

Final Report

on the work done in the project OTKA KH 130442 on the
"Preparation of lignin containing polymer blends and study of their structure-property
correlations "

1. Introduction

The proposal of this project was based on a research and a paper dealing with the preparation and study of polymer/lignin blends [1]. At the time of the submission of the proposal, the article received 17 citations within two years that indicated considerable interest in the topic from the scientific community. The number of citations increased to 35 in the meantime showing continuing interest in the research. The matrix polymer of the blends was polypropylene (PP), which can form only weak interactions with lignin through dispersion forces, which makes the dispersion of lignin particles in this particular polymer very difficult. Since lignin is a polar substance with a number of functional groups, strong interactions can form among lignin molecules, which prevent their homogenization with most polymers. Later, we prepared blends from lignin and polymers, which were capable of forming stronger, dipole-dipole, aromatic π electron [2], hydrogen bond [3] and even ionic interactions [4] with the lignosulfonate used in the experiments. The thorough analysis of the results showed that the key factor determining the structure and properties of thermoplastic/lignin blends is interaction indeed, strong interaction results in a finer dispersion of lignin particles in the polymer matrix and in better mechanical properties [5]. We summarized our results and experience on lignin blends in a review article [6], which was published in 2017 and received 98 citations since then showing the general interest in this topic and the importance of lignin as raw material. The experiments continued in the framework of this project along different lines from the use of another type of lignin, through the preparation of the hybrid materials, to the chemical modification and reactive processing of lignin. This report summarized the most important results obtained since the start of the project.

2. Lignin type

All our previous experiments have been carried out with lignosulfonates obtained from a paper plant in Italy. However, the properties of industrial lignins depend very much on the extraction technology used for their preparation. In fact lignin is usually a byproduct of other industries and it is considered a waste product with very little value. The main industries yielding lignin as side product are related to cellulose and biofuel production. Accordingly, the value added application of lignin could result in considerable environmental and financial advantages. According to the extraction technology, the four main lignin types are Kraft lignin, lignosulfonate, steam explosion lignin and organosolv lignin. The largest quantity is produced by the Kraft process, but lignin is usually burned in the technology to obtain energy. Because of the production technology, lignosulfonates contain a large amount of accompanying components mainly sugars from cellulose and inorganic salts, mostly calcium sulfonate. These components constitute about 25 % of the product. On the other hand, the Kraft lignin available on the market is much cleaner, about

98 % of the product is lignin indeed. The chemical composition of the two products do not differ significantly although some differences exist in the number and ratio of their different functional groups. Since all our previous experiments were done with lignosulfonates, we wanted to see the effect of lignin origin on the properties of polymer/lignin blends in a project. We prepared blends from polypropylene, PP and a coupling agent to improve interactions, PET and an ionomer and two types of lignin, a lignosulfonate and a Kraft lignin. **Fig. 1** compares the fracture surfaces of the ionomer blends containing the two lignins. Structure seems to be similar, lignin is dispersed in the form of small particles in the polymer matrix, but it is impossible to draw unambiguous conclusions about the effect of lignin type on blend properties from such micrographs. The analysis of all results available indicates that Kraft lignin performs better in the blends than the lignosulfonate. This might be the result of the lack of contaminants or different chemical composition, but this question remains to be resolved in the future. The preparation of a manuscript is under way, only the analysis of particle size and its dependence on composition is missing at the moment.

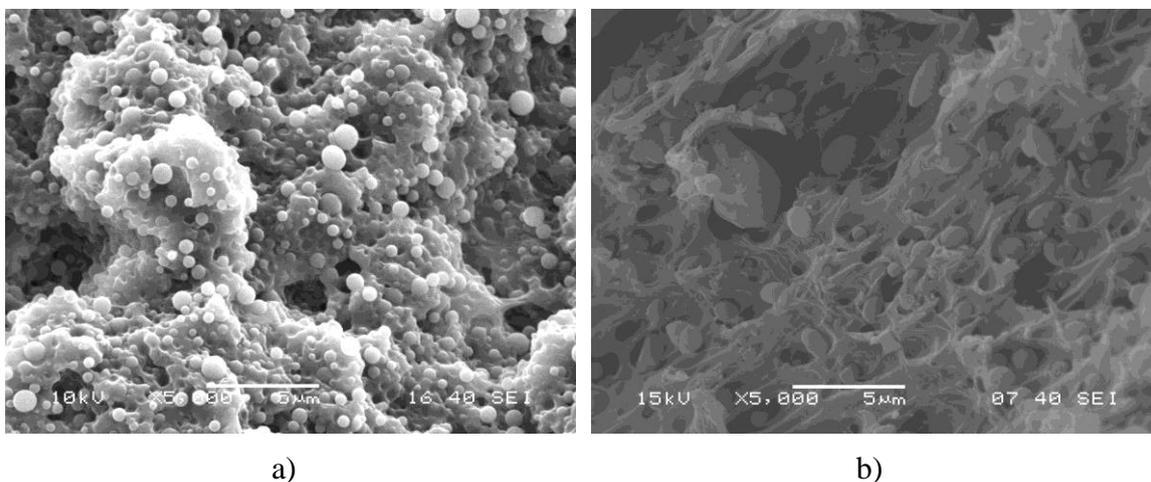


Fig. 1 Structure of ionomer/lignin blends prepared with lignins produced by dissimilar technologies. a) Kraft lignin, b) lignosulfonate. The blends contained 20 vol% lignin.

3. Structure evolution, kinetics and thermodynamics

Although interactions are very important in the determination of the structure and properties of polymer/lignin blends, kinetic factors may play a role as well. We prepared poly(ethylene-co-vinyl alcohol)/lignin blends from a series of copolymers with different vinyl alcohol contents thus changing the number of hydrogen bonds forming between the components and studied structure evolution in the blends. Low density polyethylene was used as reference in the study. The size of dispersed lignin particles is determined by particle break-up and coalescence, the original lignin particles of around 80 μm size break up to much smaller ones; particle sizes below one micrometer form at large vinyl alcohol content. Thermodynamic factors are stronger than kinetic ones in the studied system, changing shear stresses do not influence particle size much. The coalescence of particles is determined by composition and component interactions and a simple semi-empirical model was proposed to describe the correlations of these variables quantitatively. The size of dispersed lignin particles affects strongly the properties of the blends and the control of thermodynamic

factors result in blends with better properties (Pregi 2019). In Fig. 2 experimental particle sizes are compared to the prediction of existing models, two of which were published in the literature earlier and the third developed in this project. The agreement between the prediction of our model and the experimental data is obvious from the figure.

4. Ionomer/lignosulfonate blends

According to our previous results, ionomer/lignosulfonate offered the best combination of properties, thus it seemed to be worth to study them more in detail. Moreover, commercial ionomers were used in the previous project with different comonomer content, neutralization degree and neutralizing ion type. Accordingly, we wanted to control the composition of our ionomers much more thus ionomers with different degree of neutralization were prepared from an ethylene-acrylic acid copolymer of 8.5 wt% acrylic acid content. The ionomers were characterized by FTIR, SAXS, DSC and DMTA measurements as well as rheology and tensile testing. The study of the structure and properties of the ionomers prepared yielded interesting results which were summarized in a paper (Pregi 2020). The main relaxing species in ionomers are the methylene groups and the ethylene-acrylic acid copolymer segments. The mobility of these latter decreases upon neutralization and above a critical degree of neutralization a phase consisting of polyethylene segments attached to ionic clusters forms. The crystalline structure of the polymer contains primary and secondary crystallites. The amount and regularity, i.e. lamella thickness, of the latter decreases with increasing neutralization. Multiplets form from ionic species already at small degree of neutralization, which associate into clusters with increasing size as ion content increases (Fig. 3). The mechanical properties of the ionomers are determined by their crystalline structure and cluster formation. Clusters increase strength and modulus, while decrease deformability. The combined effect of the two factors (crystallinity, cluster size) on stiffness was successfully described by a simple model.

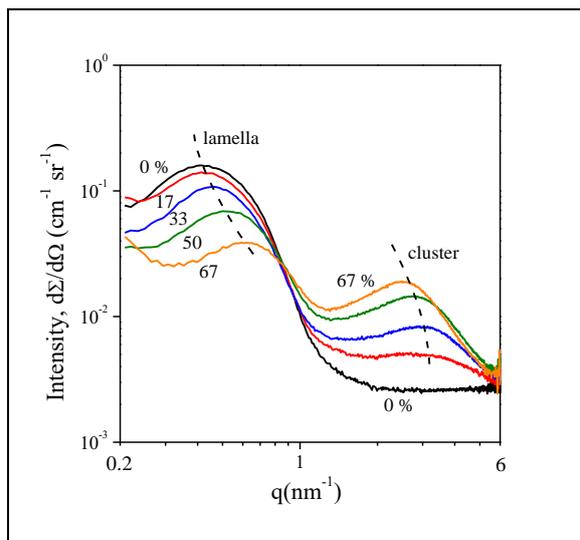


Fig. 3 Effect of neutralization on the SAXS patterns of ionomer/lignin blends; clusters and crystalline lamellae.

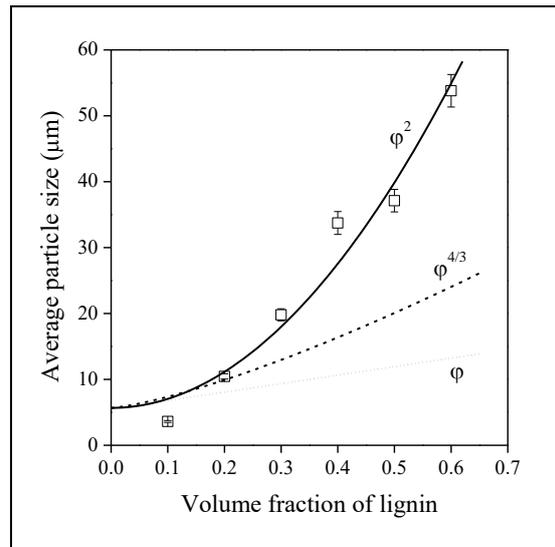


Fig. 2 Comparison of the reliability of published theories and their range of validity for LDPE/lignin blends. Models: Fortelný and Kovář [7]; ——— Huneault et al. [8]; ——— this project.

After the thorough characterization of the neat ionomers, we prepared blends from them with a lignosulfonate. The presence of

the lignosulfonate complicated structure even further. Lignin is dispersed in the form of nanosized particles in the ionomer matrix, but the presence of the lignin modified the crystalline structure of the polymer as well. Accordingly, the properties of the blends are influenced by at least three factors, lignin content, crystalline structure and cluster formation. Moreover, a further factor must be taken into account, the interaction of the components, which also may change with neutralization. Our previous study on ionomer/lignin blends proved that the two main type of interactions developing in ionomer lignin blends are hydrogen bonds and electrostatic interactions. Both are modified by the degree of neutralization. Presently we are making efforts to determine the strength of these interactions and try to estimate the relative effect of the two types, i.e. hydrogen bonds and ionic interactions. We use the results of acoustic emission experiments for the purpose and try to estimate interactions also by thermodynamic models. As soon as we obtain the results we plan to publish the results.

5. Preparation technique, homogeneity

Although the structure and properties of thermoplastic/lignin blends could be changed in a wide range by controlling interactions, the mechanical properties of the blends, mainly their deformability and fracture resistance, remained rather poor. In order to improve properties, a route different from the traditional melt blending technique was chosen for the preparation of the blends. In cooperation with a Chinese group from Donghua University in Shanghai, the blends were prepared by the Pickering emulsion technique. In this method, lignin particles stabilize the emulsion and after the evaporation of the solvent, a blend with very fine dispersed lignin particles form. The technique proved to be successful and the blends prepared possessed much better properties than their melt blended counterparts (Li 2019). In **Fig. 4** the reduced tensile strength of the PLA/lignin blends are presented as a function of lignin content. The slope of the straight lines is related to the load bearing capacity of the dispersed particles and it depends on their size as well as the strength of interactions [9]. Because of the much smaller size of lignin particles in the blend prepared by the Pickering emulsion technique, the contact surface between the phases is much larger and thus the load carried by the lignin phase is also larger. The technique has large potentials in improving the properties of immiscible polymer blends.

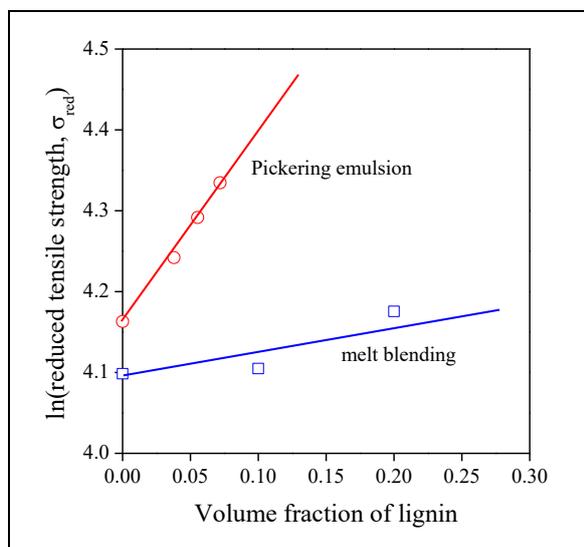


Fig. 4 Effect of the preparation technique on the load bearing capacity of lignin in PLA/lignin blends.

6. Hybrid materials

In spite of the success of the application of the Pickering emulsion technique, the results proved that new approaches must be applied if we want to prepare materials with

acceptable properties for commercial use. Accordingly, we selected a variety of approaches with different complexity to prepare new materials from lignin. The simplest way was to prepare hybrids, which contain several components with different functions to improve various properties. A hybrid material was prepared from a polypropylene reactor blend, lignin and a natural fiber, flax. A functionalized polypropylene was also added to improve interfacial adhesion between the matrix and the additives. The fracture surface of such a composite is shown in **Fig. 5**. The failure of the relatively large flax fibers is clearly visible in the figure. Because of the presence of the coupling agent lignin particles are small and they cannot be seen very well in the figure. The reactor blend contained 33 % elastomer to improve impact resistance. The results were promising, materials containing 60-70 % natural additives could be prepared with acceptable properties, with a stiffness of around 4 GPa and a strength close to 30 MPa which corresponds to the properties of a neat PP homopolymer, i.e. it can be used as structural material. The large natural material content offers a clear environmental benefit especially because of the renewable raw material content and its much smaller carbon footprint. Unfortunately fracture resistance was rather small, around 4 kJ/m², because the reactor blend cavitates during deformation, which hinders plastic deformation and does not absorb sufficient energy. However, even this small value is slightly better than the impact strength of a neat PP homopolymer. The results are being summarized at the moment and the preparation of a paper is under way. In an attempt to improve impact resistance, further experiments are going on with hybrid materials containing different components. A PP homopolymer is used as matrix and an elastomer is added separately in order to avoid cavitation. We hope that the new materials will possess even better properties than the previously prepared composites.

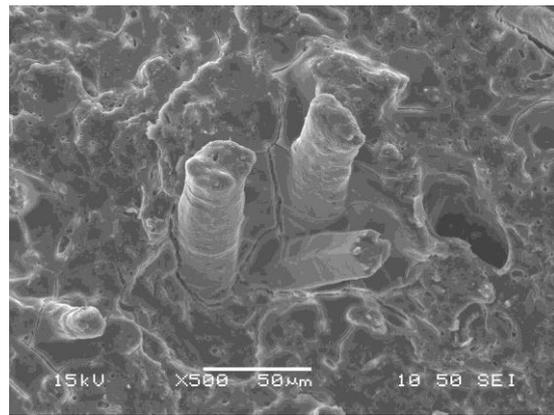


Fig. 5 *Micrograph recorded on the fracture surface of a PP hybrid composite at 20 vol% lignin and 20 vol% flax content.*

Although the PP hybrid composites described above offer good properties at very large renewable material content, they are still not completely biodegradable. In order to achieve compostability and complete biodegradation, a biopolymer must be used as matrix. The most obvious choice for this purpose is poly(lactic acid), PLA, produced and used in the largest quantity at the moment. Because it is available in large quantities, its price is also acceptable, unlike that of poly(hydroxyl butyrate) that is quite expensive. Unfortunately, the fracture resistance of PLA is even smaller than that of PP, moreover, the fast physical ageing of the polymer deteriorates it even further with time. Consequently, PLA is often modified by plasticization or blending. Polybutylene adipate terephthalate, PBAT, is a biodegradable elastomer, which is often used for the impact modification of PLA. We prepared three-components blends from PLA, PBAT and lignin and determined the structure and properties of the obtained materials. We also used a maleic anhydride modified PLA as coupling agent to improve interfacial adhesion. The experiments as well as the results are under way. Although the properties of the materials obtained are not exceptional, the structure of the blends seems to be rather interesting, the lignin is partitioned mainly in the PBAT phase, which explains the small stiffness and strength of the blends.

7. Membranes, films

The packaging industry uses a large amount of polymers, in fact plastics revolutionized packaging completely. However, plastic packaging materials increase pollution and cause environmental problems. Consequently, larger and larger amounts of materials derived from natural resources are used for packaging. Compostable and biodegradable polymers are good candidates for the purpose and natural polymers like cellulose, natural fibers, lignin, etc. can be used for the modification of their properties. With these aspects in mind, we prepared films from three-component poly(vinyl alcohol), PVA, lignin and montmorillonite (MMT) in order to study their possible application as packaging materials. The composites are completely biodegradable and the montmorillonite is expected to decrease the permeability of the membranes towards oxygen and other gases. The polymer and the lignin dissolve in water, while the layered silicate can be dispersed in the form of individual layers in water, thus a very homogeneous suspension can be prepared from the components. We expected that the layered silicate would act as compatibilizer and a homogeneous material with good mechanical properties and excellent barrier properties might be prepared in this way. The composites were prepared as a function of composition, both lignin and MMT content changed in a wide range. The first results showed a complicated effect of interactions on the structure and properties of the composites and interesting structure/property correlations. Unfortunately, the barrier properties of PVA deteriorated with the addition of the other components at small additive content, but reached the original values at larger amounts of lignin and MMT. The minimum in oxygen permeability is rather surprising and must be related to the crystalline structure of PVA. Experiments are under way to determine crystallinity more accurately than before; we hope to find close correlation between permeability and crystallinity. A publication will be prepared after completion of the experiments and the evaluation of the results.

8. Chemical modification, reactive blending

Another approach to improve properties is the chemical modification of lignin. This can be done in different ways. One is the use of lignin as reactive building block. This is done through isocyanate chemistry, lignin is coupled to poly(ethylene glycol) through its aliphatic hydroxyl groups forming polyurethanes. Changing the composition and the molecular weight of poly(ethylene glycol) results in materials with a wide range of properties. Another difficulty is the heterogeneous nature of the blends prepared from commercial polymers and lignin. As mentioned earlier, one of the obstacles before the preparation of homogeneous materials with good properties from lignin is the strong interaction among lignin molecules. Moreover, the materials obtained are usually

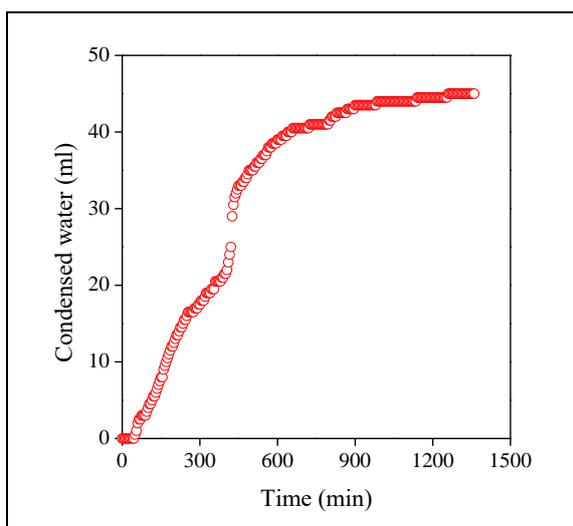


Fig. 6 Amount of water eliminated during the polycondensation of lactic acid with increasing reaction time.

quite brittle. In order to decrease interactions and improve the deformability of the final product, lignin is reacted with a monofunctional compound during the preparation of modified polyurethanes. The approach led to increased deformability as expected, but the strength of the materials is small, thus further modification is needed.

The blends of PLA and lignin have relatively poor properties even when we use the Pickering emulsion technique for their preparation (see **Section 5**). However, lignin dissolves in lactic acid and the polymerization of the monomer in the presence of lignin is expected to result in a more homogeneous material to form a fully biodegradable, natural based material. Unfortunately the polymerization of lactic acid by direct polycondensation is very slow, long reaction times and the removal of water is needed to achieve acceptable molecular weight. We built an apparatus that makes possible the following of condensation by the measurement of the eliminated water; **Fig. 6** shows the time dependence of the amount of water eliminated during the reaction. Since lactic acid can form hydrogen bonds with water, the first, faster phase is the removal of the bonded water and the second is the polycondensation reaction. The analysis of the product by GPC, Maldi spectrometry (**Fig. 7**) and NMR spectroscopy indicated that the monomer reacts with lignin indeed, but the molecular weight of the resulting block copolymer is relatively small. Molecular weight increased with reaction time as expected. A more detailed chemical analysis is needed in order to determine the exact structure of the obtained polymer including the extent of grafting. The first experiments were carried out with a liginosulfonate. As mentioned above, these products contain a larger amount of accompanying materials, which might influence the grafting reaction. Accordingly, we intend to repeat the experiments with Kraft lignin. Since the molecular weight of the products obtained is relatively small, we intend to use the obtained copolymers as coupling agents or increase their molecular weight through chain extension reactions. As mentioned earlier, the experiments are under way and we expect the development of interesting new materials, but at least the publication of several papers in leading journals of the field as a result

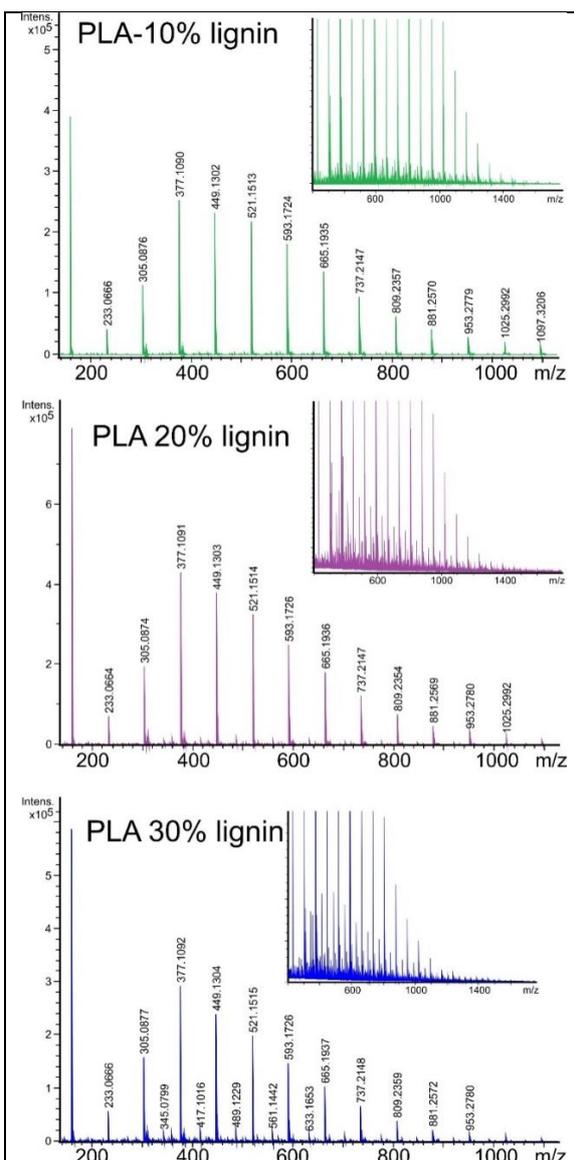


Fig. 7 Maldi spectra of lignin-g-PLA copolymers; lignin content (10-30 wt%) increases from top to bottom.

9. Summary

The financial support obtained in the framework of the OTKA K 130442 contract offered us the possibility to continue and even intensify our work related to lignin containing polymer blends and composite systems which we started a few years ago. The research was and is acknowledged internationally shown by the large number of citations obtained each year. Our review paper published in 2017, which is based on our results and experience, received almost 100 citation already. We pursued several projects in the timeframe of the contract with variable success. We continued to study polymer/lignin blends with the intention of obtaining deeper knowledge on the factors determining structure formation in various combination of polymers and lignosulfonates. We started experiments with Kraft lignin to compare its behavior and performance in blends to that of the lignosulfonate used in previous research. We studied the effect of preparation technology on the structure and properties of PLA/lignin blends in cooperation with a Chinese group. We prepared materials with practical applications in mind, mostly as structural components or for packaging. We extended the research to the chemical modification and reactive processing of lignin. The work is mostly done by young scientists, staff members, PhD, MSc and BSc students and besides doing high level scientific research, we dedicate considerable efforts to find practical application for the materials and/or the technologies developed so far. Although the number of papers written during the contract is not excessive we compiled a large amount of data from which we intend to publish many papers in the near future.

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