger in PMMA/titania NCs), and, for a given system, by functionalization of the surface of the filler, in selected cases also of the polymer. The chemistry of preparation will be checked by FTIR and NMR.

Materials will be prepared and characterized by various techniques at several levels of filler content and with systematic variation of the other parameters of synthesis (e.g. type of functional group and surface coverage), including the neat polymer matrix for comparison. The morphology of the NCs prepared will be studied by a combination of AFM, XRD, SEM, TEM, SAXS, and SANS techniques, depending on the particular system, partly in Athens and partly in the labs they will be synthesized and other collaborating labs. In addition to the quality of filler dispersion, which will be quantitatively characterized, special aspects of interest include aggregation (percolation) and in the case of CNTs straightening and alignment. Thermal transitions, in particular glass transition and polymer crystallization/melting in the case of semicrystalline polymer matrices, will be studied in detail by DSC and temperature modulated DSC (TMDSC) to reveal and quantify the effect of the filler on the transition. Dielectric techniques (broadband dielectric relaxation spectroscopy-DRS, thermally stimulated depolarization currents-TSDC, slow time domain spectroscopy-TDS) will be employed for the investigation of polymer dynamics. The broad ranges of frequency and temperature covered will allow following on the same sample processes with different length scale, from local, secondary relaxations (less than 1 nm) over segmental relaxation (dynamic glass transition, length scale about 2 nm at T_g) to conductivity (length scale in the range of μm). Conductivity studies are of particular interest for CNT NCs to quantitatively described percolation in correlation to quality of dispersion and interfacial effects (functionalization). Two kinds of properties, significant for applications and strongly dependent on interfacial interactions and quality of dispersion, will be investigated: mechanical properties by DMA and stress-strain measurements and permeability of the NCs to water, vapours and gases by sorption/diffusion measurements. Computer simulations will be employed for the investigation of morphology and polymer dynamics and the quantitative prediction of properties in close collaboration with the group of Prof. Theodorou at NTUA and in coordination with experimental work.

The main objective of the proposed project is the creation of new knowledge on the organization and the properties (thermal transitions, dynamics) of the polymer at the polymer-filler interface and in the polymer interfacial layer and on their effects on the final properties of PNCs, by a combination of targeted synthesis of the materials, several partly complementary experimental techniques of characterization, and computer simulations. Particular objectives are the contribution to a better understanding of structure-property relationships in PNCs; the development of new methodologies for the investigation of interfacial effects in PNCs on the basis of a combination of various experimental techniques, in particular DSC/DRS/TSDC/DMA; the development of a methodology for the calculation (prediction) of the segmental relaxation time as a function of the distance from the nearest nanoparticle surface on the basis of the overall dielectric response of the NC; the contribution to further development of computational tools for the prediction of morphology, dynamics and properties in PNCs in collaboration with experts and in close coordination with experimental work.

The methodology which will be followed to reach these objectives is based upon the considerable experience of the research team over a long period of time in the issues of the project and an extended network of collaborations which provides access to PNC specimens designed and synthesized by experts teams for the needs of the project, to experimental characterization techniques not available in Athens and to computer simulations in close coordination with experimental work. The project is divided into 7 Work Packages (and these into more tasks), as follows: WP1 Synthesis and physicochemical characterization; WP2 Morphological characterization; WP3 Thermal transitions; WP4 Dynamics and electrical conductivity; WP5 Mechanical properties; WP6 Permeability studies; WP7 Computer simulations.

The project will lead to creation of new knowledge on the organization and the properties (thermal transitions, dynamics) of the polymer at the polymer-filler interface and in the polymer interfacial layer and on their effects on the final properties of PNCs, as well as to a better understanding of structure-property relationships in this relatively new class of materials. Heretofore unanswered questions to be addressed within the project include the following: (1) How do interfacial polymer-filler interactions alter segmental dynamics and T_g? What is the relative contribution of the “interface” effect and of the “confinement” effect? How can the two effects be separated? (2) How do nanoparticles affect polymer matrix crystallization? Do they control the crystallization process or do the crystalline lamellae dominate particle dispersion? (3) Does the immobilized layer around nanoparticles really remain immobilized up to polymer degradation? (4) Is suppression of physical ageing in PNCs related to changes in polymer dynamics? (5) Can experiments provide a route for predicting (calculating) relaxation times as a function of the distance from the nearest nanoparticle surface in PNCs (inverse problem)? (6) Which is the best preparation method for optimizing electrical conductivity in polymer/CNT NCs? How should functionalization be tuned to simultaneously optimize mechanical performance and electrical conductivity in polymer/CNT NCs? (7) What is the route for taking full advantage of the high stiffness of CNTs in polymer/CNT NCs? Better functionalization? Straightening and aligning of CNTs? How can stiffness and toughness be simultaneously optimized in polymer/CNT NCs?

Expected results (deliverables) include: A set of well-characterized PNC specimens with various matrices and fillers available (also to other groups) for further studies, in particular of final, macroscopic properties in relation to targeted applications; Experimental results on morphology, thermal transitions, dynamics (summarized in the form of Arrhenius plots), mechanical properties, and permeability to water, alcohols, and gases (N_2, O_2, CO_2) in several PNCs; Experimental results on electrical conductivity in several CNT/polymer NCs in relation to method of preparation, and type and surface coverage of functionalization; Computational tools able to predict and explain morphology, dynamics and properties (T_g, polymer crystallization, mechanical properties etc) of PNCs; A methodology for the investigation of interfacial effects in PNCs based on DSC/DRS/TSDC/DMA studies; A methodology for the prediction of dynamics as a function of the distance from the nearest nanoparticle surface in PNCs on the basis of DRS experiments.

The results of the project will be reported in more than 15 articles in international journals of high calibre and more than 20 presentations in scientific meetings. It may be expected that the new knowledge generated within the project will contribute to the rational, knowledge-based design and production of new structural materials with optimum balance of stiffness, toughness and strength for high-performance applications; new, cost-efficient, polymer-based conducting materials for gas sensor and for electromagnetic shielding applications; new cost-saving and friendly to the environment processing technologies for preparing PNCs, contributing to sustainable development. In addition, the project will provide excellent education/training facilities for young researchers (5 post-docs, 3 PhD students, several students working for MSc and diploma thesis) by providing access to research; participation to international workshops, training schools and conferences; participation to short term visits in other labs.

The research team to carry out the project consists of 4 staff members, 5 post-docs and 3 PhD students. Several undergraduate and postgraduate students working towards diploma, resp. MSc thesis as a part of their education, will contribute to the project. In addition, 1 post-doc (Dr. C. Pandis) and 1 PhD student (Mr. P. Klonos), employed by other, strongly related projects of the Group, funded by the Ministry of Education, Lifelong Learning and Religious Affairs, will contribute to the project.

Next to the PI, Prof. P. Pissis, 3 more staff members take part to the project, Prof. E. Kontou from the Dept. of Mechanics, NTUA, and Assistant Professors V. Peoglos and A. Kyritsis from the same Dept. of Physics as the PI. Prof. Pissis will coordinate the project. Prof. Kontou, an expert in mechanical properties and calorimetry, will be responsible for WP5 and contribute also much to WP3. Assistant Professors Peoglos and Kyritsis, working closely together in the Dept. of Physics, will be responsible for WPs 2 and 3, and WPs 4 and 6, respectively. The 5 post-docs to take part to the project are S. Kripotou, K. Raftopoulos, G. Kritikos and 2 new to be named (post-doc4 and post-doc5). Dr. Kripotou will contribute to WP4, in particular to sophisticated analysis of dielectric data, and WP6. Dr. Raftopoulos will contribute to WP3 and WP5, and the new post-doc5 to WP1 (also in a process of transfer of knowledge on synthesis to Athens) and WP2. Dr. Kritikos and the new post-doc4, both with a strong background in computer simulations, will act as liaison to the group of Prof. Theodorou connecting simulations to experimental measurements (WP7). Three new PhD students to be named, PhD1, PhD2 and PhD3, will be employed by the project. The project will provide to them the possibility to complete their education and training. So, they will be involved in diverse activities of the project, with emphasis, however, in relation to the needs of the project, on WP1, WP6 for PhD1; WP2, WP3, WP4 for PhD2; WP6, WP7 for PhD3.

Collaborations with other research groups, mostly in abroad, well-established and successful in the frame of various projects, are essential for the success of the proposed research. This is particularly true for the collaborations with Prof. J. L. Gomez Ribelles (Director, Center of Biomaterials, Technical University of Valencia, Spain), Dr. D. Pospiech (Leibniz-Institute of Polymer Research, Dresden, Germany), and Prof. V. Gunko (Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine) which will provide access to nanocomposite systems, especially designed and prepared for the needs of the project. These collaborations will have an additional related beneficial action, namely transfer of knowledge on issues of synthesis to Athens. Essential for the success of the project is also the collaboration with the group of Prof. Theodorou at NTUA in computer simulation, in an attempt to connect simulations to experimental measurements in a process of permanent active interaction and feedback. Other collaborations in abroad will provide access to techniques not available in Athens.