KEEMIA- JA MATERJALITEHNOLOOGIA TEADUSKOND
POLÜMEERMATERJALIDE INSTITUUT
TEADUS- JA ARENDUSTEGEVUSE AASTAARUANNE 2013

1. Instituudi struktuur

Polümeermaterjalide instituut, *Department of Polymer Materials*
Instituudi direktor Andres Krumme

- Polümeeride tehnoloogia õppetool, Chair of Polymer Technology, prof. Andres Krumme
- Puidutöötlemise õppetool, Chair of Woodworking, prof. Jaan Kers
- Tekstiilitehnoloogia õppetool, Chair of Textile Technology, prof. Anti Viikna
- Põlevkivi ja taastuvkütuste teaduslaboratoorium, Laboratory of Oil Shale and Renewables Research, Dr. Hans Luik
- Mööbli ja puitmaterjalide katselaboratoorium, Laboratory for Furniture and Wood Materials Testing
- Tekstiili katselaboratoorium, Laboratory for Textile Testing

2. Instituudi teadus- ja arendustegevuse (edaspidi T&A) iseloomustus

2.1 struktuuriüksuse koosseisu kuuluvate uurimisgruppide teadustöö kirjeldus *(inglise keeles)*

2.1.1 Polümeermaterjalide uurimisgrupp (polümeeride tehnoloogia õppetool, puidutöötlemise õppetool, tekstiilitehnoloogia õppetool) *Research team of polymeric materials (Chair of Polymer Technology, Chair of Woodworking, Chair of Textile Technology)*

- **(AR12135: Carbon Nanotube Reinforced Electrospun Nano-fibres and Yarns - *Elektroketruse teel valmistatud ja süsinik-nanotorudega armeeritud nanokiud ning lõngad*)** Main goal of the project is to develop and industrialize a technological process for production of ultra-strong and functionalised polymer nanofibres and yarns for various applications. The process combines electro-spinning of polymers with carbon nanotube (CNT) doping and additional functionalization tools. As a result pure nanofibres, nanofibre yarns and fabrics are produced. The main applications of the novel materials are: dynamically adjustable pore size filter for special filtering applications; substrates for cell growth; ultra-strong fabric for reinforcement of plastic film laminates; yarns for special textiles having exceptional strength and special properties as piezoactivity, conductivity and shielding capacity.
- **(ETF8134: Novel polyethylenes of bimodal composition: effect of macromolecular components and branchings on crystallization, rheological and mechanical properties - *Uudsed bimodaalse koostisega polüetüleenid: makromolekulaarsete koostisosade ja hargnemiste mõju kristallisatsioonile, reoloogiale ja mehaanilistele omadustele*)** Sustainable thermoplastic polymers and composites are developed and investigated to partly or fully replace non-renewable-resources-based materials for melt processing technologies. Cellulose appears to be a nearly unlimited renewable resource for polymeric materials. Discovery of new dissolution processes in ionic liquids opens several new routes for functionalization of cellulose. Thermoplastic cellulose derivatives can be prepared without use of plasticizers. Adhesion and mechanical properties of cellulose in composites with synthetic polymers as polyolefins and polylactides can be improved. Effect of constituents and functionalization agents on rheology, crystallization behaviour, morphology and mechanical properties of the novel thermoplastic materials and composites are investigated.

- **(ERMOS78)** Polymer processing technologies requires detailed information about formation of crystalline structure on micro- and macro-level under flow stresses. The main purpose of the project is to study the flow behaviour and flow-induced crystallization process of some novel thermoplastics, derivatives of cellulose and their composites with polyolefins. Studies will be done at different shear rates and elongation stresses which similar to that appearing in situation of real polymer processing. This gives important information about how mechanical properties and processability of the novel composite materials could be improved. To achieve promoted results an influence of molecular parameters of polymers (molecular mass, chemical structure of polymer, etc.) as well as type and magnitude of applied flow on rheological, nucleation and crystallization behaviour of the materials will be studied. As a consequence, melt flow/nucleation/crystallization/crystal structure interrelations will be obtained.
- **(AR10127: Basics of new utilization processes for oil shale combustion solid wastes** - *Põlevkivi põletamisega kaasnevate tahkjäätmete uute kasutusalade alused***)** The R&D project, advised by leading research scientist Rein Kuusik (Faculty of Chemical and Materials Technology, Laboratory of Inorganic Materials) deals among others with the problem, how to use fly ash of combustion of oil shale as additive to polyethylene (PE) for formation new, more cheap composite materials (leader of this subtask is prof. Anti Viikna). The possibility of blending of oil shale ashes with PE for producing blown films of these composites is investigated. Obtained materials are tested (density, melt flow index, thermal analysis, tensile strength etc.) and selected the best composites for producing blown film.
- Two scientific research topics of **Chair of Woodworking** are wood protection by different impregnation methods and study the properties of wood plastic composites. The aim of woodpolymer composites project is to develop new WPC material on the basis of common alder (*Alnus glutinosa*) shavings and virgin PP or LLDPE polymer matrix.

2.1.2 Põlevkivi ja taastuvkütuste teaduslaboratoorium *Laboratory of Oil Shale and Renewables Research*

- **(SF0140028s09: New technologies of thermochemical processing of oil shale and blended fuels** - *Põlevkivi ja kütuste segude termokeemilise töötlemise uued tehnoloogiad*) Liquefaction and upgrading of Estonian fossil and renewable fuels and fuel blends with the aim of their more rational and appropriate utilisation will be investigated. Scientific and technological fundamentals to maximum conversion of oil shale, peat, varieties of biomass and plastic wastes into non-conventional petroleum by using novel thermal dissolution, hydrogenation and co-processing methods will be created. Bi- and multilateral interactions occurring between components at sub- and supercritical extraction and at upgrading of the viscous extracts by hydrogenation will be investigated. Probable positive synergistic effects in the yield and composition of the liquid product will be described. Mathematical models will be deduced for approximate description of the joint effect of the main factors on the yield and composition of the products in the complicated processes. The results obtained represent the science-based fundamentals for upgrading available natural fuel resources.
- **(ETF 9331: Liquefaction of the organic matter of dictyonema oil shale with supercritical solvents and reagents** - *Diktüoneema põlevkivi orgaanilise aine vedeldamine superkriitiliste lahustite ja reagentidega*) Regularities of thermochemical liquefaction and upgrading of the dictyonema oil shale with the aim of estimating its potential as a source for synthetic petroleum will be investigated. As a conversion method supercritical extraction in autoclave in the presence of various solvents and reagents is used. The effect of supercritical water, benzene, hexane, methanol, ethanol and acetone on products yield and composition will be investigated. In order to obtain the maximum yield of oil rich in hydrocarbons parametres of kerogen liquefaction process (temperature, liquefaction time, pressure in autoclave and weight ratio of initial substances) will be largely varied and some selected reagents (H-donors, NaOH, zinc) are added

to evoke the hydrogenation, cracking and other reactions. Physical-chemical and technological fundamentals for the sustainable utilisation of the huge reserve of so far industrially unused oil shale type will be created.

- **(AR12004: Fundamentals to oil shale maximum upgrading** - *Põlevkivi maksimaalse vääristamise alused*) The project is a continuation of the competence in the field of oil shale liquefaction via complex investigations leading to the new technologies, and the direct goals of the project include working out novel technologigal fundamentals of shale oil production and complex upgrading scheme of liquid, gaseous and solid products formed in thermochemical destruction of different oil shales.

2.2 aruandeaastal saadud tähtsamad teadustulemused *(inglise keeles)*

2.2.1 Polümeermaterjalide uurimisgrupp (polümeeride tehnoloogia õppetool, puidutöötlemise õppetool, tekstiilitehnoloogia õppetool) *Research team of polymeric materials (Chair of Polymer Technology, Chair of Woodworking, Chair of Textile Technology)*

- **(ETF8134)** Effect of cellulose and it's derivatives on rheological and thermal properties of low-density polyethylene (LDPE) and polylactic acid (PLA) was explained. Cellulose and it's esters had similar effect on viscosity of PLA. Cellulose laurate (CL) and cellulose stearate (CS) had moderate effect on increase of viscosity in LDPE composites compared to cellulose which is due to higher chain mobility and better compatibility of the esters with LDPE. Initial slope of the curves of storage modulus of LDPE/CL and LDPE/CS composites are similar to the curves of pure LDPE up to filler content of 20% which indicates good homogenisation of CL and CS in the LDPE matrix. Similar result was obtained with PLA matrix with filler content up to 10%. Cellulose and CL decrease degree of crystallisation of LDPE composite. However, addition of CS into LDPE matrix increases the degree of the composite due to crystallisation of CS and co-crystallisation of LDPE and CS. Contrary, overall degree of crystallisation of PLA/CS composites is determined only by crystallisation of CS, as PLA itself is amorphous in normal conditions. Ph.D. thesis is prepared by the results described above.
- **(AR12135)** industrial feasibility of production of yarns with submicron diameter of component fibres by electrospinning was investigated. Pilot process was designed and installed having increased productivity compared to the lab-scale process, the achievement of the previous period. Main focus of the materials research of the period was development of the yarns having piezoactive and conductive properties. Yarns were produced by electrospinning of polyvinylidene fluoride, a polymer known to have piezoactive properties. Different composites of non-conductive polymers with carbonous fillers (carbon-nanotubes, graphite) and polyaniline were under investigation for producing conductive yarns of good mechanical properties. Study for improving the abovementioned properties continues.
- **(ERMOS78)** Viscous and rheological properties of some cellulose esters in melt were studied at conditions near to those which usually used in industry for polymer processing. To evaluate thermoplastic properties of cellulose esters we compare them with properties of low density polyethylene at the same conditions. It was discovered that long chain fatty acid cellulose esters could be processed in the same way as commodity polymers, but these materials need further improvement for industrial application as thermoplastic polymer.
- **(AR10127)** several physical properties of composite films of polyethylene and oil-shale fly ash were investigated. Relationships between nature and concentration of the ash, tensile properties, conductivity and pH of the films were explained.
- **(The wood protection topic of Chair of Woodworking)** To prevent degradation caused by different microorganisms, the rapeseed oil in water emulsion impregnation agent was developed, technological and laboratory tests were made. Active ingredients for emulsion were chosen among boron compounds (borax, boric acid - and dioctylmethyl ammonium chloride). The

obtained results of Bio testing of impregnated pine wood specimens according to standards EN113, EN73 and EN84 demonstrated that a new penetration emulsion ensures effective protection against wood rotting fungi and discolouring fungi. It was demonstrated that rapeseed oil emulsion is about 30% more effective against mould than the emulsion based on Tanalith E tested in the same conditions.

- **(The wood plastic composites topic of Chair of Woodworking)** Firstly the size reduction of common alder (*Alnus glutinosa*) shavings by high-energy disintegrator mills was investigated. Secondly the influence of wood flour fraction size and coupling agents effect on the mechanical properties of WPC was under study. The mixture used in injection moulding (Battenfeld BA 230 E) contained 65 wt.% of polymer and 35 wt.% of food flour. The coupling agents used were polyvinylalcohol (PVA), maleic anhydride (MA), triethoxyvinylsilane (TEVS). In industrial injection moulding experiments (B-Plast Ltd) it was approved that the best wood flour fraction sizes for the WPC forks manufacturing are fractions with good aspect ratio 0.63 to 1.25 mm and from 1.25 to 2mm. The laboratory mechanical tests demonstrated that the wooden flour filler content decreased the elongation of the polymer, but it makes the material stiffer and stronger. The coupling agents MA+TEVS and PVA had best effect to the mechanical properties of the WPC. Next interesting topic for study is influence of the wood flour filler particle size to the technological and mechanical properties in rotation moulded products

2.2.2 Põlevkivi ja taastuvkütuste teaduslaboratoorium *Laboratory of Oil Shale and Renewables Research*

- The effect of reagents, catalysts, temperature and duration on the yield of products (gas, water solubles, maltenes, asphaltenes, preasphaltenes, solid residue) and group composition of the benzene soluble fraction in liquefaction of Estonian kukersite, American and Jordanian oil shales and dictyonema argillite by low-temperature pyrolysis, hydropyrolysis, supercritical extraction, and in the oil upgrading by hydrogenation was described. The optimal conditions were established where the yield of the liquid extract was substantially higher than in Fischer Assay. In water conversion of Dictyonema oil shale using NaOH, H-donors, zinc and alcohols as additives twice higher oil yields were obtained compared with semicoking.
- The co-pyrolysis of kukersite with biomass varieties and domestic wastes was studied. Depending on conditions, several positive and negative synergies were found in the yield and composition of the products. For the first time mathematical synergy model was deduced to describe the effect of the shares of the components on the actual yield and composition of the products basing on the formula of the stability constant of the synergy compound. The effects of temperature, duration and pressure on the „*synergy factor*", a new coefficient applied in the model were described in the co-pyrolysis of kukersite with pine sawdust.

2.3 Uurimisgruppide kuni 5 olulisemat publikatsiooni aastal 2013

- Ille Johannes, Laine Tiikma, Hans Luik. Synergy in co-pyrolysis of oil shale and pine sawdust in autoclaves. *Journal of Analytical and Applied Pyrolysis*, 2013, 104, 341–352.
- Ille Johannes, Vilja Palu. A synergy code in co-pyrolysis. *Oil Shale*, 2013, **30**(4), 471–490.
- Tarasova, E.; Šumigin, D.; Kudrjašova, M.; Krumme, A. (2013). Preparation of Cellulose Stearate and Cellulose Acetate Stearate in 1-Butyl-3-Methylimidazolium Chloride. J. Zicans, R. M. Meri (Toim.). Baltic Polymer Symposium (105 - 111).Trans Tech Publications Ltd
- Šumigin, D.; Tarasova, E.; Krumme, A.; Viikna, A. (2013). Influence of Cellulose Stearate (CS) Content on Thermal and Rheological Properties of Poly(lactic acid)/CS Composites. J. Zicans, R. M. Meri (Toim.). Baltic Polymer Symposium (99 - 105).Trans Tech Publications Ltd
- Hans Luik, Lea Luik, Vilja Palu, Hindrek Tamvelius. Pyrolysis and supercritical water conversion of pine *Pinus sylvestris* ingredients. In: *European Biomass Conference and*

Exhibition Proceedings 21st European Biomass Conference and Exhibition, Copenhagen, Denmark, 3-7 June 2013, 914-917.

3. Loetelu struktuuriüksuse töötajate rahvusvahelistest tunnustustest

Rahvusvahelised tunnustused 2013 aastal puuduvad.

4. Loetelu struktuuriüksuse töötajatest, kes on välisakadeemiate või muude oluliste T&A-ga seotud välisorganisatsioonide liikmed

Välisakadeemiate või muude oluliste T&A-ga seotud välisorganisatsioonide liikmed instituudis puuduvad.

5. Soovi korral lisada aruandeaastal saadud T&A-ga seotud tunnustusi (va punktis 2.3 toodud tunnustused), ülevaate teaduskorralduslikust tegevusest, teadlasmobiilsusest ning anda hinnang oma teadustulemustele

Osaletud on ettekannetega järgmistel teaduslikel konverentsidel:

- EUPOC-2013: Polymers and Ionic Liquids, 1-5 September 2013, Gargnano, Italy.
- Euroopa Biomassi Konverentsil Kopenhaagenis 3.-7. juunil 2013.
- Rahvusvahelisel Põlevkivi Sümpoosionil Tallinnas 10.-13. juunil 2013 (5 ettekannet).
- 26. Rahvusvahelisel Orgaanilise Geokeemia konverentsil Ciosta Adejes (Tenerife, Hispaania) 15.-20. septembril 2013.
- The Northern European Network of Wood Science and Engineering in Hannover 10-12 september 2013, kaks posterettekannet.
- Baltic Polymer Symposium in Trakai 18-20 september, 1 plenaarettekanne, 2 posterettekannet
- Eesti 33. Keemiapäevadel Tallinnas 11. oktoobril 2013 (5 ettekannet).

Polümeermaterjalide instituudi teadustööd võib pidada väga heaks ja osalemist teadus-arendusprojektides suurepäraseks.